

UNIVERSIDADE ESTADUAL DE CAMPINAS Faculdade de Engenharia Mecânica

MARCO CÉSAR PRADO SOARES

Photonic Materials and Devices: from Nanoparticles to Fiber Optic Chemical Sensors

Materiais e Dispositivos Fotônicos: de Nanopartículas a Sensores Químicos de Fibra Óptica

CAMPINAS 2024

MARCO CÉSAR PRADO SOARES

Photonic Materials and Devices: from Nanoparticles to Fiber Optic Chemical Sensors

Materiais e Dispositivos Fotônicos: de Nanopartículas a Sensores Químicos de Fibra Óptica

Thesis presented to the School of Mechanical Engineering of the University of Campinas in partial fulfillment of the requirements for the degree of Doctor in Mechanical Engineering, in the area of Mechatronics.

Tese apresentada à Faculdade de Engenharia Mecânica da Universidade Estadual de Campinas como parte dos requisitos exigidos para a obtenção do título de Doutor em Engenharia Mecânica, na Área de Mecatrônica.

Orientador: Prof. Dr. Éric Fujiwara

ESTE TRABALHO CORRESPONDE À VERSÃO FINAL DA TESE DEFENDIDA PELO ALUNO MARCO CÉSAR PRADO SOARES, E ORIENTADA PELO PROF. DR. ÉRIC FUJIWARA.

> CAMPINAS 2024

Ficha catalográfica Universidade Estadual de Campinas Biblioteca da Área de Engenharia e Arquitetura Elizangela Aparecida dos Santos Souza - CRB 8/8098

Soares, Marco César Prado, 1992-Photonic materials and devices : from nanoparticles to fiber optic chemical sensors / Marco César Prado Soares. – Campinas, SP : [s.n.], 2024.
Orientador: Éric Fujiwara. Tese (doutorado) – Universidade Estadual de Campinas, Faculdade de Engenharia Mecânica.
1. Carbono. 2. Nanomateriais. 3. Análise de fluorescência. 4. Tecnologia de fibra óptica. 5. Redes neurais (Computação). I. Fujiwara, Éric, 1985-. II. Universidade Estadual de Campinas. Faculdade de Engenharia Mecânica. III. Título.

Informações Complementares

Título em outro idioma: Materiais e dispositivos fotônicos : de nanopartículas a sensores químicos de fibra óptica Palavras-chave em inglês: Carbon Nanomaterials Fluorescence analysis Fiber optic technology Neural networks (Computation) Área de concentração: Mecatrônica Titulação: Doutor em Engenharia Mecânica Banca examinadora: Éric Fujiwara [Orientador] Cecilia Amelia de Carvalho Zavaglia Julio Roberto Bartoli Thiago Destri Cabral Patricio Salvatore La Rosa Data de defesa: 23-02-2024 Programa de Pós-Graduação: Engenharia Mecânica

Identificação e informações acadêmicas do(a) aluno(a)

ORCID do autor: https://orcid.org/0000-0002-5219-5124
 Curriculo Lattes do autor: https://lattes.cnpq.br/6178029647051765

UNIVERSIDADE ESTADUAL DE CAMPINAS FACULDADE DE ENGENHARIA MECÂNICA

TESE DE DOUTORADO ACADÊMICO

Photonic Materials and Devices: from Nanoparticles to Fiber Optic Chemical Sensors

Materiais e Dispositivos Fotônicos: de Nanopartículas a Sensores Químicos de Fibra Óptica

Autor: Marco César Prado Soares Orientador: Prof. Dr. Éric Fujiwara

A Banca Examinadora composta pelos membros abaixo aprovou esta Dissertação/Tese:

Prof. Dr. Éric Fujiwara, Presidente Faculdade de Engenharia Mecânica/UNICAMP Prof. Dr. Cecilia Amelia de Carvalho Zavaglia Faculdade de Engenharia Mecânica/UNICAMP Prof. Dr. Julio Roberto Bartoli Faculdade de Engenharia Química/UNICAMP Dr. Thiago Destri Cabral, R&D Engineer Instituto de Ciência e Inovação em Engenharia Mecânica e Engenharia Industrial (INEGI), Portugal

Prof. Dr. Patricio Salvatore La Rosa Washington University in St. Louis, MO, USA/Bayer St. Louis

A Ata de Defesa com as respectivas assinaturas dos membros encontra-se no SIGA/Sistema de Fluxo de Dissertação/Tese e na Secretaria do Programa da Unidade.

Campinas, 23 de fevereiro de 2024.

Acknowledgments

I thank **São Paulo Research Foundation** ("*Fundação de Amparo à Pesquisa do Estado de São Paulo*", **FAPESP**) for funding and supporting this research under grant **2019/22554-4**. Part of this work is continuation from my Master's in Science research, which was also funded by FAPESP under grant **2017/20445-8**.

Several coworkers with important contributions to this work were funded by both the Brazilian Ministry of Education, Superior Education Personnel Improvement Coordination (*"Coordenação de Aperfeiçoamento de Pessoal de Nível Superior"*, **CAPES**) and by the Brazilian National Council for Scientific and Technological Development (*"Conselho Nacional de Desenvolvimento Científico e Tecnológico"*, **CNPq**) under **Finance code 001**, so I extend my acknowledgment to both agencies. Importantly, the opinions, hypotheses and conclusions or recommendations expressed in this thesis are from author's responsibility and do not necessarily reflect the FAPESP, CAPES or CNPq views.

I also thank all Brazilian taxpayers (including myself), since we have nearly 30% of our income taxed directly at source and also contribute with cascading taxes on the acquisition of goods and services. Without this joint effort, this research would not have been possible.

Important coworkers, researchers and institutions that I need to mention here due to their significant contributions are the following, and their roles in this work are highlighted at the end of each section: Prof. S. Bosi, Dr. F. Arcudi, Dr. G. Filippini, Dr. B. Bartolomei, Dr. M. Cacioppo, Dr. P. Bertoncin and Prof. Maurizio Prato (University of Trieste, Italy); Prof. Alejandro Criado (Center for Cooperative Research in Biomaterials, Donostia San Sebastián, Spain); C. A. S. Ramos, Prof. Manuel Cid, Igor Abbe, G. S. Goveia, Prof. José F. D. Chubaci, Prof. Marcelo Carreño and Prof. Inés Pereyra (University of São Paulo, Brazil); Dr. S. Livi and Prof. Jannick Duchet-Rumeau (University of Lyon, France); Prof. Catia Ornelas, P. M. Lazari, S. Aristilde, Prof. Fabiano Fruett, Prof. Cristiano M. B. Cordeiro, Prof. Lucimara G. de la Torre, Dr. T. B. Taketa and Prof. Marisa M. Beppu (University of Campinas, Brazil); and the Brazilian Nanotechnology National Laboratory (LNNano/CNPEM).

I would like to also use this space to dedicate this work to this beautiful God, because I can do everything through the One who strengthens me. I thank the Strength even in moments of great doubt, and peace even in moments of great agony. Thank You for letting me enjoy and live this journey.

I dedicate it to my parents, Nílton and Gláucia, two giants who did not have the best lives they could have dreamed of, but who gave me their shoulders so that I could climb on them and go further than themselves, following impossible dreams. I owe everything to them. No matter how far away they are, they are always with me, so I dedicate them this work.

I dedicate it to my younger brothers, Júlio and Glauco, who despite the fights and arguments, were always present. They would always raise their voices to defend their blood, and I know they would do everything for me (at least, I hope so).

And finally, I dedicate it to all those who, in some way, were and are by my side, day after day. I want to thank my supervisor, Prof. Éric Fujiwara, who guided my work from the MSc. to the PhD and supported my decisions and ideas. Also, I thank Professor Carlos Suzuki,

his former advisor who guided me through the early stages of my Scientific Initiation and who sparkled my passion for this work. This thesis may mark the end of his outstanding career, responsible for creating the Laboratory of Integrated Quartz Cycle, which lately became the Laboratory of Photonic Materials and Devices. I owe him a lot of my personal and academic development, from many talks to and unforgettable travel to Switzerland and the fulfillment of the dream of seeing the Swiss Alps. The name of this theses is a tribute to his work and legacy as researcher. At last, this paragraph must contain my dedicatory to Prof. Julio Bartoli, not only a master, but a great friend, co-worker and discussion partner of the Italian culture, our second nation. I remember having lunch in the University's Restaurant with him, sometime between late 2018 and early 2019, when he shined the light of Carbon Nanodots and brought me to the world that would become my scientific inspiration. I also cannot put in sufficient words how much he was important to this work, but I hope his contribution will be sufficiently clear for those who read the text to the end.

In the future, people may not remember, but this work crossed the Covid-19 pandemics. Many times, I thought about giving up on finishing the PhD, but I could count not only with my family, but also with great colleagues and friends who kept telling me that I should and that I deserved to finish this work. People who not only believed in me, but also helped me in so many different ways throughout the years. I want to cite the friends from my lab: Cláudio Silveira, Thiago Cabral, Matheus Gomes, Matheus Rodrigues, Egont Schenkel and Murilo Santos; and from my collaboration labs: Gabriel Perli, Diego Bertuzzi, Francesco Amato, Thays Naves, Maria Fernanda Filippini, Bruna Gregatti, Franciele Vit, Rogerio Bataglioli and Gildo Rodrigues. Off course, I must mention my university(ies) friends: Beatriz Mendes, Paula Machado, Daniel Fernandes, Camila Oliveira, Gabriel Luz, Victor Dias, Vitor Anastácio and his wife Brunna Ardisson, Gabriel Campolina, Antonio Tomaz, Fabio "Zinho" Maia, Emerson Parazzi, Aline Miranda, Marina Ferreira, Leonardo Barddal, Yuri Olive, Bruna Rodrigues, Glauco Santiago, Lucas Pelegrini, Virgilio Santos, Guilherme Costa, Marina Martins, Bruna Miranda, Henrique Fiúza, Jean Rabelo, Eduardo Mocellin, Lucas "Uberaba" Facury, Bruno Bello, Paulo Oliveira, Gabriel Zaniboni and Lucas Fernandes; my former masters Airton Salles, Fernando Córes and André Medeiros, who always believed in me in my early days; and my "brothers in arms" Felipe Ferraz (I still owe a beer for helping me transition from Academy to the market), Otávio Rubião and Suzane Gaertner. Thank you all for each time you called me and insisted that I could not let it go. During those two lockdown years when I was isolated in Brasília, each one of you was by my side in a single special way. This work is also yours.

I know it is not the most usual thing, but I will also dedicate it to my dogs as well, my two Belgian shepherd Kitana and Jade. By the time I write this paragraph, you have almost 14, and 11 years old, respectively. Even though this hot November night may be the last one when both of you are still here with us, I will not regret about the lack of time we have. I will just be thankful for the time we were given. You cannot read it, but you were here with me from the beginning to the end of this journey. Specially during the pandemic, you were the best girls I could have by my side. My black wolves with such a will for living, a great Groenendael and a tiny Schipperke, you remember me the legend of Fenrir. By the end of the times, the Wolf would arrive and eat the Moon, the Earth and all of living things... But we should not be afraid, since everything that starts must end someday. It is not your case, though. You will live forever. You will stay forever in these pages and in my heart.

To finish it, a very brief thank to someone who was here from November 2022. Daniele, I know you did not want me to add you here, but you had a great importance pushing me

forward, inspiring me to perform important changes and overcome difficulties and fear. I also thank my daughter-in-law Catarina, and her parents Luis and Silvia Barbosa who took care of me when I was recovering from a surgery. At last, I dedicate this work to my father's uncle Aloisio Souza Costa, and to the memory of his wife, Maria do Socorro "Cecéu" Soares Souza, who left us by December 2022, but who I feel is still always with me. When I moved to São Paulo state in 2013, many times you were the family I had, and I will never forget you going to my undergraduate conclusion ceremony. You all in this paragraph are part of this family and have been a pillar for me in this life distant from my hometown.

To each one I mentioned here and to every other friend and person who gave me a small piece of contribution (some are in the chapters), thank you very much and sorry if I was unfair of not mentioning you or of not expressing all my gratitude to you in such a small space. You are all part of this, and I hope this work is worth of what you did for me.

> " If I have seen further, it is by standing upon the shoulders of giants." - Sir Isaac Newton

> > "Lasciate ogne speranza, voi ch'intrate." – Dante Alighieri

"Donde no llegan las pernas, va a llegar el corazón." – Hernán Crespo

Resumo

Atualmente, diversas técnicas e materiais estão disponíveis para a fabricação de fibras ópticas, guias de onda e sensores ópticos, mas ainda existem lacunas tecnológicas. Sensores com menores custos e menores dificuldades de fabricação, processamento de sinais e viabilidade; ou obtidos por metodologias menos agressivas como dispositivos biodegradáveis ou mais ecológicos são exigidos. No caso do monitoramento de processos químicos e bioquímicos, características inerentes às fibras ópticas como resistência ambiental e eletromagnética também são desejáveis, uma vez que condições térmicas, químicas e mecânicas severas geralmente estão presentes. Este trabalho propõe, então, o projeto e fabricação de materiais e dispositivos fotônicos nos quais nanotecnologia e tecnologia de fibra óptica são exploradas para obter processos mais sustentáveis e dispositivos com características interessantes para operação em linha. Novos nanomateriais fluorescentes da classe dos carbon nanodots (CDs, partículas com diâmetros da ordem de 10 nm ou menos) foram sintetizados a partir de três fontes naturais (xarope de cana-de-açúcar, suco de laranja e leite UHT), e as partículas à base de cana-deaçúcar foram ocluídas em uma matriz de hidrogel (gelatina) para serem introduzidas em uma fibra óptica polimérica microestruturada. Assim, um guia de onda capaz de emitir e conduzir luz visível foi fabricado como uma alternativa "verde" à incorporação de terras-raras e metais pesados na fabricação de fibras luminescentes. Outro hidrogel com melhores propriedades mecânicas (agarose) foi dopado com nanocompósitos de SiO2-CDs para obtenção de um sensor de pH fluorescente, biodegradável e biocompatível, útil na recuperação de informações para análise offline. Não bastasse, verificou-se que nanocompósitos CDs-PMMA podem ser combinados a células solares. Um aumento de 11.3% na eficiência de conversão das células foi observado, revelando um grande potencial para aplicações em optoeletrônica e energias renováveis. Sensores de fibra óptica também foram projetados e aplicados a importantes meios químicos e bioquímicos. Um sistema de sensoriamento capaz de detectar velocidade e índice de refração (IR) em misturas bifásicas gás-água, óleo-água e gás-óleo foi impresso (3D) como um dispositivo milifluídico com uma fibra com rede de Bragg inclinada, mostrando importantes aplicações em petroquímica. Um sensor de IR baseado em smartphone foi então projetado para a avaliação em tempo real de fermentadores em batelada alimentada. O projeto atende a alguns requisitos da "Indústria 4.0": o sensor é destinado ao monitoramento em campo e fabricação rápida no local, contando com um case simples impresso em 3D para acoplamento de fibras ópticas à câmera e ao LED do celular. Um aplicativo é então responsável por processar dados de intensidade de luz e correlacionar as variações de sinal ao IR do caldo fermentativo, função da concentração de sacarose segundo a lei de Fresnel. Finalmente, um sensor de espalhamento dinâmico da luz baseado em uma configuração de refletância de Fresnel totalmente óptica aplica redes neurais artificiais para detectar distúrbios de concentração e realizar a avaliação simultânea de concentração e velocidade de fluxo de nanofluidos. Esses nanofluidos foram obtidos pela síntese de nanopartículas de SiO₂ (diâmetro de 195 nm) e dispersão delas em água. Da química, petroquímica e mineração tradicionais aos alimentos e biotecnologia avançada, várias indústrias precisam lidar com nanofluidos e suspensões coloidais. Portanto, há uma gama de aplicações práticas importantes desse sensor no controle e monitoramento de instalações.

Palavras-Chave: Carbon nanodots; Fluorescência; Nanomateriais sustentáveis; Sensores de fibra óptica; Sensoriamento químico e bioquímico; Monitoramento de processos industriais; Redes neurais artificiais.

Abstract

Nowadays, several techniques and materials are available for the fabrication of optical fibers, waveguides and optic sensors, but technological gaps remain. Sensors with lower costs and minor difficulties of fabrication, signal processing, and feasibility; or obtained through lessaggressive methodologies as biodegradable or greener devices are demanded. In the case of chemical and biochemical process monitoring, characteristics inherent to optical fibers such as environmental and electromagnetic resistances are also desirable, once harsh thermal, chemical and mechanical conditions are usually present. This work proposes, then, the design and fabrication of photonic materials and devices where nanotechnology and fiber optic technology are explored to obtain more sustainable processes and devices with interesting characteristics for *inline* operation. New fluorescent nanomaterials from the class of carbon nanodots (CDs, particles with diameters in the order of 10 nm or less) were synthesized from three natural sources (sugarcane syrup, orange juice, and UHT milk), and the sugarcane-based particles were occluded into a hydrogel matrix (gelatin) for being introduced into a microstructured polymer optical fiber. So, a waveguide capable of emitting and conducting visible light was fabricated as a greener alternative to the incorporation of rare-earths and heavy metals on luminescent fibers manufacturing. Another hydrogel with better mechanical properties (agarose) was doped with SiO₂-CDs nanocomposites for obtaining a fluorescent, biodegradable and biocompatible pH sensor useful for retrieving information for offline analysis. Moreover, it was verified that CDs-PMMA nanocomposites can be combined with solar cells. An increase of 11.3% on the cell conversion efficiency was observed, revealing great potential for applications in optoelectronics and renewable energies. Fiber optic sensors were also designed and applied to important chemical and biochemical media. A sensing system capable of detecting velocity and refractive index (RI) in biphasic gas-water, oil-water and gas-oil mixtures was 3D-printed as a millifluidic device with an inserted tilted fiber Bragg grating, showing important applications on petrochemistry. A smartphone-based RI sensor was then designed for the real-time assessment of fed-batch fermentors. The project attends some "Industry 4.0" requirements: the sensor is destined to field monitoring and on-site fast fabrication, relying on a simple 3D-printed case for coupling optical fibers to the phone's camera and LED. Then, an application is responsible for processing light intensity data and correlating signal variations to the broth RI, which is function of the sucrose concentration according to Fresnel law. Finally, a dynamic light scattering sensor based on an all-optic Fresnel reflectance setup applies artificial neural networks for detecting concentration disturbances and performing the simultaneous assessment of concentration and flow speed of nanofluids. These nanofluids were obtained by synthesizing SiO₂ nanoparticles (diameter of 195 nm) and dispersing them in water. From traditional chemical, petrochemical, and mining to food and advanced biotechnology, several industries must deal with nanofluids and colloidal suspensions, so there is a range of important practical applications of this sensor on facilities control and monitoring.

Keywords: Carbon nanodots; Fluorescence; Sustainable nanomaterials; Fiber optic sensors; Chemical and Biochemical sensing; Industrial process monitoring; Artificial neural networks.

List of Abbreviations

a: Average Diameter of the Particles (*diffusivity evaluation*) A: absorbance for the samples at low concentration (quantum yield formula) **AFM:** Atomic Force Microscopy **ANN:** Artificial Neural Networks **APTES:** 3-aminopropyltriethoxysilane a-SiO₂: Amino-Functionalized Silica Nanoparticles **C:** Carbon Nanodots (*quantum yield formula*) **CDs:** Carbon Nanodots C: initial concentration of particles in sedimentation process **D**_{AB}: Diffusion Coefficient (Diffusivity) of a Particle A in a Solvent B **DI Water:** Deionized Water **DLS:** Dynamic Light Scattering **DMF:** Dimethylformamide **DSC:** Dye-Sensitized Solar Cell **EDA:** Ethylenediamine EDC·HCI: 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride **ELISA:** Enzyme-Linked Immunosorbent Assay **EQE:** External Quantum Efficiency **F**^(1st appearance): Area under the Curve at 350 nm-Fluorescence (quantum yield formula) *F*^(2nd appearance): Feed Flow (*fed-batch fermentation modelling*) FBG: Fiber Bragg Grating **FEG-TEM:** Transmission Electron Microscopy Using a Field-Emission Gun FTIR: Fourier Transform Infrared Spectroscopy FF: Fill Factor FWHM: Full Width at Half-Maximum **GC:** Gas Chromatography GC-MS: Gas Chromatography Coupled to Mass Spectrometry *h*: Planck's constant **h(t):** Height from the Bottom of a Tube to the Beginning of the Clarified Zone (*sedimentation*) HPLC: High-Performance Liquid Chromatography I: Electric Current

IDE: Integrated Development Environment **I(t):** Reflected Light Intensity (*Fresnel Law*) **IR:** Reference Light Intensity (*Fresnel Law*) **IR:** Infrared Isc: Short-Circuit Current Jsc: Short-Circuit Current Density **k:** Boltzmann constant $(1.38 \times 10^{-23} \text{ m}^2 \cdot \text{kg} \cdot \text{s}^{-2} \cdot \text{K}^{-1})$ *K_M*: Monod Constant L: Tube Characteristic Dimension LDS: Luminescent Down Shifting LDV: Laser Doppler Velocimetry LED: Light-Emitting Diode LG: Grating Length LSC: Luminescent Solar Concentrator LPG: Long-Period Grating MAE: Mean Absolute Error MMF: Multi-Mode Silica Optical Fiber m_p : Product Formation Rate Not Associated to the Cellular Growth mPOF: Microstructured Polymer Optical Fiber m_s : Substrate Consumption Rate Associated to the Metabolic Activities **MWCO:** Molecular Weight Cut-Off **n**_i: Index of Refraction from Medium *i* NA: Numerical Aperture NCNDs: Nitrogen-Doped Carbon Nanodots **NIR:** Near Infrared NHS: N-hydroxysuccinimide **OFS:** Optical Fiber Sensor **OSA:** Optical Spectrum Analyzer **OSC:** Organic Solar Cell **P:** Product Concentration **PDA:** Particle Dynamic Analysis **PDF:** Probability Density Function **Pe:** Peclet Number

PEG: Polyethylene Glycol **PETG:** Glycol-Modified Polyethylene Terephthalate **P**_{in}: Incident Irradiance Power **PL:** Photoluminescence **PMMA:** Poly(methylmethacrylate) **POF:** Polymer Optical Fiber **PVA:** Polyvinyl Alcohol q: Magnitude of the Scattering Vector **QDs:** Quantum Dots Q:: Flow Rate of a Phase i (i = D for Dispersed; or i = C for Continuous Phase) q_p : Specific Rate of Product Formation QY: Quantum Yield **R:** Reference Sample (quantum yield formula) **RI:** Refractive Index **RIU:** Refractive Index Units **S:** Substrate Concentration SEM: Scanning Electron Microscope S_F : Substrate Concentration (Feed Solution) Silica-Cdots: SiO₂-(Carboxylic Acid Terminated Carbon Nanodots) nanocomposite SMF: Silica Single-Mode Fiber **SNR:** Signal-to-Noise Ratio T: System's Temperature **TEM:** Transmission Electron Microscopy **TFBG:** Tilted Fiber Bragg Grating **TGA:** Thermogravimetric Analysis u: Flow Velocity **UHT:** Ultra-High Temperature Processed Milk **UV:** Ultraviolet UV-Vis: UV-Visible Absorbance V (1st appearance): Voltage (solar cell analysis) *V* ^(2nd appearance): Instant Volume of Fermentation Broth (*fed-batch fermentation modelling*) VAD: Vapor-phase Axial Deposition Voc: Open-Circuit Voltage

w: Beam Radius of The Light Source X: Cells' Concentration **XPS:** X-ray Photoelectron Spectroscopy **XRD:** X-ray Diffratometry $Y_{P/X}$: Theoretical Yield of Product Formation per Cell Reproduction **YPD:** Yeast-Peptone-Dextrose Medium $Y_{X/S}$: Theoretical Yield of Cell Reproduction Per Substrate Uptake a-CDs: Carboxylic Acid Terminated Carbon Nanodots Γ_m : Average Decay Rate η (1st appearance): Index of Refraction (quantum yield formula) η ^(2nd appearance): Efficiency of the Solar Cell (solar cell's efficiency formula) λ_B: Bragg Wavelength **Λ**: Grating Period μ: Specific Cell Growth Rate μ_B: Dynamic Viscosity of the Fluid μ_m : Maximum Specific Growth Rate μ_s : Specific Rate of Substrate Consumption vi: Frequency from a photon *i* τ : Arbitrary Delay Time

List of Figures

Figure 1. Schematic representation of the new methodology developed to obtain CDs from sugarcane syrup; chemical structures of the major components of sugarcane syrup; schematic representation of the resulting CDs; and FTIR spectrum of the CDs with the assignment of the most important bands
Figure 2 . (a) Pictures of the obtained pure CDs as a solid (left) and in aqueous solution (right, falcon tube); (b) pictures of the obtained pure CDs as a solid (left) and in aqueous solution (right, falcon tube) under UV light (254 nm)46
Figure 3. (a) DLS data obtained for CDs in aqueous solution; (b) 2D AFM height image of CDs deposited on a mica surface; (c) 3D topographic AFM image of CDs deposited on a mica surface (scale bar from zero to 5.8 nm)
Figure 4. (a) UV-Vis absorbance spectrum of the CDs in aqueous solution; (b) UV-Vis absorbance spectra of hydrogel and hydrogel-CDs nanocomposite; (c) emission spectra of the CDs in aqueous solution; (d) emission spectra of the hydrogel-CDs nanocomposite
Figure 5. Newly developed design of double-clad optical fiber (quotes in millimeters) 50
Figure 6. Setup for evaluation of the mPOF fluorescence and a micrograph of the fiber's cross section
Figure 7. Fluorescence emitted by the mPOF with the nanocomposite of gelatin-CDs53
Figure 8. CDs obtained from orange juice: (A) AFM; (B) 3D-profile of AFM; and (C) fluorescence spectra. CDs obtained from UHT milk: (D) fluorescence spectra (inset shows the spectra under a different scale); (E) AFM; and (F) 3D-profile of AFM. Suspensions compared: (G) under daylight (upper figures) and when emitting green fluorescence under 254 nm (bottom figures; orange juice-derived CDs on the left); (H) FTIR spectra
Figure 9. Synthesis routes of α -CDs; amino-terminated SiO ₂ nanoparticles; and hybrids of α -CDs coupled to a-SiO ₂
Figure 10. Different visual aspects observed for the nanoparticles
Figure 11. TEM images of Silica-Cdots aggregates (~50 nm) and primary particles (~6 nm).
Figure 12 . Micrographs of α -CD primary nanoparticles, with sizes between ~4 nm and ~10 nm: (A) TEM image; (B); (C); and (D): negative stained FEG-TEM images (color inverted to facilitate viewing)
Figure 13. TEM images of a-SiO ₂ aggregates and primary particles (magnifications: (A) 63 x 10 ³ times; (B) 80 x 10 ³ times)
Figure 14. TEM images of silica-Cdots aggregates and primary particles (magnifications: (A) 50×10^3 times; (B) 32×10^3 times)
Figure 15. UV-Vis absorption spectra from α -CDs (in red) and from silica-Cdots (blue)67
Figure 16. XRD patterns of the SiO ₂ , a-SiO ₂ , α-CDs and silica-Cdots nanoparticles
Figure 17. FTIR spectra collected for fumed silica, amino-functionalized silica, α-CDs, and silica-Cdots

Figure 18. Comparison between FTIR spectra of SiO ₂ and a-SiO ₂
Figure 19. Comparison between FTIR spectra of a-SiO ₂ and silica-Cdots
Figure 20. Comparison between FTIR spectra of α-CDs and silica-Cdots
Figure 21. Raman spectra (@ 532 nm) of the α -CDs and silica-Cdots nanoparticles71
Figure 22. TGA of nanoparticles of fumed silica, amino-functionalized silica, and silica-Cdots hybrids
Figure 23. (A) XPS spectrum for a-SiO ₂ ; and XPS high resolution spectra: (B) C1s; (C) N1s; (D) O1s; (E) Si2p obtained for a-SiO ₂
Figure 24. (A) XPS spectrum for α-CDs; and XPS high resolution spectra: (B) C1s; (C) O1s obtained for α-CDs74
Figure 25. (A) XPS spectrum for silica-Cdots; and XPS high resolution spectra: (B) C1s; (C) N1s; (D) O1s; (E) Si2p obtained for silica-Cdots
Figure 26. Fluorescence spectra of (A) α-CD; and (B) silica-Cdots76
Figure 27. (A) Setup for the pH evaluation using the aqueous hybrids dispersions; (B) wavelength of maximum emitted fluorescence as function of pH for the dispersions of hybrids. The inset shows the linear portion of the curve (pH ranging from 6 to 10)77
Figure 28. Assembled system with aqueous dispersions of silica-Cdots under UV-excitation, and under daylight (inset)
Figure 29. Agarose waveguide doped with the hybrids
Figure 30 . (A) Emission spectrum of the light source. (B) Intensity of light transmitted by the waveguides (excitation with the supercontinuum laser). The dashed region corresponds to the fluorescence of the hybrids
Figure 31 . (A) General aspect of the agar waveguide; (B) cross-section of the agar waveguide; (C) agar waveguide transmitting the supercontinuum laser; (D) general aspect of the waveguide with occluded silica-Cdots hybrids; (E) cross-section of the waveguide with occluded hybrids; and (F) waveguide with occluded hybrids transmitting the supercontinuum laser
Figure 32 . Refractive index of the waveguide as function of the agar concentration in the liquid precursor. The variation is in the order of only 10 ⁻⁴ refractive index units (RIU)
Figure 33. (A) Comparison between the fluorescence spectrum collected for silica-Cdots dispersed in water and the spectrum obtained for particles occluded into agarose (excitation of 403 nm and pH 4.3). A clear red-shift of the peak's wavelength is observed. (B) Wavelength of maximum emitted fluorescence as function of pH observed for the agar waveguide. The inset shows the linear portion of the curve (pHs from 6 to 10)
Figure 34 . (a) Scheme of formation of blue-emitting NCNDs; (b) brown-colored solution obtained after microwave-assisted synthesis; (c) yellow solution obtained after filtering; and (d) emission of blue fluorescence by the filtered solution when it is irradiated at 365 nm UV light
Figure 35. Lyophilized α -CDs (5 wt%) dispersed in a mixture comprised of chloroform and

Figure 35. Lyophilized α -CDs (5 wt%) dispersed in a mixture comprised of chloroform and methanol (proportion of 2:1 (v/v)) observed under: (a) daylight; (b) UV light ($\lambda = 365$ nm). 96

Figure 40. PL spectra: (a) PMMA pristine film; and different volumetric proportions of chloroform to methanol for producing PMMA-NCNDs nanocomposites (0.1 wt% of CDs). Proportions of: (b) 2:1 (selected as standard); (c) (3.3):1; and (d) 4:1 (v/v)......100

Figure 44. Different optical films observed under: (a) daylight; (b) UV light ($\lambda = 365$ nm).

Figure 45. (a) Absorbances; and (b) transmittances obtained for the different optical films.

Figure 55. Out-of-scale representation of a droplet reaching and completely leaving the TFBG sensing region from the optical fiber. The time comprised between the beginning and end of each sensing peak (peak width) is the interval needed for one droplet to go through the distance $L_G + L$. This distance should be used when there is no clear (resolved) signal maximum....121

Figure 60. Out of scale representation of the competition between the flow drag forces (blue arrows) and the Brownian random motion (red arrows) from a SiO₂ nanoparticle in water. The water flows with velocity "u", and the nanoparticle has diameter "a" and diffusivity D_{AB}...135

Figure 64. (a) Average values of the heights verified for the two tubes and concentrations estimated from Equation (13) (secondary vertical axis); (b) sequential step disturbances in the concentration detected by the OFS probe; (c) $G_2(\tau)$ obtained for Zone 1, as function of the

List of Tables

Table 1. Atomic percentages of samples obtained by high-resolution XPS spectr	a75
Table 2 . Photovoltaic data obtained for the two tested solar cells covered with PMMA-NCNDs optical films.	h pristine and 107
Table 3. Droplets lengths' L verified for each q ratio.	119
Table 4. Comparison between Monod predictions and S values calculate methodology.	d from each

Table of Contents

Preface and List of Publications
1. Introduction
2. Design of Photonic Materials and Applications: Carbon Nanodots and their Combination with Polymer Matrices
2.1. Motivation
2.2. Principles of Fluorescence of Carbon Nanodots41
2.3. Synthesis and Application of Carbon Nanodots from Sugarcane Syrup41
2.3.1. Introduction
2.3.2. Sugarcane syrup carbon dots synthesis and characterization
2.3.3. Preparation of hydrogel-CDs nanocomposites and photophysical characterization
2.3.4. Fabrication of Fluorescent Microstructured Polymer Optical Fibers (mPOF).49
2.3.5. Quantum Yield (QY) evaluation
2.3.6. Conclusions from this study
2.3.7. Contributions and acknowledgements
2.4. Synthesis of Carbon Nanodots from Orange Juice and UHT Milk55
2.4.1. Introduction
2.4.2. Synthesis and characterization of carbon nanodots
2.4.3. Conclusions from this study
2.4.4. Contributions and acknowledgements
2.5. Design and Application of Agarose-Based Fluorescent Waveguide with Embedded Silica Nanoparticle-Carbon Nanodot Hybrids for pH Sensing
2.5.1. Introduction
2.5.2. Silica-Cdots nanohybrids synthesis and characterization
2.5.3. Photophysical characterization76
2.5.4. Application of aqueous suspensions of hybrids on pH sensing76
2.5.5. Design and fabrication of agarose waveguide doped with hybrids80
2.5.6. Application of the doped agarose waveguide on pH sensing
2.5.7. Conclusions from this study
2.5.8. Contributions and acknowledgements90
2.6. Fabrication of fluorescent PMMA-Carbon Nanodots nanocomposites: improving the efficiency of solar cells through sustainable low-cost materials

	2.6.1.	Introduction	92
	2.6.2.	Nitrogen-doped carbon nanodots synthesis	93
	2.6.3.	α-CDs and Silica-Cdots hybrids production	94
	2.6.4.	Preparation of doped-PMMA optical films	96
	2.6.5.	Films' fluorescence and photovoltaic characterizations	97
	2.6.6.	Characterization of films fluorescence emission	99
	2.6.7.	Screening of the photovoltaic properties	103
	2.6.8.	Conclusions from this study	107
	2.6.9.	Contributions and acknowledgements	108
3.	Desig	n and Application of Fiber Optic Chemical and Biochemical Sensors	109
3	5.1. N	Motivation	109
3	.2. N	Monitoring of biphasic flow with tilted fiber Bragg grating optical sensor	110
	3.2.1.	Introduction	111
	3.2.2.	Droplets formation on biphasic milli- and microfluidic devices	112
	3.2.3.	TFBG detection principles	113
	3.2.4.	Sensor design and measurement setup	115
	3.2.5.	Multiphase flow assessment	119
	3.2.6.	Conclusions from this study	123
	3.2.7.	Contributions and acknowledgements	123
3	5.3. I	Portable smartphone-based optical fiber sensor for fermentation monitoring	124
	3.3.1.	Introduction	124
	3.3.2.	Fermentation process modelling and monitoring	125
	3.3.3.	Smartphone optical fiber sensor design and fabrication	127
	3.3.4.	Obtention of calibration curve and fed-batch fermentation monitoring	129
	3.3.5.	Conclusions from this study	132
	3.3.6.	Contributions and acknowledgements	132
3 d	.4. I lynamic	Dynamic light scattering optical fiber sensor for monitoring nanofluids in state conditions	tic and 133
	3.4.1.	Introduction	133
	3.4.2.	DLS and mass transfer fundamentals	135
	3.4.3.	Silica nanoparticles synthesis and characterization	137
	3.4.4.	Optical fiber sensor setup	139
	3.4.5.	Monitoring of nanofluids concentration disturbances	140
	3.4.6.	Simultaneous assessment of nanofluids concentrations and velocities	147

	3.4.7.	Conclusions from this study	
	3.4.8.	Contributions and acknowledgements	
4.	Conclusio	ons	
5.	Reference	es	
Apj (Fig	pendix 1: 2 g. 57)	3D-printed case for smartphone-based fermentation sensor - Proje	ct's blueprint
Ap	pendix 2: S	Silica nanoparticles (Fig. 61) statistics	
Ap	pendix 3: S	Supervised students	

Preface and List of Publications

This thesis is comprised of *11 peer-reviewed publications listed and numbered below*: 2 patents; 3 international conference proceedings papers indexed in IEEE, Scopus or Web of Science; and 6 full international scientific journal articles. It is divided into two main sections, each one with its own motivation and containing several subsections. Each section may be read completely independently: it represents a given study published as one or more papers and contains its own introduction, methodology and conclusions.

Firstly, section "2. Design of Photonic Materials and Applications: Carbon Nanodots and their Combination with Polymer Matrices" explores the publications [1] to [7] below, presenting the design of photonic materials based on carbon nanodots and their applications. Firstly, [1] and [2] show the synthesis of green-fluorescent carbon nanodots from sugarcane syrup. Then, publication [3] demonstrates how this method can be extended to incorporate CDs into gelatin matrices, allowing the immobilization of the nanomaterials into a microstructured polymer optical fiber (mPOF) holes. This process is a sustainable alternative to the incorporation of rare-earths and heavy metals when fabricating luminescent fibers. After that, [4] demonstrates how this CDs synthesis from sugarcane syrup can be adapted to obtain fluorescent nanoparticles from milk and from orange juice, broadening the portfolio of sustainable raw materials that may be used.

Continuing the carbon nanodots work, article [5] presents a biodegradable and biocompatible hydrogel (agarose) waveguide where hybrid silica-carbon nanodots particles were occluded. This material was used for fabricating a soft and permeable pH-sensor based on the shift of luminescent emission. This sensor is capable of retrieving information for posterior offline analysis, an important feature for biochemical and biomedical applications. Finally, publications [6] and [7] demonstrate the use of acrylic-based nanodots nanocomposites for optoelectronic applications. These materials were used for coating photovoltaic cells, resulting in a significant increase on the energy conversion efficiency. It is an improvement that could be translated into enormous potential gains on large-scale solar (renewable) energy systems.

Section "3. Design and Application of Fiber Optic Chemical and Biochemical Sensors" shifts the effort from the development of photonic materials to the design of photonic sensors based on silica optical fibers. Firstly, publications [8] and [9] present a 3D-printed millifluidic device with a tilted fiber Bragg grating sensor used for the simultaneous assessment of velocity and refractive index on biphasic systems (air-in-oil, water-in-oil and water-in-air suspensions). Such systems are present in many petrochemical processes where this sensor can be leveraged. Then, [10] shows the development of a portable smartphone-based optical fiber sensing platform for the online monitoring of fed-batch fermentation systems. This setup may be produced on-site through 3D-printing and can be economically and industrially explored in the context of "*Industry 4.0*". Finally, article [11] demonstrates a dynamic light scattering sensor that applies artificial neural networks and a simplified all-optic Fresnel reflectance setup for nanofluids' concentration and flow speed evaluation. Several industries must deal with nanofluids and colloidal suspensions, so it is a system with a range of important practical applications on facilities control and monitoring.

Publications discussed in this thesis (mentioned above, in order of appearance in the text):

[1] SOARES, Marco César Prado; PERLI, Gabriel; FUJIWARA, Eric; BARTOLI, Julio Roberto; ORNELAS MEGIATTO, Cátia Cristina Capêlo; BERTUZZI, Diego Luan; SUZUKI, Carlos Kenichi. Processo de Produção de Nanopartículas Fluorescentes de Carbono a Partir de Derivados da Cana-De-Açúcar e Uso Dessas Nanopartículas. Universidade Estadual de Campinas, 2019. Processo BR 10 2019 014881 0. Data de depósito: 19/07/2019. In: https://patentscope.wipo.int/search/en/detail.jsf?docId=BR318494329& cid=P20-KRH3FL-47876-1. Informações em: https://patentes.inova.unicamp.br/item/1402 fluorescentes/.

Type: Patent

My contributions: project and methodology design with G. Perli, J. R. Bartoli and E. Fujiwara, nanoparticles fabrication, patent writing, conduction of experiments, data analysis, discussion of the results.

[2] <u>Marco C. P. Soares</u>, Gabriel Perli, Júlio R. Bartoli, Diego L. Bertuzzi, Thiago B. Taketa, Rogério A. Bataglioli, Carlos K. Suzuki, Cátia C. C. Ornelas, and Eric Fujiwara. Fast Microwave-Assisted Synthesis of Green-Fluorescent Carbon Nanodots from Sugarcane Syrup. In: IEEE Proceedings: 2019 SBFoton International Optics and Photonics Conference (SBFoton IOPC 2019), Oct 7-Oct 9; São Paulo, SP, Brazil. <u>https://doi.org/10.1109/SBFoton-IOPC.2019.8910216</u>.

Type: Conference Proceedings Paper (In: IEEE, Scopus and Web of Science)

My contributions: project and methodology design with G. Perli, J. R. Bartoli and E. Fujiwara, nanoparticles fabrication, paper writing, conduction of experiments, data analysis, discussion of the results.

[3] Gabriel Perli, <u>Marco C. P. Soares</u>, Thiago D. Cabral, Diego L. Bertuzzi, Julio R. Bartoli, Sébastien Livi, Jannick Duchet-Rumeau, Cristiano M. B. Cordeiro, Eric Fujiwara and Catia Ornelas. Synthesis of Carbon Nanodots from Sugarcane Syrup, and Their Incorporation into a Hydrogel-Based Composite to Fabricate Innovative Fluorescent Microstructured Polymer Optical Fibers. **Gels**, 8(9), 553, 1 September 2022. <u>https://doi.org/10.3390/gels8090553</u>.

Type: Journal Article

My contributions: project and methodology design with G. Perli, J. R. Bartoli (carbon nanodots); T. D. Cabral, E. Fujiwara and C. M. B Cordeiro (optical fibers), contextualization of optics and hydrogel applications, nanoparticles and hydrogel fabrication, paper writing, conduction of optical fiber and nanoparticles experiments with T. D. Cabral, data analysis review, discussion of the results.

[4] <u>Marco C. P. Soares</u>, Gabriel Perli, Diego L. Bertuzzi, Thiago D. Cabral, Cristiano M. B. Cordeiro, Cátia C. C. Ornelas, Julio R. Bartoli, Eric Fujiwara. One-Step Synthesis of Fluorescent Carbon Nanodots from Two Widely Available Natural Sources. In: **Optics InfoBase Conference Papers, OSA Advanced Photonics Congress** (AP) 2020 (IPR, NP, NOMA, Networks, PVLED, PSC, SPPCom, SOF), 13-16 July. L. Caspani, A. Tauke-Pedretti, F. Leo, and B. Yang, eds., **OSA Technical Digest (Optica, Formerly Optical Society of America, OSA, 2020)**, paper JTh3G.4. From the session LEDs, Lasers and Flourescing Materials (Joint NOMA/PVLED session), JTh3G. Presentation in: https://youtu.be/MuUxDCXP1Z0. https://doi.org/10.1364/NOMA.2020.JTh3G.4.

Type: Conference Proceedings Paper (In: Optica (formerly OSA), Optics InfoBase, and Scopus)

My contributions: project and methodology design with G. Perli, J. R. Bartoli and E. Fujiwara, nanoparticles fabrication, paper writing, conduction of experiments, data analysis, discussion of the results.

[5] Francesco Amato, <u>Marco César Prado Soares</u>, Thiago Destri Cabral, Eric Fujiwara, Cristiano Monteiro de Barros Cordeiro, Alejandro Criado, Maurizio Prato, and Julio Roberto Bartoli. Agarose-

Based Fluorescent Waveguide with Embedded Silica Nanoparticle–Carbon Nanodot Hybrids for pH Sensing. ACS Applied Nano Materials, 4, 9, 9738–9751, August 20, 2021. https://doi.org/10.1021/acsanm.1c02127.

Type: Journal Article

My contributions: project and methodology design of the agarose-based pH sensor with T. D. Cabral, J. R. Bartoli, E. Fujiwara and C. M. B. Cordeiro, contextualization of hydrogel and optics applications, hydrogel waveguide fabrication, paper writing, conduction waveguide and pH sensing experiments with T. D. Cabral, data analysis review, discussion and compiling of the results.

[6] <u>Marco Soares</u>, Francesco Amato, Thiago Cabral, Michele Cacioppo, Marcelo Carreño, Inés Pereyra, Carlos Ramos, Manuel Cid, Gilson Goveia, José Chubaci, Maurizio Prato, Julio Bartoli, and Eric Fujiwara. Improving Solar Cells Efficiency with PMMA-Carbon Dots Nanocomposites. In: IEEE Proceedings: 2023 International Conference on Optical MEMS and Nanophotonics (OMN) and SBFoton International Optics and Photonics Conference (SBFoton IOPC), 31 Jul. - 03 Aug.; Campinas, SP, Brazil. <u>https://doi.org/10.1109/OMN/SBFotonIOPC58971.2023.10230988</u>.

Type: Conference Proceedings Paper (In: IEEE, Scopus and Web of Science)

My contributions: project and methodology design with J. R. Bartoli, M. Carreño, I. Pereyra and F. Amato, paper writing, data analysis, discussion of the results.

[7] <u>Marco C. P. Soares</u>, Michele Cacioppo, Francesco Amato, Thiago D. Cabral, Marcelo N. P. Carreño, Inés Pereyra, Carlos A. S. Ramos, Manuel Cid, Gilson S. Goveia, José F. D. Chubaci, Eric Fujiwara and Julio R. Bartoli. Fabrication of fluorescent PMMA-carbon nanodots optical films and their feasibility in improving solar cells efficiency using low-cost sustainable materials. **Brazilian Journal of Chemical Engineering**, 2023. <u>https://doi.org/10.1007/s43153-023-00408-w</u>.

Type: Journal Article

My contributions: project and methodology design with J. R. Bartoli, M. Carreño, I. Pereyra and F. Amato, paper writing, data analysis, discussion of the results.

[8] CORDEIRO, Cristiano Monteiro de Barros; ARISTILDE, Stenio; SOARES, Marco César Prado; FUJIWARA, Eric; RODRIGUES, Gildo Santos; FRUETT, Fabiano. Sistema Óptico Para Caracterização de Escoamento Multifásico em Tubulações e Processo de Análise de Tubulações para a Caracterização de Escoamento Multifásico. Universidade Estadual de Campinas, 2019. 2019 020966 Processo BR 10 6. Data de depósito: 04/10/2019. In: https://patentscope.wipo.int/search/en/detail.jsf?docId=BR323741005& cid=P20-KRH3FL-47876-1. Informações em: https://patentes.inova.unicamp.br/item/1463 flow/.

Type: Patent

My contributions: experiments design, chemical, industrial and fluidodynamics contextualization, patent writing, conduction of sensing experiments with S. Aristilde, data analysis review, discussion and compiling of the results.

[9] Stenio Aristilde, <u>Marco Soares</u>, Thiago Cabral, Gildo Rodrigues, Eric Fujiwara, Fabiano Fruett, Cristiano Cordeiro. Measurement of Multiphase Flow by Tilted Optical Fiber Bragg Grating Sensor. **IEEE Sensors Journal**, v.21, n.2, pp.1534-1539, 2021. <u>https://doi.org/10.1109/JSEN.2020.3016616</u>.

Type: Journal Article

My contributions: experiments design, chemical, industrial and fluidodynamics contextualization, paper writing, conduction of sensing experiments with S. Aristilde and T. D. Cabral, data analysis review, discussion and compiling of the results.

[10] <u>Marco César Prado Soares</u>, Thiago Destri Cabral, Pedro Machado Lazari, Matheus dos Santos Rodrigues, Gildo Santos Rodrigues, and Eric Fujiwara. Smartphone-Based Optical Fiber Sensor for the Assessment of a Fed-Batch Bioreactor. Engineering Proceedings, v.2, n.1, pp.26, 2020. Available online: <u>https://ecsa-7.sciforum.net/</u>. At: <u>https://youtu.be/yv1KQfVwpA0</u>. <u>https://doi.org/10.3390/ecsa-7-08157</u>.

Type: Journal Article

My contributions: project and methodology design with T. D. Cabral and E. Fujiwara, biochemical and industrial contextualization, guiding and supervision of students P. M. Lazari, M. S. Rodrigues and G. S. Rodrigues, paper writing, data analysis review, discussion and compiling of the results.

[11] <u>M. C. P. Soares</u>, M. S. Rodrigues, E. A. Schenkel, G. Perli, W. H. A. Silva, M. K. Gomes, E. Fujiwara, and C. K. Suzuki. Evaluation of silica nanofluids in static and dynamic conditions by optical fiber sensor. **Sensors**, v.20, n.3, pp.707, 2020. <u>https://doi.org/10.3390/s20030707</u>.

Type: Journal Article

My contributions: project and methodology design with M. S. Rodrigues and E. Fujiwara, chemical, industrial, fluidodynamics and mass transfer contextualization, guiding and supervision of students M. S. Rodrigues, W. H. A. Silva and M. K. Gomes, paper writing, data analysis review, discussion and compiling of the results.

Other works published during activities in the Laboratory of Photonic Materials and Devices (in chronological order):

School of Mechanical Engineering, University of Campinas, SP, Brazil, supervision of Prof. Eric Fujiwara and Prof. Carlos K. Suzuki

Academic Awards

[1] 3rd-Place Student Paper Award SBFoton International Optics and Photonics Conference (SBFoton IOPC 2019, October 7-9th, 2019, São Paulo, Brazil). Awarded paper: "Online Monitoring of Cell Growth on PDMS Reversible Microfluidic Bioreactor Integrated to Optical Fiber Sensor". IEEE Photonics Society, 2019.

[2] INOVA Scientific Initiation Award ("Prêmio INOVA de Iniciação Científica", undergraduate research award) 2016, "Technological" ("Tecnológicas") category. Awarded Paper: "Use of Optical Fiber Sensor and Design of Experiments Statistical Methodology for Improving Dye Retention in a Quartz Ceramic Porous Material". INOVA UNICAMP Innovation Agency, University of Campinas, SP, Brazil, 2016.

Patents

SOARES, Marco César Prado;FUJIWARA, Eric; SUZUKI, Carlos Kenichi. Método deQuantificação de Partículas. Universidade Estadual de Campinas, 2017. Processo BR 10 2017 0251926.Datadedepósito:23/11/2017.In:https://patentscope.wipo.int/search/en/detail.jsf;jsessionid=D42FAC7C77C9361FBC8B9E2DF7A213E1.wapp2nA?docId=BR246645263&_cid=P20-KBA709-87308-9.Informaçõesem:https://patentes.inova.unicamp.br/item/1250dls/.Metodo deCarlos Marco César Prado;Metodo de

[2] <u>SOARES, Marco César Prado</u>; VIT, Franciele; FUJIWARA, Eric; DE LA TORRE, Lucimara Gaziola. **Dispositivo Microfluídico para Sensoriamento Óptico**. Universidade Estadual de Campinas, 2019. Processo **BR 10 2019 020984 4**. Data de depósito: 04/10/2019. In: <u>https://patentscope.wipo.int/search/en/detail.jsf?docId=BR323741012&_cid=P20-KRH3FL-47876-1</u>. Informações em: <u>https://patentes.inova.unicamp.br/item/1414_microfermentador/</u>.

[3] PERLI, Gabriel; BRAGA, Carolyne Brustolin; BERTUZZI, Diego Luan; SOARES, Marco César Prado; ORNELAS MEGIATTO, Cátia Cristina Capêlo. Processo de Obtenção de Nanocápsulas Antimicrobianas e Nanocápsulas Antimicrobianas. Universidade Estadual de Campinas, 2020. Processo BR 10 2020 026307 2. Data de depósito: 21/12/2020. In: https://patentscope.wipo.int/search/en/detail.jsf?docId=WO2022133561& cid=P11-LA12YK-21497-1. Informações em: https://patentes.inova.unicamp.br/item/1599 nanoparticula/.

[4] PERLI, Gabriel; BRAGA, Carolyne Brustolin; BERTUZZI, Diego Luan; <u>SOARES, Marco César</u> <u>Prado</u>; ORNELAS MEGIATTO, Cátia Cristina Capêlo. International Patent: WO2022133561 -Method for Obtaining Antimicrobial Nanocapsules, and Antimicrobial Nanocapsules. International Filing Date: 29 Nov. 2021. Publication Date: 30 Jun. 2022. Universidade Estadual de Campinas, World Intellectual Property Organization, WIPO. In: <u>https://patentscope.wipo.int/search/en/detail.jsf?docId=WO2022133561&_cid=P11-LA12YK-21497-</u> <u>1</u>. Info in: <u>https://patentes.inova.unicamp.br/item/1599_nanoparticula/</u>.

Journal Articles

[1] <u>M. C. P. Soares</u>, B. F. Mendes, E. A. Schenkel, M. F. Santos, E. Fujiwara, and C. K. Suzuki. Kinetic and thermodynamic study in pozzolanic chemical systems as an alternative for Chapelle test. **Materials Research - Ibero-American Journal of Materials**, v.21, n.4, pp.e20180131, 2018. https://doi.org/10.1590/1980-5373-MR-2018-0131.

[2] <u>Marco César Prado Soares</u>, Franciele Flores Vit, Carlos Kenichi Suzuki, Lucimara Gaziola de la Torre, and Eric Fujiwara. Perfusion Microfermentor Integrated into a Fiber Optic Quasi-Elastic Light Scattering Sensor for Fast Screening of Microbial Growth Parameters. **Sensors**, vol.19, n.11, pp.2493, 2019. <u>https://doi.org/10.3390/s19112493</u>.

[3] <u>M. C. P. Soares</u>, M. K. Gomes, E. A. Schenkel, M. S. Rodrigues, C. K. Suzuki, L. G. la Torre, and E. Fujiwara. Evaluation of Silica Nanoparticles Colloidal Stability with Fiber Optic Quasi-Elastic Light Scattering Sensor. **Brazilian Journal of Chemical Engineering**, v.36, n.4, pp.1519-1534, 2019. https://doi.org/10.1590/0104-6632.20190364s20190042.

[4] Brino Ruy Negri, Antonio Carlos Luz Lisboa, Julio Roberto Bartoli, <u>Marco César Prado Soares</u>. Estudo sobre Sistemas de Baixo Custo para Aquecimento de Água por Energia Solar Utilizando Coletores Solares e Reservatórios Térmicos à base de Materiais Poliméricos. Revista Brasileira de Energia Solar, v.10, n.2, pp.111-120, 2019. ISSN: 2526-2831. In: https://rbens.emnuvens.com.br/rbens/article/view/285. https://doi.org/10.13140/RG.2.2.19957.50406.

[5] Clarissa Cruz; Thiago Lima; <u>Marco Soares</u>; Emmanuelle Freitas; Eric Fujiwara; Amauri Garcia; and Noé Cheung. Effect of microstructure features on the corrosion behavior of the Sn-2.1 wt%Mg solder alloy. Electronic Materials Letters, v.16, pp.276-292, 2020. <u>https://doi.org/10.1007/s13391-020-00202-7</u>.

[6] <u>Marco C. P. Soares</u>, Egont A. Schenkel, Beatriz F. Mendes, Eric Fujiwara, Murilo F. M. Santos, Gabriel Perli, and Carlos K. Suzuki. Vapor-Phase Axial Deposition Synthesis of SiO₂ and SiO₂-TiO₂ Sponge-Shaped Nanostructures. **Key Engineering Materials**, v.846, pp.3-8, 2020. https://doi.org/10.4028/www.scientific.net/KEM.846.3.

[7] <u>Marco C. P. Soares</u>, Thiago D. Cabral, Gabriel Perli, Jéssica M. Bressanin, Julio R. Bartoli. Estimating Polymer Properties and Practicing Statistical Tools in Undergraduate Level through Simple

Experiments. Chemical Engineering Transactions, v.86, pp.1375-1380, 2021. https://doi.org/10.3303/CET2186230. Presentation in: https://youtu.be/0dq7ITmV Uo.

[8] Gabriel Perli, Qi Wang, Carolyne B. Braga, Diego L. Bertuzzi, Liniquer A. Fontana, <u>Marco C. P.</u> <u>Soares</u>, Jaime Ruiz, Jackson D. Megiatto Jr., Didier Astruc, and Catia Ornelas. Self-Assembly of a Triazolylferrocenyl Dendrimer in Water Yields Nontraditional Intrinsic Green Fluorescent Vesosomes for Nanotheranostic Applications. Journal of the American Chemical Society, 2021. <u>https://doi.org/10.1021/jacs.1c05551</u>.

[9] Franciele Flores Vit, Rony Nunes, Yu Tzu Wu, <u>Marco César Prado Soares</u>, Naiara Godoi, Eric Fujiwara, Hernandes F. Carvalho, Lucimara Gaziola de la Torre. A modular, reversible sealing, and reusable microfluidic device for drug screening. **Analytica Chimica Acta**, v.1185, 339068, 15 November 2021. <u>https://doi.org/10.1016/j.aca.2021.339068</u>

International Conference Proceedings Papers

[1] <u>M.C.P. Soares</u>, M. Novotná, Zdeněk Marušák. Determination of the Effects of Chemical Solutions in Membrane's Physical Properties. In: **3rd MemBrain Innovation Centre Workshop of Students' Presentations**; 2015, 21 Oct, Straž pod Ralskem, Czech Republic. <u>https://doi.org/10.13140/RG.2.2.12500.96643</u>.

[2] <u>M. C. P. Soares</u>, E. Fujiwara, M. K. Gomes, B. F. Mendes, L. G. la Torre, and C. K. Suzuki. Application of Optical Fiber Sensor on Fermentation Monitoring. In: 26th International Conference on Optical Fiber Sensors, OSA Technical Digest (Optical Society of America, 2018), paper ThE39; 2018, Sep 24-Sep 28; Lausanne, Switzerland. <u>https://doi.org/10.1364/OFS.2018.ThE39</u>.

[3] <u>Marco C. P. Soares</u>, Beatriz F. Mendes, Matheus K. Gomes, Rogério A. Bataglioli, Egont A. Schenkel, Franciele F. Vit, Lucimara G. de la Torre, Eric Fujiwara, and Carlos K. Suzuki. Optical Fiber Sensor as an Alternative for Colorimetric Image Processing for the Assessment of Dye Concentration. In: IEEE Proceedings: 2018 SBFoton International Optics and Photonics Conference (SBFoton IOPC 2018); 2018, Oct 8-Oct 10; Campinas, SP, Brazil. <u>https://doi.org/10.1109/SBFoton-IOPC.2018.8610912</u>.

[4] Eric Fujiwara, Matheus K. Gomes, <u>Marco C. P. Soares</u>, Matheus S. Rodrigues, Egont A. Schenkel, and Carlos K. Suzuki. Characterization of Colloidal Silica by Optical Fiber Sensor. In: IEEE Proceedings: 2018 SBFoton International Optics and Photonics Conference (SBFoton IOPC 2018); 2018, Oct 8-Oct 10; Campinas, SP, Brazil. <u>https://doi.org/10.1109/SBFoton-IOPC.2018.8610896</u>.

[5] Eric Fujiwara, Yu Tzu Wu, Caio S. Villela, Matheus, K. Gomes, <u>Marco C. P. Soares</u>, Carlos K. Suzuki, Antonio Ribas Neto, and Eric Rohmer. Design and Application of Optical Fiber Sensors for Force Myography. In: IEEE Proceedings: 2018 SBFoton International Optics and Photonics Conference (SBFoton IOPC 2018); 2018, Oct 8-Oct 10; Campinas, SP, Brazil. https://doi.org/10.1109/SBFoton-IOPC.2018.8610923.

[6] <u>Marco C. P. Soares</u>, Franciele F. Vit, Lucimara G. de la Torre, and Eric Fujiwara. Online Monitoring of Cell Growth on PDMS-PDMS Reversible Microfluidic Bioreactor Integrated to Optical Fiber Sensor. In: IEEE Proceedings: 2019 SBFoton International Optics and Photonics Conference (SBFoton IOPC 2019), Oct 7-Oct 9; São Paulo, SP, Brazil. <u>https://doi.org/10.1109/SBFoton-IOPC.2019.8910241</u>.

[7] Eric Fujiwara, Pedro L. Machado, Tarcísio C. D. Oliveira, <u>Marco C. P. Soares</u>, Thiago D. Cabral, and Cristiano M. B. Cordeiro. Using the Smartphone as an Ubiquitous Platform for Implementing Optical Fiber Sensors. In: IEEE Proceedings: 2019 SBFoton International Optics and Photonics Conference (SBFoton IOPC 2019), Oct 7-Oct 9; São Paulo, SP, Brazil. <u>https://doi.org/10.1109/SBFoton-IOPC.2019.8910250</u>.

[8] Ângela Maria Moraes, Monize Caiado Decarli, Cecília Buzatto Westin, <u>Marco César Prado</u> <u>Soares</u>, Franciele Flores Vit, Fernan David Martinez Jimenez and Lucimara Gaziola de la Torre. Use of Business Model Canvas in Bioprocesses Engineering Education at Undergraduation Level: Encouraging Entrepreneurship and Increasing Motivation. 2019 AIChE Annual Meeting, 10-15 November, Orlando, FL, USA, 2019. In: **2019 AIChE Annual Meeting Proceedings**: Education Division, Area: Education, Poster Session: Chemical Engineering Education, pp.375f, Code 164325. ISBN: 978-0-8169-1112-7. In: <u>https://www.scopus.com/record/display.uri?eid=2-s2.0-85095684435&origin=resultslist. In: https://www.researchgate.net/publication/340032318_Use_of_Business_Model_Canvas in_Bioproces ses_Engineering_Education at Undergraduation_Level_Encouraging_Entrepreneurship and Increasi</u>

ng Motivation. [9] <u>Marco César Prado Soares</u>, Gabriel Perli, Matheus Kauê Gomes, Carolyne Brustolin Braga, Diego Luan Bertuzzi, Eric Fujiwara and Carlos Kenichi Suzuki, Use of Optical Fiber Sensor for Monitoring

Luan Bertuzzi, Eric Fujiwara and Carlos Kenichi Suzuki. Use of Optical Fiber Sensor for Monitoring the Degradation of Ac-Dex Biopolymeric Nanoparticles. In: **Proceedings**, v.42, n.1, pp.12, 2020: 6th International Electronic Conference on Sensors and Applications, 15–30 November, 2019; Available online: <u>https://ecsa-6.sciforum.net/</u>. <u>https://doi.org/10.3390/ecsa-6-06535</u>.

[10] <u>Marco César Prado Soares</u>, Matheus Santos Rodrigues, Egont Alexandre Schenkel, Willian Hideak Arita Silva, Gabriel Perli, Matheus Kauê Gomes, Eric Fujiwara, and Carlos Kenichi Suzuki. Dynamic Monitoring of Multi-Concentrated Silica Nanoparticles Colloidal Environment with Optical Fiber Sensor. In: Proceedings, v.42, n.1, pp.6, 2020: 6th International Electronic Conference on Sensors and Applications, 15–30 November, 2019; Available online: <u>https://ecsa-6.sciforum.net/</u>. <u>https://doi.org/10.3390/ecsa-6-06546</u>.

[11] <u>Marco C. P. Soares</u>, Beatriz F. Mendes, Matheus K. Gomes, Franciele F. Vit, Lucimara G. de la Torre, Eric Fujiwara. Fiber Optic Quasi-Elastic Light Scattering Sensor Monitoring of a Mixed Bacteria Culture Applied to Yogurt Fermentation. **8th International Conference on Food Proteins and Colloids (CIPCA 2020)**, 17-19 February, Campinas, Brazil, Identifier PO.14, 2020. In: Book of Abstracts of the VIII CIPCA International Conference on Food Proteins and Colloids de Engenharia de Alimentos, Universidade Estadual de Campinas: Campinas SP, Brazil, 2020. pp.71. ISBN: 978-65-5093-005-9. <u>https://doi.org/10.13140/RG.2.2.35077.58083</u>.

[12] Brino Ruy Negri, <u>Marco César Prado Soares</u>, Antonio Carlos Luz Lisboa, and Julio Roberto Bartoli. Low-Cost Solar Heating Reservoir Manufactured by Double-Coating a Water Tank with Polymeric Materials. In: Materials Proceedings, v.2, n.1, pp.14, 2020: 2nd Coatings and Interfaces Web Conference (CIWC-2 2020), 15-31 May, 2020; Available online: <u>https://ciwc2020.sciforum.net/</u>. <u>https://doi.org/10.3390/CIWC2020-06784</u>.

[13] Matheus S. Rodrigues, Pedro M. Lazari, <u>Marco C. P. Soares</u> and Eric Fujiwara. Characterization of hand gestures by a smartphone-based optical fiber force myography sensor. In: Engineering Proceedings, v.2, n.1, pp.46, 2020: 7th International Electronic Conference on Sensors and Applications, 15–30 November, 2020; Available online: <u>https://ecsa-7.sciforum.net/</u>. <u>https://doi.org/10.3390/ecsa-7-08178</u>.

[14] <u>Marco César Prado Soares</u>, Thiago Destri Cabral, Beatriz Ferreira Mendes, Vitor Anastacio da Silva, Elias Basile Tambourgi and Eric Fujiwara. Technical and Economic Viability Analysis of Optical Fiber Sensors for Monitoring Industrial Bioreactors. In: Engineering Proceedings, v.2, n.1, pp.57, 2020: 7th International Electronic Conference on Sensors and Applications, 15–30 November, 2020; Available online: <u>https://ecsa-7.sciforum.net/</u>. <u>https://doi.org/10.3390/ecsa-7-08161</u>.

[15] <u>Marco César Prado Soares</u>, Paula Rocha Machado and Roger Eike Guinosa. Technical and Economic Supercritical Extraction of Essential Oils from Dry Clove: A Technical and Economic Viability Study of a Simulated Industrial Plant. In: Environmental Sciences Proceedings, v.13, n.1, pp.11, 2022: 2nd International Electronic Conference on Forests - Sustainable Forests: Ecology,

Management, Products and Trade, 1–15 September 2021; Available online: https://iecf2021.sciforum.net/. https://doi.org/10.3390/IECF2021-10778.

Open-Source Educational Report

[1] <u>Marco César Prado Soares</u>. Fermentação: Modelagem Matemática e Resolução das Equações Diferenciais. 15p., Dezembro 2020. Universidade Estadual de Campinas, Campinas, SP, Brasil. In: https://doi.org/10.13140/RG.2.2.11104.92161/1.

Book Chapters

[1] <u>Soares, Marco César Prado</u>; Luz, Gabriel Fernandes; Costa, Aline Carvalho da; Gomes, Matheus Kauê; Mendes, Beatriz Ferreira; Torre, Lucimara Gaziola de la; Fujiwara, Eric. *Saccharomyces cerevisiae* Fed-Batch Fermentation and Artificial Intelligence Method for Adjusting Model Parameters to Experimental Data. In: Voigt, Carmen Lúcia (Ed.). **Impactos das Tecnologias na Engenharia Química 2**. 1 Ed., pp. 111-117. Atena Ed., 2019. <u>https://doi.org/10.22533/at.ed.36419030411</u>. ISBN: 978-85-7247-236-4.

[2] <u>Soares, Marco César Prado</u>; Santos, Murilo Ferreira Marques; Schenkel, Egont Alexandre; Mendes, Beatriz Ferreira; Perli, Gabriel; Ferreira, Samuel Fontenelle; Fujiwara, Eric; Suzuki, C. K. On the Assessment of Dye Retention in Quartz-Based Ceramic Porous Material by Optical Fiber Sensor. In: Rodrigues, Tayronne de Almeida; Neto, João Leandro; Galvão, Dennyura Oliveira (Ed.). **Meio Ambiente, Sustentabilidade e Agroecologia 4**. 1 Ed., pp. 290-295. Atena Ed., 2019. https://doi.org/10.22533/at.ed.30919160430. ISBN: 978-85-7247-330-9.

Local and National Conference Proceedings Papers and Abstracts

[1] <u>SOARES, Marco César Prado</u>. Determination of the Effects of Chemical Solutions in Membranes' Physical Properties. Supervision: Marie Novotná, Laboratory of Materials, MemBrain Innovation Centre, Straž pod Ralskem, Czech Republic. In: INCBAC UNIGOU Academic Exchange Program (Brazil - Czech Republic) Conference, Prague, Czech Republic, February 2015. Available in: <u>https://incbacnews.wordpress.com/_2015-marco-cesar-prado-soares/. https://doi.org/10.13140/RG.2.2.36231.01442</u>.

[2] FUJIWARA, Eric; SCHENKEL, Egont Alexandre; SANTOS, Murilo Ferreira Marques; <u>SOARES, Marco</u> <u>César</u>; SUZUKI, Carlos K. Characterization of silica nanofluids by optical fiber sensor. In: Proceedings of XIV Brazil Materials Research Society Meeting, September 27 to October 01, Rio de Janeiro, RJ, Brazil, 2015, Identifier AQFV, pp.278. ISBN: 978-85-63273-29-1.

[3] <u>SOARES, Marco César</u>; SANTOS, Murilo Ferreira Marques; SCHENKEL, Egont Alexandre; FUJIWARA, Eric; SUZUKI, Carlos K. Sintering behavior of quartz nanocrystals. In: **Proceedings of XIV Brazil Materials Research Society Meeting, September 27 to October 01**, Rio de Janeiro, RJ, Brazil, 2015, Identifier AQFZ, pp.276. ISBN: 978-85-63273-29-1.

[4] <u>SOARES, Marco César Prado</u>; SANTOS, Murilo F. M.; SCHENKEL, Egont A.; FUJIWARA, Eric; SUZUKI, Carlos K. Ultrasound effect in nanoquartz pressing behavior. In: **XXIII Congresso de Iniciação** Científica da Unicamp, 17 a 19 de outubro, Campinas, São Paulo, Brasil, pp.38064, 2015. ISSN: 2447-5114. https://doi.org/10.19146/pibic-2015-38064.

[5] SCHENKEL, Egont Alexandre; PACHECO, Antônia Alana Lima; <u>SOARES, Marco César Prado</u>; Murilo Ferreira Marques; FUJIWARA, Eric; SUZUKI, Carlos Kenichi. Characterization of amorphous fraction in nanoquartz particles obtained by ball milling process. In: 6th TEM Summer School, LNNano - Brazilian Nanotechnology National Laboratory, CNPEM - Brazilian Center for Research in Energy and Materials, 2016, Campinas, São Paulo, Brazil.

[6] PACHECO, A. A. L.; SUZUKI, C. K; SANTOS, M. F. M.; SCHENKEL, E. A.; FUJIWARA, E.; <u>SOARES,</u> <u>M. C. P.</u>; MENDES, B. F. Efeito da adição de pó fino de quartzo na trabalhabilidade, resistência e microestrutura do concreto convencional. In: 60° Congresso Brasileiro de Cerâmica, Associação Brasileira de Cerâmica (ABCERAM), 15 a 18 de maio de 2016, Águas de Lindóia, São Paulo, Brasil. Anais do 60º Congresso Brasileiro de Cerâmica, Trabalho Técnico 06-017TT, pp.840-851, 2016. ISSN: 2175-8891.

[7] <u>SOARES, M. C. P.</u>; PACHECO, A. A. L.; SANTOS, M. F. M.; SCHENKEL, E. A.; MENDES, B. F.; FUJIWARA, E.; SUZUKI, C. K. Porous material sintered from quartz nanoparticles. In: **60° Congresso Brasileiro de Cerâmica, Associação Brasileira de Cerâmica (ABCERAM), 15 a 18 de maio de 2016**, Águas de Lindóia, São Paulo, Brasil. Anais do 60° Congresso Brasileiro de Cerâmica, Trabalho Técnico 17-016TT, pp.2346-2354, 2016. ISSN: 2175-8891. <u>https://doi.org/10.13140/RG.2.2.35916.44167</u>.

[8] MENDES, Beatriz Ferreira; <u>SOARES, Marco César</u>; SANTOS, Murilo Ferreira Marques; SCHENKEL, Egont Alexandre; Antônia Alana Lima; FUJIWARA, Eric; SUZUKI, Carlos K. The Influence of morphology and crystalline structure in the kinetics of nanoquartz and amorphous silica. In: **Proceedings of XV Brazil Materials Research Society Meeting, September 25 to September 29**, Campinas, Brazil. Identifier B4EF, pp.841, 2016. ISBN: 978-85-63273-29-1.

[9] <u>SOARES, Marco César</u>; SANTOS, Murilo Ferreira Marques; SCHENKEL, Egont Alexandre; PACHECO, Antônia Alana Lima; MENDES, Beatriz Ferreira; FUJIWARA, Eric; SUZUKI, Carlos K. On the assessment of dye retention in quartz-based ceramic porous material by optical fiber sensor. In: **Proceedings of XV Brazil Materials Research Society Meeting, September 25 to September 29**, Campinas, Brazil. Identifier AZRA, pp.1899-1900, 2016. ISBN: 978-85-63273-29-1.

[10] <u>SOARES, Marco C. P.</u>; SANTOS, Murilo F. M.; SCHENKEL, Egont A; MENDES, Beatriz F.; PACHECO, Antônia A. L.; FUJIWARA, Eric; SUZUKI, Carlos K. Use of Optical Fiber Sensor and Design of Experiments Statistical Methodology for Improving Dye Retention in a Quartz Ceramic Porous Material. In: XXIV Congresso de Iniciação Científica da Unicamp, 19 a 21 de outubro, Campinas, São Paulo, Brasil, pp.51467, 2016. ISSN: 2447-5114. <u>https://doi.org/10.19146/pibic-2016-51467</u>.

[11] MENDES, Beatriz Ferreira; <u>SOARES, Marco César</u>; SANTOS, Murilo Ferreira Marques; SCHENKEL, Egont Alexandre; PACHECO, Antônia Alana Lima; FUJIWARA, Eric; SUZUKI, Carlos K. Study of the activation energy of sílica nanoparticles. In: XXIV Congresso de Iniciação Científica da Unicamp, 19 a 21 de outubro, Campinas, São Paulo, Brasil, pp.51802, 2016. ISSN: 2447-5114. <u>https://doi.org/10.19146/pibic-2016-51802</u>.

[12] <u>SOARES, Marco C. P.</u>; SANTOS, Murilo F. M.; SCHENKEL, Egont A; MENDES, Beatriz F.; FUJIWARA, Eric; SUZUKI, Carlos K. Initial development of a high-performance filtration device with Vapor-Phase Axial Deposition Process. In: **XXV Congresso de Iniciação Científica da Unicamp**, 18 a 20 de outubro de 2017, Campinas, São Paulo, Brasil, pp.78288, 2017. ISSN: 2447-5114. <u>https://doi.org/10.19146/pibic-2017-78288</u>.

[13] MENDES, Beatriz Ferreira; <u>SOARES, Marco César</u>; SANTOS, Murilo Ferreira Marques; SCHENKEL, Egont Alexandre; FUJIWARA, Eric; SUZUKI, Carlos K. Study of the activation energy and reaction parameters on the pozzolanic reaction using quartz and silica nanoparticles In: **XXV Congresso de Iniciação Científica da Unicamp**, 18 a 20 de outubro de 2017, Campinas, São Paulo, Brasil, pp.78252, 2017. ISSN: 2447-5114. https://doi.org/10.19146/pibic-2017-78252.

[14] <u>SOARES, Marco César Prado</u>; SILVA, Flávio Vasconcelos; DE LA TORRE, Lucimara Gaziola; RODRIGUES, Maria Teresa. Ensino baseado em problema combinado à construção coletiva e compartilhamento de aprendizado, aplicado ao curso de Introdução às Indústrias e Processos Químicos. In: VI Seminário Inovações Curriculares Edição 2017, 30 de novembro a 2 de dezembro de 2017, Campinas, São Paulo, Brasil, 2017 (Trabalho apresentado). Página do trabalho: <u>https://eventos.ea2.unicamp.br/event/1/contributions/32</u>.

[15] <u>SOARES, Marco César Prado</u>; LUZ, Gabriel Fernandes. Simulação dinâmica de um processo de fermentação alcoólica, em batelada, utilizando *Saccharomyces cerevisiae*: medição de viscosidade e sensoriamento óptico. 2017, 48p. Trabalho de Conclusão de Curso. Orientadora: Prof. Dr^a. Aline Carvalho da Costa. Faculdade de Engenharia Química, Universidade Estadual de Campinas, Campinas, Brasil. https://doi.org/10.13140/RG.2.2.31830.80968.

[16] <u>M. C. P. Soares;</u> G. F. Luz; A. C. Costa; M. K. Gomes; B. F. Mendes; L. G. Torre; E. Fujiwara. *Saccharomyces cerevisiae* Fed-Batch Fermentation and Artificial Intelligence Method for Adjusting Model Parameters to Experimental Data. Blucher Chemical Engineering Proceedings, v.1, n.5, Sep. 2018, XXII Congresso Brasileiro de Engenharia Química – COBEQ 2018, 23 Sep.-26 Sep.; São Paulo, SP, Brazil, 2018, pp.2010-2014. ISSN: 2359-1757. <u>https://doi.org/10.5151/cobeq2018-PT.0532</u>.

[17] GOMES, Matheus K.; FUJIWARA, Eric; <u>SOARES, Marco C. P.</u>; SUZUKI, Carlos K. Caracterização de Nanopartículas de Dióxido de Silício Utilizando Sensor de Fibra Óptica. In: XXVI Congresso de Iniciação Científica da Unicamp, 17 a 19 de outubro de 2018, Campinas, São Paulo, Brasil. In: Revista dos Trabalhos de Iniciação Científica da Unicamp, n.26, pp.1041, Campinas, 2018. ISSN: 2596-1969. https://doi.org/10.20396/revpibic2620181041.

[18] MENDES, Beatriz F.; <u>SOARES, Marco C. P.</u>; GOMES, Matheus K.; SCHENKEL, Egont Alexandre; FUJIWARA, Eric; SUZUKI, Carlos K. Study of dye adsorption from water on silica materials using an optical fiber sensor. In: XXVI Congresso de Iniciação Científica da Unicamp, 17 a 19 de outubro de 2018, Campinas, São Paulo, Brasil. In: **Revista dos Trabalhos de Iniciação Científica da Unicamp, n.26**, pp.196, Campinas, 2018. ISSN: 2596-1969. <u>https://doi.org/10.20396/revpibic262018196</u>.

[19] MORAIS, Guilherme A. D.; <u>SOARES, Marco C. P.</u>; FUJIWARA, Eric; LA TORRE, Lucimara G. Development of an Image Processing MATLAB Algorithm for Cell Growth Analysis. In: XXVI Congresso de Iniciação Científica da Unicamp, 17 a 19 de outubro de 2018, Campinas, São Paulo, Brasil. In: **Revista dos Trabalhos de Iniciação Científica da Unicamp, n.26**, pp.557, Campinas, 2018. ISSN: 2596-1969. https://doi.org/10.20396/revpibic262018557.

[20] <u>SOARES, Marco César</u>; BARTOLI, Julio Roberto; AMATO, Francesco; CACIOPPO, Michele; ARCUDI, Francesca; CARREÑO, Marcelo N. P.; PEREYRA, Inès; FUJIWARA, Eric; SUZUKI, Carlos K.; PRATO, Maurizio. Synthesis and Applications of Nitrogen-Doped Carbon Dots with Blue Fluorescence. In: **Proceedings of XVIII Brazil Materials Research Society Meeting, September 22-26**, Balneário Camboriú, Santa Catarina, Brazil, Sep. 22-26. Identifier 4FMT, pp.1542-1543, 2019. ISBN: 978-85-63273-40-60.

[21] RODRIGUES, Matheus S.; <u>SOARES, Marco C. P.</u>; FUJIWARA, Eric. Development of an optical fiber sensor for monitoring the flow of colloidal nanoparticles. In: XXVII Congresso de Iniciação Científica da Unicamp, 16 a 18 de outubro de 2019, Campinas, São Paulo, Brasil. In: **Revista dos Trabalhos de Iniciação** Científica da Unicamp, n.27, pp.1749, Campinas, 2019. ISSN: 2596-1969. https://doi.org/10.20396/revpibic2720191749.

1. Introduction

Nowadays, several techniques and materials are available for the fabrication of optical fibers, waveguides and optic sensors, but technological gaps remain. Sensors with lower costs and minor difficulties of fabrication, signal processing, and feasibility; or obtained through less-aggressive methodologies as biodegradable or greener devices are demanded (ELSHERIF et al., 2019). An important technological gap, on the other hand, is to combine the solution of these problems with the environmental point of view, producing biodegradable devices and less-aggressive processes. In this context, the use of biocompatible hydrogels arises as a promising methodology for manufacturing photonic devices. In the case of chemical and biochemical process monitoring, characteristics inherent to optical fibers such as environmental and electromagnetic resistances are also desirable, once harsh thermal, chemical and mechanical conditions are usually present (CHOI et al., 2013; OLIVERIO et al., 2017; OMENETTO; KAPLAN, 2008; SHEPPARD; TUCKER; SALEHI-HAD, 1993).

Hydrogel-based waveguides combine the electromagnetic interference shielding to the possibility of miniaturization, allowing the detection of different parameters with high sensitivity (CENNAMO et al., 2016). They usually explore the properties of hydrogels on suffering volumetric variations as response to different parameters, including: pH; temperature; ionic strength; and concentration of analytes, such as glucose, proteins, and DNA. These different potential applications in industrial biotechnology, environmental monitoring, and biosensing (ELSHERIF et al., 2019; JIANG et al., 2018b; WOLFBEIS, 2008) can be also increased by doping the polymeric matrix with luminous agents.

The doping strategy is based on the variation of the pattern of the light transmitted by the waveguide due to luminescence and to other light-matter interaction phenomena. Studies showed the possibility of producing step-index cylindrical optical fibers by coating a polyethylene glycol (PEG) core with an alginate layer. These materials were doped with fluorophores and Au nanoparticles and allowed the guiding of light inside living tissues and the detection of avidin (CHOI et al., 2015). A PEG optical fiber was also doped with functionalized-CdTe quantum dots (QDs) for monitoring Fe³⁺ (ZHOU; GUO; YANG, 2018). Meantime, practical applications of these devices are still limited by the fact that inorganic nanoparticles such as the semiconductor QDs usually present high toxicity (CHOI et al., 2013).

This work proposes, then, the design and fabrication of photonic materials and devices where nanotechnology and fiber optic technology are explored to obtain more sustainable processes and devices with interesting characteristics for *inline* operation. Thus, new fluorescent nanomaterials from the class of carbon nanodots (CDs) were synthesized and applied. The advantages of CDs when compared to inorganic QDs (considered superior fluorescent emitters) include the fact that they are low-cost and environmentally safe materials (ĐORĐEVIĆ et al., 2018), and show good biological and biocompatibility properties, being excreted in urine (HUANG et al., 2013; WANG; HU, 2014). Moreover, they present chemical robustness and high solubility in water, and are easily doped and chemically modified (ARCUDI; ĐORĐEVIĆ; PRATO, 2016).

Carbon Nanodots are nanoparticles constituted by a carbon core and superficial functional groups, notable for their quasi-spherical and discrete morphologies, usually with dimensions lower than 10 nm (ĐORĐEVIĆ et al., 2018; PARK et al., 2016; WANG; HU, 2014; XIA et al., 2019). They present unique assets such as strong fluorescence both in solution and

in the solid state, high photostability, low toxicity, high biocompatibility, high solubility in water, chemical robustness, and are easily doped and chemically modified (HUANG et al., 2013; PANWAR et al., 2019; SUN et al., 2006; TIAN; YIN, 2019; YUAN et al., 2016).

Interestingly, CDs exhibit excitation-wavelength dependent emission, and the emission wavelength is strongly affected by the electronic bandgap transitions of conjugated π -systems, surface defects, and by element doping (GAN; XU; HAO, 2016; YAN et al., 2019; ZUO et al., 2016). It has been demonstrated that variations of the CDs' sizes shift the maximum emission wavelength: smaller particles usually emit at lower wavelengths, whereas larger particles tend to emit at higher wavelengths (LI et al., 2010; ZUO et al., 2016).

The unique emission properties of CDs allied to their easily tailored nanosize and to the high abundance of carbon sources have made them attractive for a wide variety of potential applications including bioimaging, drug-delivery, sensors, optoelectronics, photovoltaic devices, photocatalysis, renewable energy devices, and anti-counterfeiting materials (ARCUDI; ĐORĐEVIĆ; PRATO, 2017, 2019; CHEN et al., 2019; GAO et al., 2016; GUPTA et al., 2011; JI et al., 2018; LI et al., 2018a; MENG et al., 2019; PANWAR et al., 2019; SHARMA; TIWARI; MOBIN, 2017; TIAN et al., 2017). Moreover, the semiconductor-like properties of CDs enabled their incorporation into optical fibers to obtain optical devices with innovative features (GONÇALVES; DUARTE; ESTEVES DA SILVA, 2010; LIN; HUANG; DING, 2019).

Particularly, the CDs biomedical and biosensing applications are quite extensive and interesting. Examples reported include the use of CDs: for the bioimaging and monitoring of human breast cancer MCF-7 cells (CAO et al., 2007); as probes for several theranostics applications and for the fluorescence-based monitoring of tissues in mice (DONG et al., 2020; WANG; HU, 2014); as nanoprobes for single-molecular tracking and for real-time imaging on biomedical analysis; as confocal microscopy fluorescent probes; and even as nanocarriers in cellular transfection. Indeed, CDs functionalized with gold nanoparticles and plasmid DNA (pDNA) allowed the gene delivery with real-time optical monitoring of the transfection process (YUAN et al., 2016). Moreover, CDs with surface functionalized with biological molecules were described for the optical fluorescence-based tracking and selective detection of DNA (ZUO et al., 2016); and CDs obtained from the latex of *Euphorbia milii* were used for detection of glutathione in human blood serum (BANO et al., 2019).

There is a continuous search for greener and cheaper methods to produce CDs with low polydispersity from renewable sources (DEVI; DHAMODHARAN, 2018; DUARAH; KARAK, 2017; RAN et al., 2018; RAVISHANKAR et al., 2019; WU et al., 2016). Nature offers a plethora of carbon sources that has motivated the investigation of a wide variety of raw materials to obtain CDs, including lignin biomass, waste paper, kitchen waste, starch, orange peels, potato, grass, soy milk, papaya, eggs, coffee grounds, hair, cow manure, among others (MENG et al., 2019; SHARMA; TIWARI; MOBIN, 2017; SURENDRAN et al., 2020; XU; XIE; HAKKARAINEN, 2017; ZHANG; SUN; WU, 2015).

The use of specific routes and chemical precursors on CDs synthesis results in nanomaterials with different photonic properties (ARCUDI; ĎORĎEVIĆ; PRATO, 2019; ĐORĐEVIĆ; ARCUDI; PRATO, 2019; GONG et al., 2018). In fact, the conversion of organic precursors containing carboxylic acids (or nitrogen as doping element) results in the formation of CDs rich in carboxylic (or amine) surface groups with enhanced luminescence (ĐORĐEVIĆ et al., 2022). Martindale *et al.* (MARTINDALE et al., 2015), for instance, demonstrated the application of citric acid CDs on the light-driven fabrication of chemical products, performing an artificial photosynthesis by preparing a photocatalytic hybrid system (CD-NiP) for solar H₂

production. Also, Boobalan *et al.* (BOOBALAN et al., 2020) obtained CDs by hydrothermal synthesis using oyster mushroom. Their material was capable of selectively sensing Pb^{2+} ions in aqueous solutions and presented antibacterial and anticancer activity. Also, Mn-doped CDs with ultra-high quantum yield of luminescence were demonstrated for the selective detection of Hg²⁺ ions in water (XU et al., 2018).

CDs may also present energy applications, which include their use to increase the efficiency of energy conversion in solar cells; to photosensitize or photocatalyze the conversion of solar energy into fuels; or to employ their fluorescence to prepare light-emitting diodes (ĐORĐEVIĆ et al., 2022). Their fluorescence properties also find use in light converters for photovoltaic cells and solar concentrators, and may replace dye sensitizers (TUERHONG; XU; YIN, 2017; WANG; LU, 2022). Recently, advanced approaches like the use of mechanochemistry, flow chemistry and laser synthesis in the liquid phase are widening the range of properties and applications of these promising nanomaterials. Besides, these novel synthesis methodologies present the advantage of being scalable. Finally, machine learning could be also applied to go beyond the trial-and-error approach commonly used to explore the chemistry of CDs (BARTOLOMEI; DOSSO; PRATO, 2021).

Thus, this work shows the synthesis of new fluorescent nanomaterials from the class of carbon nanodots from three natural sources (sugarcane syrup, orange juice, and milk). The sugarcane-based particles were occluded into a hydrogel matrix (gelatin) for being introduced into a microstructured polymer optical fiber. So, a waveguide capable of emitting and conducting visible light was fabricated as a greener alternative to the incorporation of rareearths and heavy metals on luminescent fibers manufacturing. Another hydrogel with better mechanical properties (agarose) was doped with SiO₂-CDs nanocomposites for obtaining a fluorescent, biodegradable and biocompatible pH sensor useful for retrieving information for *offline* analysis. Finally, it was verified that nanocomposites from CDs and poly(methylmethacrylate), PMMA (CDs-PMMA nanocomposites) can be combined with solar cells to achieve an increase of 11.3% on the cell conversion efficiency.

Fiber optic sensors were also designed and applied to important chemical and biochemical media. Optical fibers are cylindrical waveguides formed by dielectric materials with low loss of light power, which have a central core (where the light is guided) surrounded by a cladding with refractive index slightly lower than the core's. Light rays incident on the core-cladding interface with angles greater than a certain critical value suffer total internal reflection, being guided through the core without suffering refraction. Rays that do not follow this critical angle condition are transmitted through the cladding: they suffer high loss of power and are not effectively guided (SALEH; TEICH, 1991). In optical fiber-based systems, the transmitted or reflected light is captured by a photodetector (KEISER, 2013). The detector, then, converts the optical stimulus into an electrical signal to be electronically or computationally processed (GHATAK; THYAGARAJAN, 2000).

Fiber optic sensors may be used on various types of measurements, like rotation, acceleration, temperature, pressure, mechanical deformation, voltage and electric current (UDD, 2002). The technical advantages inherent to the use of optical fibers include: typically reduced mass of these devices; small dimensions of the sensors; low energy consumption by the equipment; resistance to electromagnetic interference; and biocompatibility. Other interesting optical fiber sensors properties are high: sensitivity; stability; measurement resolution; bandwidth; and resistance to the environment, both from the chemical and from the

thermal point of view, with possibility of remote operation and under aggressive conditions (LI et al., 2018c; UDD, 2002).

Such features are very interesting for practical cases, once contemporary industry is in a period of great expansion. It is the so-called "*Industry 4.0*", where novel mathematical and computer-based methods are leveraged to optimize and monitor the systems and processes, with social, economic, and environmental repercussions on many human activities (PAN et al., 2015). As a matter of fact, this new period relies on the development of new sensor technologies capable of collecting, distributing, and delivering information by themselves.

In chemical and biochemical industries, the increase on the data availability and on the portability of the monitoring devices has potential for enhancing safety; productivity; energy-use efficiency; environmental sustainability; product quality; and general process performance (REIS; KENETT, 2018). However, the analysis and evaluation of many chemical and biochemical agents (from pesticides to pharmacological drugs) is still based on high-performance liquid chromatography (HPLC); gas chromatography (GC); combined techniques like GC coupled to mass spectrometry (GC-MS); and enzyme-linked immunosorbent assay (ELISA). Such methods are sensitive, reliable, and precise, but demand expensive and bulky instrumentation; highly trained technicians; and procedures with long times of analysis. The use of compact and real-time sensors, on the other hand, allows the monitoring, control, and screening of the best process conditions (JU; KANDIMALLA, 2008; REIS; KENETT, 2018; SOARES et al., 2019e)

Then, optical fiber sensors systems show several potential applications in chemical and biochemical monitoring: detection of gases and vapors; chemical and biomedical analysis; molecular biotechnology; environmental analysis (from the analysis of agricultural pesticides to the monitoring of marine environments); industrial production monitoring; bioprocess control; monitoring of the production of catalysts and other components in automotive industry (WANG; WOLFBEIS, 2020; WOLFBEIS, 2008); and even monitoring of cell proliferation in microfermentors (SOARES et al., 2019b, 2019e).

Traditionally, the set of optical fiber chemical sensing systems is divided into two main classes: direct sensing schemes (called "label-free" sensors); and indirect ones, based on the addition of indicators (e.g., a dye with fluorescence dependent on the presence of a target analyte). In the first case, intrinsic optical properties of the analyte (e.g., its refractive index, its absorption, or its emission) are assessed. In the second one, either the fluorescence or the color of an immobilized indicator agent (the "label") is evaluated; or another optical property of the "probe" is selected for being monitored (WANG; WOLFBEIS, 2020; WOLFBEIS, 2008). Some authors also consider that there is a subclass of chemical sensors called biosensors, but there is no consensual definition regarding this subclass.

One useful definition of fiber optic biosensors is a set of devices derived from optical fibers that use the optical field for the detection of biological molecules (including proteins, antibodies, nucleic acids, and even cells). Such devices are commonly modified with biological species to improve their selectivity (LEUNG; SHANKAR; MUTHARASAN, 2007; WANG; WOLFBEIS, 2020; WOLFBEIS, 2008). Ideally, biosensors should not only respond to low analyte concentrations, but also be capable of differentiating species according to the recognition molecules attached to their surfaces. It is noted, therefore, that they have several applications in the health area, including the detection of biological markers for clinical diagnosis and the detection of pathogens and toxins in water and food (LEUNG; SHANKAR; MUTHARASAN, 2007). So, as with CDs, there are many examples of optical fiber sensors
already used for biomedical and biochemical monitoring, including: an optical fiber Etched-SMS (single mode - multimode - single mode) immunosensor functionalized for the specific detection of anti-goat IgG antigen in solution (CARDONA-MAYA et al., 2018); a Sagnac interferometer based on a core-exposed microstructured optical fiber where the core was functionalized with biotin, used for the detection of streptavidin biomolecules (LI et al., 2018c); an optical fiber speckelgram sensor with very high sensitivity to DNA molecules, capable of detecting concentrations of DNA as low as 10⁻¹⁶ M in aqueous solution (FENG et al., 2018); a flow cytometer capable of performing the continuous detection of microparticles, manufactured as a fiber Bragg grating/Fabry-Pérot interferometer (JIANG et al., 2018a); and a Mach-Zender interferometer based on a twin-core hollow optical fiber sensor functionalized with biotin for detecting streptavidin in solution (YANG et al., 2018).

Thus, considering the importance of such photonic devices, another objective of this work was the design of optical fiber sensors (OFSs) for applications on chemical and biochemical systems. Firstly, a sensing system capable of detecting velocity and refractive index (RI) in biphasic gas-water, oil-water and gas-oil mixtures was described. It was 3D-printed as a millifluidic device with an inserted tilted fiber Bragg grating. The multiphase flows are characterized by the simultaneous transport of immiscible substances, the dispersed and continuous phases. They are observed in the oil and gas industries during the extraction of light and heavy oils containing dispersed components like minerals, gases, and water (ANGELI; HEWITT, 2000); in nuclear reactors (COLOMBO; FAIRWEATHER, 2015); and in biomedical applications (YAO; TAKEI, 2017). So, this device provides reliable results with a straightforward, easy-to-implement setup that may be applied to several industries. It presents the advantage of employing a simplified interrogation system based on a single photodetector where the response time only depends on the sampling rate of the data acquisition hardware.

Another system developed consisted of a smartphone-based RI sensor designed for the real-time assessment of fed-batch fermentors. The project attends some "*Industry 4.0*" requirements: the sensor is destined to field monitoring and on-site fast fabrication, relying on a simple 3D-printed case for coupling optical fibers to the phone's camera and LED. Then, an application is responsible for processing light intensity data (retrieved as intensity of pixels in captured images); and for correlating the signal variations to the broth's RI, which is function of the sucrose concentration according to the Fresnel law. The fed-batch mode was chosen for the study because most of the alcoholic fermentation industries in Brazil operate with this methodology (CARLOS; OLITTA; NITSCHE, 2011). The results were validated through comparison with a handheld refractometer and with the Monod mathematical model.

Finally, a dynamic light scattering (DLS) sensor based on an all-optic Fresnel reflectance setup applies artificial neural networks for detecting concentration disturbances and performing the simultaneous assessment of concentration and flow speed of nanofluids. Nanofluids are stable suspensions of nanoparticles in a base-fluid, and their physical and chemical properties can be tailored according to the characteristics of both the dispersed and the continuous phases (LI et al., 2009). In particular, silica-based nanofluids have been developed for use in thermal conductivity enhancement (CHEN et al., 2008); *in-vivo* fluorescence imaging (KOBAYASHI et al., 2013); and tunable optical filters (TAYLOR et al., 2013). The assessment of micro- and nanoparticles subjected to flow and other dynamic conditions (e.g., concentration gradients and disturbances) is essential not only for silica nanofluids applications, but also for several other biochemical, biomedical, and food engineering uses. Examples include the monitoring of red cells in blood streams (NILSSON;

TENLAND; OBERG, 1980); the flow of polymeric particles (e.g., polystyrene) obtained by chemical emulsion processes (CHEN et al., 1997); and the fabrication of food emulsions based on the nanoencapsulation of nutrients (QUINTANILLA-CARVAJAL et al., 2010).

Then, this research proposes an optical fiber DLS sensor for the evaluation of silica nanofluids' static and dynamic conditions. These nanofluids were obtained by synthesizing SiO₂ nanoparticles (195 nm-diameter) and dispersing them in water. Firstly, the sedimentation of colloidal silica in test tubes was done to create environments with different concentration zones, allowing the evaluation of the dynamic response of the sensor in relation to concentration disturbances. Finally, the OFS was applied to the detection of velocity of nanofluids with different concentrations and flow conditions. Contrary to previous works, the present system is capable of simultaneously estimating the sample concentration and flow velocity by using artificial neural networks, providing a simple, minimally invasive, and nondestructive approach to assess particles dispersions.

From traditional chemical, petrochemical, and mining to food and advanced biotechnology, several industries must deal with nanofluids and colloidal suspensions, so there is a range of important practical applications of this sensor on facilities control and monitoring.

2. Design of Photonic Materials and Applications: Carbon Nanodots and their Combination with Polymer Matrices

2.1. Motivation

Despite of all the different techniques and materials available for fabricating optical fibers, waveguides and optical sensors, the development of devices with lower costs and minor difficulties of fabrication, signal processing, and feasibility is still needed (ELSHERIF et al., 2019). An important technological gap, on the other hand, is to combine the solution of these problems with the environmental point of view, producing biodegradable devices and less-aggressive processes. In this context, the use of biocompatible hydrogels arises as a promising methodology for manufacturing photonic devices. Hydrogels are reticulated hydrophilic polymers. Typically, up to ~30% of the hydrogel mass corresponds to water occluded into its structure or adsorbed on the macromolecules' surfaces. Silk-based hydrogels have already been used for fabricating thin films, diffraction gratings, and organic photonic crystals. When comparing photonic devices for biomedical applications, important advantages are observed for hydrogel-based equipment, like the obtention of implantable sensors and the reduction of undesirable effects typical from traditional optical fibers and other glass-based devices, like the formation of sharp points that may inflame an implant region (CHOI et al., 2013; OLIVERIO et al., 2017; OMENETTO; KAPLAN, 2008; SHEPPARD; TUCKER; SALEHI-HAD, 1993).

Hydrogel-based waveguides allow the detection of several physical and biochemical parameters with high sensitivity (CENNAMO et al., 2016). They usually explore the properties of hydrogels on suffering volumetric variations as response to different parameters, including pH, temperature, ionic strength, and concentration of analytes, such as glucose, proteins, and DNA. These different potential applications in industrial biotechnology, environmental monitoring, and biosensing (ELSHERIF et al., 2019; JIANG et al., 2018b; WOLFBEIS, 2008) can be also increased by doping the polymeric matrix with luminous agents.

The doping strategy affects the waveguide luminescence and other light-matter interaction phenomena. Studies have shown the possibility of producing step-index cylindrical optical fibers by coating a polyethylene glycol (PEG) core with an alginate layer. These materials allowed light guidance through living tissues and were doped with fluorophores and Au nanoparticles to selectively detect avidin (CHOI et al., 2015). A PEG optical fiber was also doped with functionalized-CdTe quantum dots (QDs) for monitoring Fe³⁺ (ZHOU; GUO; YANG, 2018). Meantime, practical applications of these devices are still limited by the fact that the waveguides are usually doped with organic dyes; or with inorganic nanoparticles such as QDs, which present high toxicity (CHOI et al., 2013). It is a drawback that could be overcome by replacing the particles or dyes with carbon nanodots (CDs) (ĐORĐEVIĆ et al., 2018).

These carbon nanodots are emerging materials from the carbon nanotechnology family (as well as graphene, fullerene, and carbon nanotubes). They present quasi-spherical morphology; sizes lower than 10 nm (ARCUDI; ĐORĐEVIĆ; PRATO, 2017; ĐORĐEVIĆ et al., 2018); and are constituted by a carbonaceous core with plenty of functional groups on their surfaces. Those groups allow their solubility in polar solvents, and may include hydroxyl, amine, and carboxylic acids. The peculiar behavior of carbon nanodots is their fluorescence, which arises from molecular domains that are formed during their syntheses (ARCUDI;

ĐORĐEVIĆ; PRATO, 2016, 2017; ĐORĐEVIĆ et al., 2018; HUANG et al., 2013; SALEH; TEICH, 1991; SUN et al., 2006; WANG et al., 2011; WANG; HU, 2014; YUAN et al., 2016).

This luminescent behavior of CDs may be modulated by different factors, especially the excitation wavelength (SUN et al., 2006), pH (PAN et al., 2012), and solvent used (ZHU et al., 2011). Moreover, the surroundings of the particles are responsible for the stabilization of the fluorophore electronic states, and red-shifted emissions are expected when the neighboring particles stabilize such states (solvatochromic effect) (SUPPAN, 1990). Due to these unique features, CDs find applications into several fields, such as: biomarking; bioimaging; drug-delivery; optoelectronics (in which they can be used for manufacturing LEDs with controlled emission wavelength) (WANG et al., 2011; WANG; HU, 2014); covalent asymmetric catalysis (FILIPPINI et al., 2020); photocatalysis; renewable energies (WANG; HU, 2014); luminescent down shifting; and solar concentrator devices (CHOI et al., 2017; GONG et al., 2018).

CDs may show different photonic properties depending on the particular routes and chemical precursors applied (ARCUDI; ĎORĎEVIĆ; PRATO, 2019; ĐORĐEVIĆ; ARCUDI; PRATO, 2019; GONG et al., 2018). Some examples include: small and highly fluorescent nitrogen-doped carbon nanodots obtained from inexpensive L-arginine and ethylenediamine by microwave-assisted hydrothermal carbonization (ARCUDI; ĐORĐEVIĆ; PRATO, 2017); citric acid CDs used on artificial photosynthesis by preparing a photocatalytic hybrid system (CD-NiP) for solar H₂ production (MARTINDALE et al., 2015); CDs hydrothermally synthesized from a green source (oyster mushroom) to fabricate a material capable of selectively sensing Pb²⁺ ions in aqueous solutions and with antibacterial and anticancer activity (BOOBALAN et al., 2020); and CDs doped with Mn obtained from the hydrothermal treatment (195 °C, 2h) of mixtures of sodium citrate, citric acid, and manganese (II) carbonate, showing ultra-high quantum yield of luminescence and the possibility of being used to selectively detect Hg²⁺ ions in water (XU et al., 2018). A detailed review describing synthetic routes for obtaining CDs from both artificial and natural sources (such as silk and grass); difficulties found by researchers; and applications already demonstrated for those particles was published and is referred to those interested in this topic (XU et al., 2019).

Thus, the goal of this work was to produce new photonic materials from the class of carbon nanodots and to use them for fabricating non-conventional optical sensors and optoelectronic devices. For that, CDs were synthesized from three natural sources (sugarcane syrup, orange juice, and UHT milk). The sugarcane-based carbon nanodots were also occluded into a hydrogel matrix (gelatin) for being introduced into a microstructured optical fiber. So, a waveguide capable of emitting and conducting visible light was obtained, constituting a sustainable alternative to the incorporation of rare-earths and heavy metals on luminescent fibers production. Also, silica-carbon nanodots nanocomposites were used for doping agarose and fabricating a fluorescent, biodegradable and biocompatible pH optical sensor capable of retrieving information for offline analysis (a work performed in extensive collaboration with groups from Italy and Spain). Finally, carbon nanodots were occluded into PMMA matrices and the feasibility of using such nanocomposites for improving the efficiency of photovoltaic cells was verified. It is a work with impactful applications in renewable energy systems, with potential of enormous gains in terms of reduction of land-use and fabrication costs on large-scale solar plants.

2.2. Principles of Fluorescence of Carbon Nanodots

As mentioned, carbon nanodots show the interesting property of emitting visible fluorescence (light) when stimulated by ultraviolet radiation. In other words: such particles are capable of converting UV into visible, a property that may be explored for the development of chemical sensors (ARCUDI; ĐORĐEVIĆ; PRATO, 2019; BANO et al., 2019).

Basically, given that a CD is reached by a certain packet of radiant energy (a photon) in the ultraviolet (frequency v_1), Planck's Equation states that the energy of this photon is given by hv_1 , where h is Planck's constant. A fraction of this energy is dissipated by the medium (e.g., water, solvent, or hydrogel matrix). The more conductive the medium is, the more energy will be dissipated through this mechanism. In addition, electrical energy transfer can occur between the atoms of the particle itself. Such processes that are not involved in the secondary emission of radiation are denominated non-radiative decays. These non-radiative phenomena are always present (JIANG et al., 2020; LAKOWICZ, 2006).

Thus, after the non-radiative losses, a smaller amount of energy (hv_2) remains, and the difference ($hv_1 - hv_2$) is known as the Stokes shift. Since violet has the highest and red has the lowest frequency in visible spectrum, this Stokes shift always results in a second energy hv_2 closer to red, a phenomenon called "red-shift". The hv_2 energy excites the electrons in the outermost orbitals of the atoms that form the CDs, leading them to an unstable electronic state. Then, to return to its stable state, the CDs re-emit a photon hv_2 to the external environment: while the hv_1 photon corresponds to UV radiation, the hv_2 photon is usually visible light (JIANG et al., 2020; LAKOWICZ, 2006).

The observed light emission is the fluorescence. The ratio between the total number of photons that the particle re-emits and the number of photons it absorbs is called the quantum yield (QY). QY is a very important parameter for evaluating the performance of light emitters (LAKOWICZ, 2006). It is worth noting that fluorescence is an extremely fast phenomenon with a lifetime of just nanoseconds, impossible to be detected by the human eye. Therefore, unlike phosphorescence and delayed fluorescence (processes with lifetimes ranging from microseconds to seconds), fluorescence seems to disappear as soon as the UV source is interrupted (JIANG et al., 2020; LAKOWICZ, 2006).

2.3. Synthesis and Application of Carbon Nanodots from Sugarcane Syrup

The work published by the Institute of Electrical and Electronics Engineers (IEEE) is presented here (SOARES et al., 2019a). It shows the synthesis of green-fluorescent carbon nanodots from sugarcane syrup, a method that was patented for the intellectual protection of the fabrication process (SOARES et al., 2019d).

This method was extended to incorporate the CDs into gelatin matrices, allowing their immobilization into the holes of a microstructured polymer optical fiber (mPOF). This approach was published by the open-source journal Gels from the Multidisciplinary Digital Publishing Institute, MDPI (PERLI et al., 2022). Thus, an optical fiber with intrinsic fluorescence was obtained, providing a sustainable alternative to the incorporation of rare-earths and heavy metals when fabricating luminescent fibers.

2.3.1. Introduction

Carbon Nanodots (CDs) are nanoparticles constituted by a carbon core and superficial functional groups, notable for their quasi-spherical and discrete morphologies, usually with dimensions lower than 10 nm (ĐORĐEVIĆ et al., 2018; PARK et al., 2016; WANG; HU, 2014; XIA et al., 2019).

CDs present unique assets such as strong fluorescence both in solution and in the solid state, high photostability, low toxicity, high biocompatibility, high solubility in water, chemical robustness, and are easily doped and chemically modified (HUANG et al., 2013; PANWAR et al., 2019; SUN et al., 2006; TIAN; YIN, 2019; YUAN et al., 2016). In terms of charge transfer chemistry, CDs have the particularity of acting as either electron donors or acceptors (CADRANEL et al., 2019). These properties are intrinsic to CDs and distinct from other carbon-based nanostructures such as graphene, fullerene, and carbon nanotubes.

CDs were discovered by Scrivens and co-workers as a fluorescent by-product from single-walled carbon nanotube synthesis (XU et al., 2004). Since then, several methodologies were developed to obtain CDs that involve top-down nanocutting procedures and bottom-up organic approaches, which include arc discharge, laser ablation, electrochemical oxidation, combustion methods, hydrothermal carbonization, templated carbonization, pyrolysis in concentrated acid, and microwave irradiation (ARCUDI; ĐORĐEVIĆ; PRATO, 2016; WANG et al., 2011; WANG; HU, 2014; XIA et al., 2019). Some of these processes are difficult to control, resulting in CDs with high polydispersity. The size, polydispersity, and surface functional groups nature depend on the synthetic methodology used to obtain the CDs (WANG; HU, 2014).

There is a continuous search for greener and cheaper methods to produce CDs with low polydispersity from renewable sources (DEVI; DHAMODHARAN, 2018; DUARAH; KARAK, 2017; RAN et al., 2018; RAVISHANKAR et al., 2019; WU et al., 2016). Nature offers a plethora of carbon sources that has motivated the investigation of a wide variety of raw materials to obtain CDs, which include lignin biomass, waste paper, kitchen waste, starch, orange peels, potato, grass, soy milk, papaya, eggs, coffee grounds, hair, cow manure, among others (MENG et al., 2019; SHARMA; TIWARI; MOBIN, 2017; SURENDRAN et al., 2020; XU; XIE; HAKKARAINEN, 2017; ZHANG; SUN; WU, 2015). Since CDs obtained from different sources were synthesized through diverse protocols, they present different properties and size ranges, varying from 1 nm to 50 nm (MENG et al., 2019). Therefore, there is room for improvement in terms of searching for reliable and renewable carbon sources and for the development of greener, cheaper, and environmentally friendly synthetic protocols.

The molecular structure of the CDs has not been fully elucidated, but infrared (IR) and Raman studies suggest that these carbon nanoparticles are not perfect crystals and that they present a high degree of structural defects and peripheral functional groups (CADRANEL et al., 2019). The structural defects on the carbon core and the peripheral functional groups are both dependent on the synthetic protocol and have a strong influence on the photoluminescence behavior of the CDs.

The mechanism involved in the CDs fluorescence is still under debate in the literature, and some theories propose: (i) generation and recombination of electron-hole pairs; (ii) quantum confinement effect; and (iii) defective state emission (WANG; HU, 2014; ZHU et al., 2015). CDs usually exhibit a strong absorption band in the UV region around 230 nm that may be assigned to a $\pi \rightarrow \pi^*$ transition concerning sp² carbons on the carbon core, and a tail extending to the visible region that might be attributed to a $n \rightarrow \pi^*$ transition involving the peripheral functional groups that bear electron lone pairs (BAKER; BAKER, 2010; LUO et al., 2009).

Interestingly, CDs exhibit excitation-wavelength dependent emission, and the emission wavelength is strongly affected by the electronic bandgap transitions of conjugated π -systems, surface defects, and element doping (GAN; XU; HAO, 2016; YAN et al., 2019; ZUO et al., 2016). It has been demonstrated that variations of the CDs' sizes shift the maximum emission wavelength, resulting in maximum emissions on ultraviolet (UV, around 350 nm), on visible (400–700 nm), and on near infrared (NIR, about 800 nm) depending on the carbon core's dimensions (smaller particles emit at lower wavelengths, whereas larger particles emit at higher wavelengths) (LI et al., 2010; ZUO et al., 2016).

The unique emission properties of CDs allied to their easily tailored nanosize and to the high abundance of carbon sources have made them attractive for a wide variety of potential applications including bioimaging, drug-delivery, sensors, optoelectronics, photovoltaic devices, photocatalysis, renewable energy devices, and anti-counterfeiting materials (ARCUDI; ĐORĐEVIĆ; PRATO, 2017, 2019; CHEN et al., 2019; GAO et al., 2016; GUPTA et al., 2011; JI et al., 2018; LI et al., 2018a; MENG et al., 2019; PANWAR et al., 2019; SHARMA; TIWARI; MOBIN, 2017; TIAN et al., 2017). Moreover, the semiconductor-like properties of CDs enabled their incorporation into optical fibers to obtain optical devices with innovative features (GONÇALVES; DUARTE; ESTEVES DA SILVA, 2010; LIN; HUANG; DING, 2019).

2.3.2. Sugarcane syrup carbon dots synthesis and characterization

A green, sustainable, and simple methodology to obtain CDs from sugarcane syrup was developed, as shown on Figure 1. The major components of sugarcane syrup are sucrose, glucose, fructose, amino acids, lipids, and inorganic salts containing K, Ca, Na, Fe, and Mg, among others.

Sugarcane syrup was obtained from a local plant (Usina da Pedra, SP, Brazil) in commercial grade. Contrary to molasses, which is usually obtained as a residue from ethanol production, the syrup is produced as a step from the sugar process: part of the clarified broth is evaporated to concentrate the sucrose without crystallizing it.

The syrup (5 mL) was diluted with deionized water (5 mL) and placed into a ceramic crucible. The mixture was heated in a domestic microwave oven (700 W, 20 L), using a two-cycle process (1 min + 30 s): (i) 1 min; followed by (ii) a second cycle of 30 s. After the first heating cycle, the microwave oven was carefully opened to relieve the internal pressure. After the carbonizing process, the ceramic crucible was left to cool up to room temperature. The carbonized solid was scraped out and redispersed in deionized water (30 mL) using an ultrasound bath for 1 h. The ultrasonication process was repeated until the full consumption of the carbonized bulk material.

The resulting mixture was filtered through filter paper to remove the bulk material, yielding a homogeneous brownish solution. The filtered solution containing the CDs was further filtered using centrifugal filter tubes with molecular weight cut-off (MWCO) of 3000 Da (Merck Millipore, Danvers, MA, USA). The ultracentrifugation process was carried out under 7000 g (7873 rpm) for 15 min. Deionized water was added to the dispersion of CDs until the centrifugal filtered water exhibits absorbance close to zero (absorbance < 0.005 UA). The sample was lyophilized, resulting in 135 mg of a dark brown solid (yield of 67.5% in wt). Part

of this solid material was subsequently redispersed in deionized water to generate a CDs solution in a concentration of 32.3 mg/mL and the remaining material was characterized.

Fourier Transform Infrared Spectroscopy (FTIR) was used to detect and identify the functional groups present in the CDs surface (Figure 1) using an Antaris FTIR-NIR Absorption Spectrophotometer (Thermo Fisher Scientific, Waltham, Massachusetts, USA) in ATR reflectance mode. For the FTIR analysis, the solid CD sample was directly placed onto the ATR crystal.

Typical absorption bands for alcohol, carboxylic acids, amines, aldehydes, and ketones were observed. The intense and broad band at 3360 cm⁻¹ corresponds to the stretching and bending vibrations of O-H and N-H bonds present on amines, alcohols, and carboxylic acids. The double band at 2850 cm⁻¹ is assigned to C-H stretching on aldehydes. The peak observed at 1720 cm⁻¹ corresponds to the C=O bending on carboxylic acids, aldehydes, and ketones. The presence of amines is evidenced by the bands at 1650 cm⁻¹ (N-H bending) and at 1040 cm⁻¹ (C-N stretching vibrations). The presence of these functional groups bearing lone electron pairs contribute to the CDs fluorescence and makes these nanoparticles polar and water-soluble. Moreover, these functional groups on the CDs periphery allow their further functionalization through covalent attachment or interaction with other nanomaterials through hydrogen bonding. The resulting CDs are fluorescent in solution and in the solid-state after lyophilization, which was easily confirmed using an UV lamp with a wavelength of 254 nm (photographs of CDs in solution and powder are shown in Figure 2).

The sizes of the CDs were analyzed in the solid-state by Atomic Force Microscopy (AFM) using a Park NX10 Atomic Force Microscope (Park Systems, Suwon, Korea) with scan width of $100 \times 100 \mu$ m, z-hub of ca. 15 μ m, and out-of-plane resolution of 0.006 nm. The samples were prepared by diluting the original solution of CDs (32.3 mg/mL) in deionized water ($100 \times dilution$); dropping it on a freshly cleaved mica surface; and allowing it to dry for 24 h. Figures 3b-c show the 2D-AFM height image and the 3D-topographic AFM image of the CDs on the mica surface. In the AFM equipment, spherical nanoparticles result in circular bidimensional profiles observed on the image's plane. Therefore, it is possible to infer that the heights indicated by the color scale of the AFM image correspond to the diameters of the individual particles. The AFM images reveal the presence of semispherical nanoparticles with average dimensions of 3.0 nm (sizes vary between 2.0 nm and 5.8 nm).

Particle size distribution was also assessed through Dynamic Light Scattering (DLS). The measurement was carried out at 25 °C on a Zetasizer Nano–ZS ZEN3600 instrument (Malvern Instruments, Malvern, UK) equipped with a 4 mW He–Ne laser with a light wavelength of 632.8 nm and backscattering angle of 173°, using a disposable DTS 1070 cell. The solid sample of CDs was redispersed in deionized water at a concentration of 1 mg/mL. Data are presented as % by number.

The DLS analysis (Figure 3a) reveals particles with an average hydrodynamic diameter of 5 nm and low polydispersity. It is important to note that there is no evidence for the presence of other populations of particles with higher diameters, demonstrating the efficacy of the newly developed synthetic protocol.

When comparing the values obtained by DLS and AFM, it is possible to notice consistency, since the size obtained by DLS refers to the nanoparticle's hydrodynamic diameter in solution, which includes at least one layer of surrounding solvent. AFM images, in turn, are acquired in the solid state on a flat surface in which a slight flattening of the nanoparticles is expected due to their interaction with the mica surface and to their contact with the AFM probe (ASTRUC; ORNELAS; RUIZ, 2009; ORNELAS et al., 2009). Moreover, the 3.0 nm size is consistent with the dimensions of CDs with green emission obtained in previous reports (LI et al., 2010).



Figure 1. Schematic representation of the new methodology developed to obtain CDs from sugarcane syrup; chemical structures of the major components of sugarcane syrup; schematic representation of the resulting CDs; and FTIR spectrum of the CDs with the assignment of the most important bands.



Figure 2. (a) Pictures of the obtained pure CDs as a solid (left) and in aqueous solution (right, falcon tube); (b) pictures of the obtained pure CDs as a solid (left) and in aqueous solution (right, falcon tube) under UV light (254 nm).



Figure 3. (a) DLS data obtained for CDs in aqueous solution; (b) 2D AFM height image of CDs deposited on a mica surface; (c) 3D topographic AFM image of CDs deposited on a mica surface (scale bar from zero to 5.8 nm).

2.3.3. Preparation of hydrogel-CDs nanocomposites and photophysical characterization

The fluorescent CDs were further immobilized into a hydrogel matrix (gelatin) to produce a green-fluorescent polymeric nanocomposite. The idea was that the carbon nanodots would be firstly immobilized using gelatin as the polymeric gelator to be used for the fabrication of fluorescent optical fibers.

Gelatin is a natural high molecular weight polypeptide biopolymer derived from the hydrolysis of collagen. Gelatin easily forms thermoreversible hydrogels in aqueous solutions in concentrations as low as 1% w/w by constituting a micro-structural network (HAN; LV, 2019).

Gelatin possesses both positively and negatively charged amino acids. It is a unique polyampholyte polypeptide, what confers an excellent versatility to this hydrogel material. Also, this material presents a series of advantages when compared to the more common acrylic and glycolic-based hydrogels such as: low-cost; wide commercial availability; low viscosity (before curing); and spontaneous heat-induced curing. Also, it does not require aggressive crosslinking conditions like photocure equipment, extreme pH, radical initiators, or metalbased catalysts (BUREY et al., 2008; CAMPIGLIO et al., 2019; ZHOU; GUO; YANG, 2018).

Moreover, gelatin hydrogels have been successfully used in fiber optic devices for sensing applications (SCHYRR et al., 2015). For instance, a previous report showed that a membrane formed by a gelatin-CDs nanocomposite performed as a fluorescence sensor for the detection of potassium (RAHIMI; MAHANI; HASSANI, 2019).

The preparation of the hydrogel matrix started by dissolving 3 g of colorless and odorless gelatin (food grade) in 94 mL of deionized water using a 250 mL beaker. The solution was heated at 90 °C under magnetic stirring until the elimination of the air bubbles dissolved in the solution (temperature control is crucial to avoid degradation of the polypeptide material). Indeed, the presence of air bubbles is a common problem in hydrogel matrices and has a negative impact on the optical properties of the final materials. Different strategies may be used for minimizing this effect, including simultaneously heating and stirring, or treatment of the suspension in vacuum chamber for eliminating the occluded air (CHOI et al., 2013, 2015).

Once more aggressive approaches could impact the properties of the nanocomposite and increase the cost and complexity of the overall process, the simple heating and stirring under relatively low temperature and velocity (for reducing the shear stresses) was used. To the transparent gelatin solution, 6 mL of the CDs solution (32.3 mg/mL) were added and kept under magnetic stirring for 5 min until the complete homogenization.

The resulting yellowish solution was cooled in the refrigerator at 10 °C overnight. A thermoreversible hydrogel was obtained through the formation of a micro-structural tridimensional network (DJABOUROV, 1991). Above 40 °C, the aqueous solution of gelatin behaves as a homogeneous solution of macromolecules with a typical molar mass of 2×10^5 Da. The macromolecules assume random coil configurations (single polypeptide chains termed α -chains) which may be entangled (BOHIDAR; JENA, 1993). When these α -chains are cooled further, they undergo a coil-to-helix transition that leads to the formation of a tridimensional network with water molecules and to the consequent gelation process (FINER et al., 1975).

During gelation, the CDs remained within the hydrogel matrix: they were probably stabilized by hydrogen bonding between the terminal functional groups on the CDs surfaces and the amino acids present on the gelatin polymer. The resulting hydrogel-CDs nanocomposite presents a yellowish coloration that fluoresces upon irradiation with UV light (254 nm).

The refractive index (RI) of the hydrogel-CDs nanocomposite was evaluated with a MISCO PA 202 Refractometer before and after curing (Palm Abbe, Cleveland, OH, USA). For that, a liquid suspension is dropped on the analytical surface of the equipment, which indicates the index. In the case of the hydrogels, there may be a slight variation of this index over time due to temperature changes and to the curing process of the drop. Therefore, the value of the index was evaluated immediately after dropping the solution on the equipment; and after the reading became stationary, which usually takes from 15 min to 1 h depending on the environmental temperature. On the other hand, due to the high amount of occluded water, the indices are very close to the one obtained for water.

The analysis showed RI values of 1.3389 and 1.3390 before and after curing, respectively. Such values are close to the one measured for DI water (1.3330) and lower than PMMA's RI (1.49) (BEADIE et al., 2015). It indicates that the total internal reflection in the PMMA-nanocomposite interface will prevent the fluorescence from leaking back into the hydrogel-filled holes.

The absorbance spectra in the UV-Visible range that were obtained for CDs, hydrogel matrix, and hydrogel-CDs nanocomposite are presented in Figures 4a,b. Data were acquired using a 1 cm cuvette in an Agilent 8453 UV-Vis Spectrophotometer (Agilent Technologies, Santa Clara, CA, USA).

The CDs present an absorption band with λ_{max} at 279 nm that corresponds to the $\pi \rightarrow \pi^*$ transition assigned the sp² carbons from the CDs core, which is within the expected range for CDs with 3-5 nm (Figure 4a). The CDs also present a shoulder at 360 nm with a tail extending to the visible range assigned to the $n \rightarrow \pi^*$ transitions involving the electron lone pairs from functional groups present at the CDs periphery.

The absorption spectrum of the hydrogel matrix confirms the high transparency of this material in the visible range (Figure 4b). In contrast, the absorption spectrum of the hydrogel-CDs nanocomposite shows a higher absorption in the 360 nm region with a tail in the visible region related to the absorption spectra of the CDs encapsulated in the hydrogel matrix (Figure 4b).

The emission spectra were obtained in a Varioskan LUX Multimode Microplate Reader (Thermo Fisher Scientific, Waltham, Massachusetts, USA), by irradiating it with wavelengths ranging from 300 to 430 nm with intervals of 10 nm. Results were normalized in terms of the maximum detected fluorescence intensity.

The spectra collected for CDs in aqueous solution and in the hydrogel-CDs nanocomposite are dependent on the excitation wavelength, which is a well-known characteristic of CDs (Figures 4c,d). The emission spectrum in solution shows that the maximum intensity of the fluorescence emission is around 450 nm, obtained when irradiating the sample with an excitation wavelength of 360 nm. In contrast, the emission spectrum of the hydrogel-CDs nanocomposite shows that the maximum intensity of the fluorescence emission is around 450 nm. In contrast, the emission spectrum of the hydrogel-CDs nanocomposite shows that the maximum intensity of the fluorescence emission is around 420 nm, obtained when it is irradiated with an excitation wavelength of 340 nm.

As a matter of fact, when comparing the nanocomposite with the dispersion of CDs in water, it is possible to notice that the encapsulation into the hydrogel matrix broadens all emission bands towards blue, but without a substantial change on the wavelength of the respective peaks (i.e., the maximum emission intensities).

This broadening to the blue might be explained by the changes in the microenvironment around the CDs. Emissions at shorter wavelengths are usually observed when the surrounding environment destabilizes the excited state of the fluorophore groups on the nanoparticle's surface. Therefore, our data suggest that, upon immobilization inside the hydrogel tridimensional network, new intermolecular interactions arise between the functional groups in the periphery of the CDs and the amino acid residues in the polypeptide. Once these new forces are weaker than those present in the aqueous medium, the particles are less stable in the polymer matrix than in water. This loss of stability causes the blue-broadening on the emission spectra (SUPPAN, 1990).



Figure 4. (a) UV-Vis absorbance spectrum of the CDs in aqueous solution; (b) UV-Vis absorbance spectra of hydrogel and hydrogel-CDs nanocomposite; (c) emission spectra of the CDs in aqueous solution; (d) emission spectra of the hydrogel-CDs nanocomposite.

2.3.4. Fabrication of Fluorescent Microstructured Polymer Optical Fibers (mPOF)

An innovative microstructured polymer optical fiber (mPOF) with intrinsic fluorescence was obtained by incorporating the hydrogel-CDs nanocomposite into a double-clad optical fiber with a newly developed design.

The mPOFs consist of waveguides containing well-defined hole patterns in their crosssections, allowing the control of the light-guiding through the appropriate design and configuration of the holes (VAN EIJKELENBORG et al., 2001). The holes can be filled with different materials and substances, providing direct interaction between the enclosed materials and the evanescent field of the light throughout the whole fiber length (YANG et al., 2018). Among the different possible designs for mPOFs, the double-clad fiber is one that patterns the holes to create an internal clad (usually filled with air) for improving the guiding efficiency (LIMPERT et al., 2003).

The double-clad design has been successfully employed in several applications, including the fabrication of fiber lasers with enhanced Q-switching and high-efficiency amplifiers. For these applications, the fibers are usually doped with rare-earth elements (ZENTENO, 1993) such as Nd (CHEN et al., 1998), Yb (FILIPPOV et al., 2008, 2010; HIDEUR et al., 2000; LIMPERT et al., 2005, 2003; YE et al., 2007; YONG WANG; HONG

PO, 2003), Er (ABEDIN et al., 2014; AMRANI et al., 2009; DOYA; LEGRAND; MORTESSAGNE, 2001), Tm (LIU et al., 2013; ZHENGQIAN LUO et al., 2014), and combinations of Er-Yb (LAROCHE et al., 2002; SOBON et al., 2011) to explore the fluorescence of those chemicals. Moreover, given the high efficiency to confine light, the double-clad design also finds applications in fluorescence spectroscopy and biomedicine, where it can be used for endoscopy, intravascular imaging, and optical coherence tomography (LEMIRE-RENAUD et al., 2010; LIANG et al., 2012; WANG et al., 2007; YELIN et al., 2004).

Despite their inherent versatility, these fibers are commonly combined with rare-earths and other heavy metals with superior fluorescence, like inorganic quantum dots (QDs) of high costs and toxicity. An alternative to this cost and toxicity problem is to substitute such materials for the harmless CDs by properly immobilizing the nanoparticles into the fiber holes. For this purpose, the hydrogel-CDs nanocomposite was used, since it is a green, sustainable, safe, and biodegradable material obtained from biomass and with low production cost.

An innovative design of waveguide was proposed, which is essentially different from the ones of other double-clad mPOFs previously fabricated. In other works, the reported cavities are arranged according to hexagonal profiles (BELTRÁN-MEJÍA et al., 2012; LIMPERT et al., 2005, 2003); the fibers create a pattern of tangential circular cavities for field enhancement (WIEDERHECKER et al., 2007); or the fibers present successive layers of non-tangential cavities, both in hexagonal and circular patterns (ZHANG et al., 2017).

The design developed in this work presents advantages for the liquid matrix incorporation. The presence of the central cavity of higher diameter and of the two tangential layers of circular cavities (with four diametrically opposed holes of higher diameters) facilitates the introduction of the hydrogel containing CDs by both external pressure and capillary forces (Figure 5). That is due to the wide and symmetrical distribution of hollow spaces through the cylindrical volume.



Figure 5. Newly developed design of double-clad optical fiber (quotes in millimeters).

The mPOF fiber was designed in the Laboratory of Specialty Fibers and Photonic Materials from the University of Campinas, which has large experience in the project and fabrication of polymer and microstructured optical fibers (CABRAL et al., 2019; CORDEIRO;

NG; EBENDORFF-HEIDEPRIEM, 2020; FUJIWARA et al., 2020; TALATAISONG et al., 2018). The fiber was obtained by pulling a structured poly(methylmethacrylate), PMMA, preform on a POF draw tower in a two-step process. The preform started as a PMMA rod with an external diameter of 70 mm. Using a CNC drilling machine, several holes were introduced in the preform. This fabricated preform has two rings of 2.5 mm holes; the innermost ring has 36 equally spaced holes; and the outer ring has 44 holes. A group of 4 larger holes (5 mm diameter) centered along the midpoint between the inner and outer rings are placed in the cardinal directions. The preform also contains a 15 mm-wide central hole.

On the first step of the drawing process, the diameter of the preform is reduced from 70 mm to 12 mm, while the second drawing step reduces the 12 mm-preform to a fiber with external diameter of \sim 500 µm. Drawing parameters for the first step are: furnace temperature of 190 °C, preform feed speed of 0.5 mm/min, and drawing speed around 0.02 m/min. The same furnace temperature was used for the second step, but now with 5 mm/min preform feed speed and around 3 m/min of drawing speed.

The hydrogel-CDs nanocomposite preparation procedure was essentially repeated, but now the curing took place inside the fiber. For that, a syringe was attached to one end of the fiber to flow the gelatin-CDs heated suspension (which was not cured yet) through capillary and external pressure forces. Thus, part of the solution was introduced into the holes of the mPOF for curing. The two ends of the mPOF were sealed, and the system was left on the refrigerator overnight for allowing the thermal-crosslinking of the matrix and the immobilization of the hydrogel-CDs nanocomposite.

Figure 6 shows the cross-section of the final fiber obtained. Light is directed to the fiber in a direction normal to its cross-section plane (the fiber's circumference). It allows the light to get transmitted through the holey structure and to excite the fluorescent material inside the central hole. Due to the contrast of refractive indices (RIs), the fluorescence emitted by the CDs is confined and guided through the inner PMMA ring (RI \approx 1.49) (BEADIE et al., 2015) and can be captured by a photodetector or spectrometer positioned by the tip of the fiber.

Therefore, a (370 ± 10) nm LED operated at 48 mA was positioned perpendicular to the axis from a mPOF piece, and it was used to externally irradiate the fiber. The visible light emerging from the tip was finally focused by an external lens to an HR4000 Spectrometer (Ocean Optics, Largo, FL, USA) for detection and analysis. This full setup and a micrograph of the mPOF cross section are also shown in Figure 6.

One could expect here that the detected power would be substantially inferior to the LED nominal power. Considering the absorption properties of CDs and the immobilization of the nanocomposite into the mPOF cavities, the light guided through the mPOF (including both the UV excitation and the fluorescent emission) is expected to lose power due to the intrinsic mechanisms of molecular absorption. Also, the guided light may lose intensity due to attenuation or scattering by the macromolecules or by the nanoparticles themselves. Finally, it is not the totality of the irradiated light that will penetrate the fiber structure for being guided. Part of the light can be absorbed, scattered or even reflected back by the external waveguide's surface.



Figure 6. Setup for evaluation of the mPOF fluorescence and a micrograph of the fiber's cross section.

The application of the hydrogel-CDs nanocomposite for obtaining a microstructured optical fiber with intrinsic fluorescence was verified by analyzing the light guided by the new mPOF system. Once the internal volume of the cavities of the mPOF is very low (diameter on the order of micrometers), the total number of luminescent emitters inside it is very reduced. Thus, a relatively low total intensity was expected to be verified on the fiber tip, requiring the experiment to be performed in the absence of environmental light.

The spectral data regarding the visible emission of interest that was collected from the mPOF are shown in Figure 7. It is possible to notice that the fluorescence with the highest intensity is on the range 445-550 nm, what was already expected from the hydrogel-CDs nanocomposite emission spectra. Above this range, the fluorescence is progressively lower, and no emission is observed above 650 nm. Specially for the maximum intensity range, there is a substantial noise (e.g., at 470 and 475 nm) impairing the signal-to-noise ratio (SNR). It is probably a consequence of the low number of fluorescent particles present in the microchannels, which reduces the detected intensity as predicted.

The detection of the fluorescence on the range predicted by Figure 4 shows that the immobilization into the fiber does not shift the emission and that the methodology of retaining the CDs with hydrogel into the microstructured fiber is effective for the fabrication of a fluorescent mPOF.

The fluorescent emission and the SNR could be further improved by using a higherpowered LED; by increasing the concentration of CDs in the hydrogel-CDs nanocomposite; or by increasing the diameter of the central mPOF hole (enhancement of the number of emitters).



Figure 7. Fluorescence emitted by the mPOF with the nanocomposite of gelatin-CDs.

2.3.5. Quantum Yield (QY) evaluation

As previously observed in Section 2.2, the ratio between the total number of photons that the particle re-emits and the number of photons it absorbs is known as its quantum yield (LAKOWICZ, 2006). Quantum yields (QYs) for CDs in water and the hydrogel matrix were calculated with Equation (1) (WILLIAMS; WINFIELD; MILLER, 1983).

$$QY_C = \frac{QY_R F_C A_R \eta_C^2}{F_R A_C \eta_R^2} \tag{1}$$

In Equation (1), QY_C is the quantum yield; F is the area under the curve of the fluorescence spectrum at 350 nm; A is the absorbance of the samples at low concentration (absorbance < 0.1 AU); and η is the index of refraction. Here, subscript C denotes carbon nanodots, whereas subscript R denotes the reference sample. The reference sample is quinine sulfate in 0.1 M sulfuric acid, which has a QY of 54.5% (BROUWER, 2011; LAKOWICZ, 2006).

Remarkably, the occlusion of the CDs into the polymeric matrix did not significantly affect the quantum yield: QY_C was reduced from 34.5% to 33.1%.

2.3.6. Conclusions from this study

This study resulted in a sustainable, cheap, scalable, and straightforward methodology to obtain carbon nanodots with low polydispersity. The resulting CDs have average diameters of 3 nm and are fluorescent upon irradiation with UV light. A fluorescent hydrogel-CDs nanocomposite was obtained using cheap gelatin polypeptide as the polymeric matrix. The CDs emission spectrum bands broadened towards blue upon incorporation into the hydrogel tridimensional network; and the occlusion of the particles into the polymeric matrix did not significantly affect the quantum yield, which reduced from 34.5% to 33.1%.

The new hydrogel-CDs nanocomposite was incorporated into the cavities of a doubleclad polymer optical fiber fabricated with an innovative design. This mPOF has a central empty hole surrounded by a PMMA ring, which is, in turn, limited by two tangential layers of airfilled holes, forming an external ring with lower refractive index. The fluorescent fiber showed similar emission profiles than the nanocomposite when UV-irradiated. Therefore, this work demonstrates a potential alternative for the substitution of rare-earths and other inorganic heavy metals (which present high costs and toxicity) for applications in luminescent microstructured optical fibers.

- 2.3.7. Contributions and acknowledgements
 - Financial support from São Paulo Research Foundation (FAPESP) under grant 2019/22554-4.
 - Financial support to other contributors of this work: FAPESP grants: 2015/04929-0 and 18/02093-0; Coordenação de Aperfeiçoamento de Pessoal de Nivel Superior (CAPES), finance code 001; National Council for Scientific and Technological Development (CNPq, productivity award for CO 307403/2018-1) grant 309989/2021-3.
 - Prof. Carlos K. Suzuki from the Laboratory of Photonic Materials and Devices, School of Mechanical Engineering, University of Campinas, SP, Brazil (FEM/UNICAMP) for the technical support and for scientific discussions and insights.
 - Laboratory for Surface Science (LSC) of the Brazilian Nanotechnology National Laboratory, SP, Brazil (LNNano, CNPEM/MCTI) for the AFM images.
 - Dr. Bruna Gregatti and Prof. Lucimara Gaziola de la Torre from the Laboratory of Advanced Development of Nano and Biotechnology, School of Chemical Engineering, University of Campinas, SP, Brazil (FEQ/UNICAMP) for the centrifuge equipment.
 - Dr. Thiago B. Taketa, Dr. Rogério A. Bataglioli and Prof. Marisa M. Beppu from the Laboratory of Chemistry and Products Engineering (LEQUIP), School of Chemical Engineering, University of Campinas, SP, Brazil (FEQ/UNICAMP) for the fluorescence spectra characterization and the lyophilization equipment.
 - Dr. Sébastien Livi and Prof. Jannick Duchet-Rumeau from Ingénierie des Matériaux Polymères, Université de Lyon (France) for the characterization of the quantum yields.
 - Gabriel Perli, Dr. Diego L. Bertuzzi and Prof. Catia Ornelas from the Institute of Chemistry, University of Campinas, SP, Brazil (IQ/UNICAMP) for the chemistry theory, contextualization and interpretation support, as well as UV-Vis, DLS and FTIR characterization.
 - Dr. Thiago D. Cabral and Prof. Cristiano M. B. Cordeiro from the Laboratory of Specialty Fibers and Photonic Materials, "Gleb Wataghin" Institute of Physics, University of Campinas, SP, Brazil (IFGW/UNICAMP) for the physics theory, contextualization and interpretation support, fabrication of the double-clad mPOF, and optical characterization equipment (RI and OSA).
 - Prof. Julio Roberto Bartoli from the School of Chemical Engineering, University of Campinas, SP, Brazil (FEQ/UNICAMP); and Prof. Maurizio Prato from the Carbon Nanotechnology Group, Dept. of Chemical and Pharmaceutical Sciences, University of Trieste (Italy) for the support on both the development of the synthetic carbon nanodots methodology and on the project idealization.

2.4. Synthesis of Carbon Nanodots from Orange Juice and UHT Milk

Here, the work published by Optica Publishing Group (SOARES et al., 2020a) is presented, demonstrating the possibility of easily obtaining fluorescent nanoparticles from ultra-high temperature processed (UHT) milk and orange juice. It consists on the adaptation of the methods shown in Section 2.3 for synthesizing CDs from these two other natural sources.

2.4.1. Introduction

Carbon nanodots can be obtained directly from natural sources, allowing the use of ecofriendly processes which apply renewable and biocompatible raw materials of low cost and wide availability on nanoparticles syntheses. Moreover, since many of these natural sources contain carbon and heteroatoms (e.g. N, O and S), no other chemical reactant is necessary: doped CDs can be directly obtained from biomass waste, for example (ZHANG et al., 2018).

Even though CDs usually present diameters lower than 10 nm (ARCUDI; ĐORĐEVIĆ; PRATO, 2019; DAS; BANDYOPADHYAY; PRAMANIK, 2018), particles with sizes up to ~50 nm are reported for the syntheses from natural products (ZHANG et al., 2018). For instance, the hydrothermal treatment was applied to the fabrication of CDs from orange juice (120 °C, 2.5 h) (SAHU et al., 2012) and from milk (180 °C, 2.0 h) (WANG; ZHOU, 2014).

Then, this work demonstrates a faster (2 min) and more energetically efficient approach (microwave-assisted synthesis) for the fabrication of CDs using these last two natural sources, orange juice and milk. Both raw materials are rich in organic acids (ascorbic and citric acids in the orange juice, and lactic acid in milk), and milk also contains nitrogen sources (proteins). It is known that the conversion of organic materials containing carboxylic acids (or N) results in the formation of CDs rich in carboxylic (or amine) surface groups. These groups are considered the major contributors for the luminescence (ARCUDI; ĐORĐEVIĆ; PRATO, 2019).

2.4.2. Synthesis and characterization of carbon nanodots

10 mL of orange juice; and 10 mL from a solution comprised of ultra-high temperature (UHT) processed whole milk powder dissolved in deionized water (concentration of 70 g/L of milk in water) were separately submitted to an adaptation of the procedure previously reported for the synthesis of CDs from sugarcane syrup - the one described in Section 2.3 (PERLI et al., 2022; SOARES et al., 2019a). Both raw materials were of food grade and were used as available in standard local markets. The orange juice was fabricated by fruit squeezing, maintaining oranges' original composition and organoleptic properties.

In both cases, the procedure consisted of putting the liquid solutions on a ceramic crucible prior to heating them in a domestic microwave oven (700 W, 20 L). 2 heating cycles of 1 min were performed; and the microwave was slowly opened between each cycle to relieve internal pressure. After that, the crucible with carbonized material (brown color) was cooled to room temperature; deionized water was added; and the solid was scraped out with a spatula and redispersed. The colloidal dispersions were then: sonicated for 5 min; filtered in cotton for removal of larger particles; and sonicated again for 5 min.

The suspensions rested in the refrigerator for 3 days (~10 °C); and were submitted to a last filtering before being centrifuged under 7000 g (7873 rpm) for 15 min using centrifugal

filter tubes with molecular weight cut-off (MWCO) of 3000 Da (Merck Millipore, Danvers, MA, USA). Deionized water was added to the dispersions of CDs until the centrifugal filtered water exhibits absorbance close to zero (absorbance < 0.005 UA).

An orange and a pale-yellow dispersion were obtained from the orange juice and from the UHT milk, respectively, and both showed light green fluorescence when irradiated by a 254 nm UV lamp (suspensions under daylight and emitting luminescence under UV-irradiation are depicted on Figure 8g).

The sizes of the CDs were analyzed in the solid-state by AFM using a Park NX10 Atomic Force Microscope (Park Systems, Suwon, Korea) with scan width of $100 \times 100 \mu m$, z-hub of ca. 15 μm , and out-of-plane resolution of 0.006 nm. The samples were prepared by diluting the original solutions of CDs in deionized water ($100 \times dilution$); dropping them on a freshly cleaved mica surface; and allowing them to dry for 24 h. Figures 8a and 8e show 2D-AFM height images for the CDs from orange juice and from milk, respectively; whereas Figures 8b and 8f present the 3D-topographic AFM images of the CDs on the mica surface for the materials from orange juice and from milk, respectively.

It is possible to observe that the AFM analysis shows particles smaller than 5 nm for the CDs obtained from orange juice and up to 53 nm for the ones from UHT milk. These results are in accordance with those observed for other natural-derived CDs (ZHANG et al., 2018). These diameters suggest a higher organic content for the milk and the possibility of optimizing the heating time for fabricating particles with lower diameters and narrower dimensional distributions (ARCUDI; ĐORĐEVIĆ; PRATO, 2019; DAS; BANDYOPADHYAY; PRAMANIK, 2018; ZHANG et al., 2018).

The solutions of carbon nanodots were also lyophilized for FTIR characterization with an Antaris FTIR-NIR Absorption Spectrophotometer (Thermo Fisher Scientific, Waltham, Massachusetts, USA) in ATR reflectance mode. For the FTIR analysis, solid CDs samples were directly placed onto the ATR crystal for the detection and identification of the functional groups present in particles' surfaces. Figure 8h compares the spectra collected for both materials.

The physicochemical characterization by FTIR showed spectra similar to the one previously obtained from sugarcane syrup, with organic functional groups -C-O; -CN (only in milk); -C=C; -C=O; -OH; -NH (only in milk); and carboxylic -OH. These last two (amine and carboxylic acid) are usually considered the major responsible for the luminescent emission (ARCUDI; ĐORĐEVIĆ; PRATO, 2019; DAS; BANDYOPADHYAY; PRAMANIK, 2018; PERLI et al., 2022; ZHANG et al., 2018).

The CDs derived from orange juice present an apparently more intense carboxylic -OH signal. This was already expected due to the higher amount of organic acids usually observed on citric fruit juice (ARCUDI; ĐORĐEVIĆ; PRATO, 2019; LI et al., 2018b).

Finally, the original solutions (suspensions with no further dilution) of carbon nanodots were simultaneously analyzed in liquid phase in terms of their fluorescence spectra using a Varioskan LUX Multimode Microplate Reader (Thermo Fisher Scientific, Waltham, Massachusetts, USA). For that, samples were irradiated with wavelengths ranging from 300 to 430 nm with intervals of 10 nm, and the results were normalized in terms of the maximum detected fluorescence intensity. Figures 8c and 8d show the spectra collected for CDs from orange juice and from UHT milk, respectively.

The fluorescence spectra peak at 426 nm when the sample is irradiated at 350 nm (orange juice-derived CDs, Fig. 8c); and at 425 nm when the sample is irradiated at 330 nm (UHT milk-derived CDs, Fig. 8d). Both profiles show excitation-dependent behavior and decrease of intensity as the peaks red-shift.

The variation of the wavelength correspondent to the maximum emitted fluorescence is also similar for both profiles. However, substantially lower intensities are observed for the milkderived CDs. It is in accordance with other studies that compared CDs synthesized with similar methodologies, but with different diameters. Indeed, a general tendency that is usually observed is the reduction of the luminescent intensity when the particles' diameters increase (ARCUDI; ĐORĐEVIĆ; PRATO, 2019; DAS; BANDYOPADHYAY; PRAMANIK, 2018; PERLI et al., 2022; SAHU et al., 2012; WANG; ZHOU, 2014; ZHANG et al., 2018).



Figure 8. CDs obtained from orange juice: (A) AFM; (B) 3D-profile of AFM; and (C) fluorescence spectra. CDs obtained from UHT milk: (D) fluorescence spectra (inset shows the spectra under a different scale); (E) AFM; and (F) 3D-profile of AFM. Suspensions compared: (G) under daylight (upper figures) and when emitting green fluorescence under 254 nm (bottom figures; orange juice-derived CDs on the left); (H) FTIR spectra.

This reduction of the intensity may be also resultant from the lower content of carboxylic acid groups (as predicted from chemical compositions and as empirically observed on the FTIR spectra). It indicates that, among the organic groups present in these particles, COOH is probably the main fluorescence contributor; and that the presence of amine groups in milk-derived CDs is not sufficient for compensating for this effect.

2.4.3. Conclusions from this study

This study showed the feasibility of extending the methodology used for the synthesis of carbon nanodots from sugarcane syrup to other two widely available natural sources (orange juice and milk), opening the possibility of applying a broad portfolio of natural raw materials.

Fluorescent organic nanoparticles rich in carboxylic groups and with excitationdependent behavior were obtained; and it was verified that the heating time (the main process parameter) could be optimized for each raw material to obtain lower particle dimensions and a consequent increase on the fluorescence intensity. This optimization would be particularly important for the milk-derived materials, which showed high diameters. Such diameter increase was possibly caused by a heating time excessively large for their total organic content.

Since the orange juice derived dots are rich in carboxylic groups and show higher emission intensities, they are promising for use in applications that explore the chemistry of the -COOH groups. Examples include the bounding of CDs to silica for fabricating nanocomposites with applications on sensors and on the fabrication of fluorescent dyes for anti-counterfeiting (AMATO et al., 2021).

2.4.4. Contributions and acknowledgements

- Financial support from São Paulo Research Foundation (FAPESP) under grant 2019/22554-4.
- Prof. Carlos K. Suzuki from the Laboratory of Photonic Materials and Devices, School of Mechanical Engineering, University of Campinas, SP, Brazil (FEM/UNICAMP) for the technical support and for scientific discussions and insights.
- Laboratory for Surface Science (LSC) of the Brazilian Nanotechnology National Laboratory, SP, Brazil (LNNano, CNPEM/MCTI) for the AFM images.
- Dr. Bruna Gregatti and Prof. Lucimara Gaziola de la Torre from the Laboratory of Advanced Development of Nano and Biotechnology, School of Chemical Engineering, University of Campinas, SP, Brazil (FEQ/UNICAMP) for the centrifuge equipment.
- Dr. Thiago B. Taketa, Dr. Rogério A. Bataglioli, and Prof. Marisa M. Beppu from the Laboratory of Chemistry and Products Engineering (LEQUIP), School of Chemical Engineering, University of Campinas, SP, Brazil (FEQ/UNICAMP) for the fluorescence spectra characterization and the lyophilization equipment.
- Gabriel Perli, Dr. Diego L. Bertuzzi and Prof. Catia Ornelas from the Institute of Chemistry, University of Campinas, SP, Brazil (IQ/UNICAMP) for the chemistry theory, contextualization and interpretation support, as well as UV-Vis and FTIR characterization.
- Dr. Thiago D. Cabral and Prof. Cristiano M. B. Cordeiro from the Laboratory of Specialty Fibers and Photonic Materials, "Gleb Wataghin" Institute of Physics, University of Campinas, SP, Brazil (IFGW/UNICAMP) for the physics theory support.
- Prof. Julio Roberto Bartoli from the School of Chemical Engineering, University of Campinas, SP, Brazil (FEQ/UNICAMP); and Prof. Maurizio Prato from the Carbon Nanotechnology Group, Dept. of Chemical and Pharmaceutical Sciences, University of Trieste (Italy) for the support on both the development of the synthetic carbon nanodots methodology and on the project idealization.

2.5. Design and Application of Agarose-Based Fluorescent Waveguide with Embedded Silica Nanoparticle-Carbon Nanodot Hybrids for pH Sensing

This work presents a novel biodegradable and biocompatible hydrogel waveguide. It uses agarose matrix and is fabricated through the incorporation of hybrid nanoparticles. Such hybrids, in turn, are formed by the chemical combination of silica nanoparticles with carbon nanodots derived from citric acid, showing tunable fluorescence sensitive to the external pH.

This project was conducted in close and extensive collaboration with the groups led by Prof. Maurizio Prato (University of Trieste, Italy), Prof. Alejandro Criado (Center for Cooperative Research in Biomaterials, Donostia San Sebastián, Spain), and Prof. Julio R. Bartoli (School of Chemical Engineering, UNICAMP), resulting in an open-source publication in ACS Applied Nano Materials, a journal from the prestigious American Chemical Society (AMATO et al., 2021).

2.5.1. Introduction

Despite all of the different techniques and fabrication materials available for the production of optical fibers, waveguides and optical sensors, the development of devices with lower costs and minor difficulties of fabrication, signal interpretation, and practicality is still needed (ELSHERIF et al., 2019). An important technological gap, on the other hand, is to combine the solution of these problems with the environmental point of view, producing biodegradable devices and less aggressive processes.

In this context, the use of biocompatible hydrogels arises as a promising methodology for manufacturing photonic platforms. This approach allows obtaining implantable sensors and reducing undesirable effects of the traditional silica optical fibers, such as the formation of sharp points that may inflame the implant region. For instance, silk-based hydrogels have already been used for fabricating thin films, diffraction gratings, and organic photonic crystals (OLIVERIO et al., 2017; OMENETTO; KAPLAN, 2008).

Hydrogel-based waveguides combine, then, the electromagnetic interference shielding to the possibility of miniaturization, allowing the detection of different parameters with high sensitivity (CENNAMO et al., 2016). They usually explore the properties of hydrogels on suffering volumetric variations as response to different parameters, including: pH; temperature; ionic strength; and concentration of analytes, such as glucose, proteins, and DNA. These different potential applications in industrial biotechnology, environmental monitoring, and biosensing (ELSHERIF et al., 2019; JIANG et al., 2018b; WOLFBEIS, 2008) can be also increased by doping the polymeric matrix with luminous agents.

The doping strategy is based on the variation of the pattern of the light transmitted by the waveguide due to luminescence and to other light-matter interaction phenomena. Studies have shown, for example, the possibility of producing step-index cylindrical optical fibers by coating a polyethylene glycol (PEG) core with an alginate layer. These materials, which allowed the guiding of light inside living tissues, were doped with fluorophores and Au nanoparticles. Both types of doping allowed the sensor to selectively detect avidin (CHOI et al., 2015). A PEG optical fiber was also doped with functionalized-CdTe quantum dots (QDs) for monitoring Fe³⁺ (ZHOU; GUO; YANG, 2018).

Meantime, practical applications of these devices are still limited by the fact that inorganic nanoparticles such as the semiconductor QDs usually present high toxicity (CHOI et al., 2013), which could be overcome by their substitution with carbon nanodots (ĐORĐEVIĆ et al., 2018). CDs are constituted by a carbonaceous core with plenty of functional groups on their surfaces, such as hydroxyl, amine, and carboxylic acids, allowing their solubility in polar solvents. The peculiar fluorescent behavior of carbon nanodots, in turns, arises from molecular domains that are formed during their syntheses at high temperatures (ARCUDI; ĐORĐEVIĆ; PRATO, 2016, 2017; ĐORĐEVIĆ et al., 2018; HUANG et al., 2013; SALEH; TEICH, 1991; SUN et al., 2006; WANG et al., 2011; WANG; HU, 2014; YUAN et al., 2016)[.]

It is known that this luminescent behavior of CDs may be modulated by different factors, especially the excitation wavelength (SUN et al., 2006); pH (PAN et al., 2012); and solvent used for dispersing them (ZHU et al., 2011). Moreover, the surroundings of the particles are responsible for the stabilization of the fluorophore electronic states, and red-shifted emissions are expected when the neighboring particles stabilize such states (solvatochromic effect) (SUPPAN, 1990).

The advantages of CDs when compared to inorganic QDs (considered superior fluorescent emitters) include the fact that they are low-cost and environmentally safe materials (ĐORĐEVIĆ et al., 2018), and show good biological and biocompatibility properties, being excreted in urine (HUANG et al., 2013; WANG; HU, 2014). Moreover, they present chemical robustness and high solubility in water, and are easily doped and chemically modified (ARCUDI; ĐORĐEVIĆ; PRATO, 2016).

CDs have been produced with different photonic properties that rely on the particular routes and chemical precursors applied (ARCUDI; ĎORĎEVIĆ; PRATO, 2019; ĐORĐEVIĆ; ARCUDI; PRATO, 2019; GONG et al., 2018). Some examples of syntheses include the one from Arcudi *et al.* (ARCUDI; ĐORĐEVIĆ; PRATO, 2017), who obtained small and highly fluorescent nitrogen-doped carbon nanodots (NCNDs) using a bottom-up approach by microwave-assisted hydrothermal carbonization, starting from inexpensive L-arginine and ethylenediamine. The study from Martindale *et al.* (MARTINDALE et al., 2015), in turns, has shown the application of citric acid CDs on the light-driven fabrication of chemical products, performing an artificial photosynthesis by preparing a photocatalytic hybrid system (CD-NiP) for solar H₂ production.

Also, previous studies showed that CDs can be easily fabricated in domestic microwave ovens using sugarcane syrup, a low-cost and renewable source (SOARES et al., 2019a). Boobalan *et al.* (BOOBALAN et al., 2020) obtained CDs by hydrothermal synthesis using another green source, oyster mushroom. The fabricated material is capable of selectively sensing Pb²⁺ ions in aqueous solutions and presents antibacterial and anticancer activity. CDs may even be doped with Mn by submitting mixtures of sodium citrate, citric acid, and manganese (II) carbonate to the hydrothermal treatment (195 °C, 2h). These Mn-doped particles present ultra-high quantum yield of luminescence and may be used to selectively detect Hg²⁺ ions in water (XU et al., 2018). A detailed review describing synthetic routes for obtaining CDs from both artificial and natural sources (such as silk and grass), as well as some applications already demonstrated for these materials was published and is referred to those interested in this particular topic (XU et al., 2019).

In the work presented here (Section 2.5), in turns, carboxylic acid carbon nanodots obtained from the thermolysis of citric acid were used to produce amorphous nanohybrids (named Silica-Cdots) by coupling CDs to silica, and the particles were tested for pH detection.

Then, particles were occluded into agarose to produce a waveguide with intrinsic fluorescence, obtaining a device suitable for pH sensing. The use of the hybrids instead of the net CDs is related to their physical properties: since the hybrid nanoparticles present slightly higher densities and are less hygroscopic, they are easier to manipulate under larger scales.

The chemical attainment of the silicon dioxide-CD hybrids was based on the report from An *et al.* (AN et al., 2007). These authors described a method to assemble silica nanoparticles into silicon wafers through the direct amidation between the amine group of the silicon surface and the carboxyl groups of modified silica nanoparticles. More recently, a second route was proposed by An *et al.* (AN et al., 2020), which consists on the hydrothermal synthesis of hybrids of carbon dots/SiO₂ and gold nanoclusters. They showed that the particles were suitable to detect Ag^+ in water.

In a very comprehensive review about the incorporation of CDs into different polymer and ceramic matrices, Jiang *et al.* (JIANG et al., 2020) concluded that matrices with a plethora of sites containing hydroxyl and other oxidized groups can stabilize the excited state of the carbon dots. In particular, the authors highlighted the composites of polyvinyl alcohol (PVA), in which hydrogel networks may form numerous hydrogen bonds with the polar groups of CDs, stabilizing the emission.

Thus, agar was selected as the material for fabricating the waveguides because a similar stabilization of the CDs' emissions related to the presence of C-OH and C-O-C groups of agarose was expected (BUREY et al., 2008); and due to the large availability of this material, which may be usually bought at local markets in food grade. Agar also shows satisfactory mechanical properties for many biomedical and monitoring applications, with the possibility of thermal curing. This last characteristic facilitates the manufacturing and reduces costs, since no curing agent or equipment is needed (BUREY et al., 2008; JIANG et al., 2020; ZHOU; GUO; YANG, 2018). Finally, ions and molecules from the external environment may diffuse through the matrix, allowing the chemical sensing (BUREY et al., 2008; ZHOU; GUO; YANG, 2018).

Even though some studies have already reported the pH assessment based on the use of fluorescent nanoparticles, there are important peculiarities that distinguish them from this research. These differences include the synthetic routes and chemical identities of the obtained particles; and difficulties and complexity of their interrogation strategies or of their integration and application in biosystems. For instance, Wang *et al.* (WANG et al., 2018) hydrothermally synthesized crystalline (graphitic) CDs by introducing a solution of 1,2,4-triaminobenzene and NaOH into an autoclave (heating under 180 °C for 12 h). The dots were firstly dispersed in water to be used on the colorimetric analysis of pH: the solutions were excited with either daylight or ultraviolet (UV) and analyzed by UV-Visible and fluorescence spectroscopy. Then, the particles were loaded into pH test papers to obtain a colorimetric pH sensor interrogated by image processing. Not only pH paper is not as easily integrated to biosystems as hydrogels, but it is also a device that is not designed to conduct light.

In turn, this approach is similar to the one used by Zhang *et al.* (ZHANG et al., 2019), who obtained core-shell CDs from the hydrothermal treatment of an aqueous solution of 5amino-1,10-phenanthroline and citric acid (heating in a Teflon-lined 50-mL autoclave under 200 °C, over 7 h). After being purified with a dialysis membrane, the particles were applied to color-based pH detection by dispersing them in water, or by printing that solution into filter papers, which were further stuck onto A4 papers. As in the study from Wang *et al* (WANG et al., 2018), the samples were excited by either sunlight or UV light, and then image processing was used to obtain the luminescence intensity. Finally, the intensity was correlated to the pH through calibration curves.

Both studies (WANG et al., 2018; ZHANG et al., 2019) experience some concerns, as the colorimetric analysis of samples' images may be influenced by external factors. Examples of factors that may affect this type of assessment are: variation of the camera's position or of the object's location; oscillations of the environmental light or of the brightness level of the recorded images; sensitivity and resolution of the image detector; differences among the focal length of each lens; and particular methods chosen for image calibration and distortion correction. Additionally, the detection often requires the removal of samples from the analyzed medium (for off-line analysis), as well as constant recalibration procedures when applying the sensor to practical applications. This is not observed when an optical waveguide sensor is used as in this study. That is because wavelength interrogation and other optical fiber sensing technologies are usually robust regarding the above-mentioned factors (SKIBICKI; GOLIJANEK-JĘDRZEJCZYK; DZWONKOWSKI, 2020; SOARES et al., 2018b).

An important final example to be mentioned is the fluorescent pH sensor reported by Chen *et al.* (CHEN et al., 2020). They fabricated inorganic CdTe QDs (particles with environmental and safe issues) and mixed then to CDs hydrothermally obtained from an aqueous solution of chitosan and hydrogen peroxide (heating under 180 °C for 5 h). The CDs-QDs dispersions were used for the ratiometric detection of pHs ranging from 3.0 to 11.0. For that, CDs-QDs suspensions under different pHs were obtained, and samples from these mixtures were collected and introduced into quartz cuvettes to be analyzed in a fluorometer. Then, the ratios between the maximum intensity peaks corresponding to the emissions from each nanoparticle were obtained and correlated to the pH. Again, this is a system that is not easily integrated to simple standard optical instrumentation. Besides, it does not show neither the possibility of on-site monitoring nor the biocompatibility characteristic of the hydrogel.

2.5.2. Silica-Cdots nanohybrids synthesis and characterization

Carboxylic acid terminated carbon nanodots, denominated here as α -CDs, were synthetized from the thermolysis of 200 g of citric acid (Fluka, 99.5%). The synthesis was performed in a muffle furnace under air atmosphere at 180 °C for 40 h (MARTINDALE et al., 2015). A yellow-orange powder was obtained after the thermal treatment, as represented in Figure 9 and shown in Figure 10.

Amino-functionalized silica nanoparticles (a-SiO₂), in their turn, were prepared from commercial amorphous fumed silica nanoparticles treated with 3-aminopropyltriethoxysilane (APTES). Briefly, 206 mg of commercial fumed nanosilica (Aerosil 300, Synthetic Amorphous Silica, average primary particle size ~7 nm, Evonik) previously dried for 2 days at 105 °C were added to ethanol (50 mL), and the mixture was stirred for 3 min. Then, APTES (5 mL, Sigma-Aldrich) was added and sonicated for 5 min, and the dispersion was stirred at room temperature (r.t.) overnight (o.n.). After this step, the mixture was purified by centrifugation and was then dispersed in ethanol (procedure repeated three times). The dispersion was lyophilized, leading to the a-SiO₂ nanoparticles. Then, the hybrid silica-Cdots were synthetized through an amidic coupling reaction between a-SiO₂ and the carboxyl rich α -CDs, as also depicted in Figure 9.

For this last synthesis, 223 mg of α -CDs dispersed in 10 mL of anhydrous dimethylformamide (DMF) were mixed with 50 mg of a-SiO₂ under inert environment (Ar) and with 200 mg (1.04 mmol) of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride

(EDC·HCl, Alfa Aesar). 120 mg (1.04 mmol) of N-hydroxysuccinimide (NHS, Sigma-Aldrich) were also added. Finally, this mixture was sonicated for 10 s and stirred at 70 °C for two days at r.t. DMF was removed through azeotropic distillation with toluene under reduced pressure, and Milli-Q water was added. In order to purify the product, two cycles of centrifugation (20 min at 3000 rpm) were performed, followed by freeze-drying. The changes of color of the three dried materials (a-SiO₂, α -CD and silica-Cdots) are shown in Fig. 9.



Figure 9. Synthesis routes of α -CDs; amino-terminated SiO₂ nanoparticles; and hybrids of α -CDs coupled to a-SiO₂.



Figure 10. Different visual aspects observed for the nanoparticles.

The images of the a-SiO₂, α -CD and silica-Cdots nanoparticles were obtained by Transmission Electron Microscopy (TEM) on a Philips EM 208 (FEI, operation under 100 kV, magnification of 50 x 10³ times). The samples were prepared by dropping the nanoparticles aqueous dispersion onto a carbon-coated copper grid. Additional TEM analyses were performed for the α -CD nanoparticles using a Field-Emission Gun (FEG-TEM) JEOL JEM-2100F (80kV - 200 kV), Ultra High-Resolution pole piece, under low electron dose conditions and equipped with a TVIPS F216 CMOS camera (2048 x 2048 pixels resolution). The α -CDs samples were negative stained with ammonium molybdate, which allows the formation of an uniform, consistent and high contrast staining. The specimen preparation was: α -CDs powder diluted in 30% (v/v) DMF (1/3 DMF : 2/3 H₂O), sonicated for 90 min; afterwards centrifuged with a small table centrifuge for 10 min, using the supernatant as a sample and negative-staining with 2% of ammonium molybdate. Conventional bright field TEM images were acquired for the α -CDs negative stained specimens.

The TEM image of fumed silica-carbon nanodots hybrids (silica-Cdots), Fig. 11, shows aggregates (~50 nm) formed by primary amorphous particles with sizes around 6 nm. Since the carboxylic acid carbon nanodots (α -CDs) are amorphous, they are hardly identified by TEM analysis. Nevertheless, variations on diameter and morphology were observed by TEM for the α -CDs, a-SiO₂, and silica-Cdots particles (Figures 12 to 14). The sizes of α -CDs found are in accordance with Martindale *et al.* (MARTINDALE et al., 2015), who obtained an average size of 6.8 ± 2.3 nm for amorphous carboxylic acid carbon nanodots and a relatively broad size distribution. It is also in accordance with the average primary particle size reported for the used amorphous fumed silica (Aerosil 300), 7 nm measured through dynamic light scattering (AEROSIL 300 TECHNICAL DATASHEET, [s.d.]).

The TEM images of the α -CDs (Fig. 12a) showed dispersed primary, spherical, amorphous nanoparticles with diameters around 6 nm. The images of amino-terminated silica, a-SiO₂ (Fig. 13), showed dispersed primary particles and aggregates of around 6 nm and 100 nm, respectively. The primary particles of fumed silica do not occur just isolated or evenly dispersed; they also merge to form aggregates (AEROSIL 300 TECHNICAL DATASHEET, [s.d.]). They are held together because of weak interactions, such as van der Waals forces or hydrogen bonds. Consequently, amorphous silica-Cdots hybrids are not seen as dispersed as α -CDs (Fig. 14), showing overlapping or agglomeration of particles aggregates (100 - 300 nm) and primary particles (~ 6 nm).

FEG-TEM high resolution images of carbon nanodots (α -CD) were also obtained after negative staining of the nanoparticles (an attempt to make the morphology visible). They are seen as dark blob-alike spots embedded in the grey background (Fig. 12b-c). No lattice fringes or contrast lines were observed, as expected for amorphous particles. The appearance is typical of objects composed of very light elements negatively stained with ammonium molybdate. The carbon nanodots appear in sizes between approximately 4 nm and 10 nm. Very tiny white dots that become visible everywhere in the images are considered grains derived from ammonium molybdate. Brighter grey islands much bigger than the dark blobs (sometimes also containing even bright tiny spots) could be formed by sodium. EDX analysis confirmed that Na is present in the TEM sample. The origin of this Na is likely from the staining solution containing Na from pH adjustments.



Figure 11. TEM images of Silica-Cdots aggregates (~50 nm) and primary particles (~6 nm).

Although it is difficult to distinguish carbon dots in the TEM images of the silica-Cdots due to their amorphous nature, their presence was confirmed by the several analyses presented below:

- UV-Visible (UV-Vis) absorbance analyses of aqueous suspensions of α-CDs in NaOH 0.1M and of silica-Cdots in NaOH 0.1M. The analyses were performed at room temperature with a Cary Ellipse-Varian Fluorescence Spectrophotometer (Agilent Technologies);
- X-ray Diffratometry (XRD) using a Philips X'pert PRO automatic diffractometer operating at 40 kV and 40 mA, secondary monochromator with Cu-K α radiation ($\lambda = 1.5418$ Å), PIXcel solid state detector, scan speed 0.01°/s at room temperature;
- Fourier Transform Infrared Spectroscopy (FTIR) using a 2000 Spectrometer (Perkin Elmer). Transmission spectra of the powder samples were recorded using KBr and resolutions of 3 and 10 scans;
- X-ray Photoelectron Spectroscopy (XPS), with a SPECS Sage HR 100 spectrometer equipped with a 100 mm mean radius PHOIBOS analyzer (SPECS Surface Nano Analysis). A MgKa X-ray source was used, and XPS data fitting was carried out using CasaXPS software;
- Raman Spectroscopy using a Renishaw inVia Confocal Raman Microscope at 532 nm, 633 nm and 785 nm laser lines, 10% laser power, 10 s exposition time;
- Thermogravimetric Analysis (TGA) using a TGA Q500 (TA Instruments) was performed by imposing an isotherm at 100 °C for 20 min, followed by a ramp of 10° C/min under N₂ at flow rates of 90 and 10 mL/min on the sample and balance, respectively.

The UV-Visible absorption spectra of both the α -CDs and of the silica-Cdots (Fig. 15) show maximum absorbance at 300 nm, corresponding to the $\pi \to \pi^*$ transition of the sp² carbons of the CDs cores. The α -CDs spectrum shows a shoulder at 360 - 390 nm with a tail that extends to the visible range, assigned to the $n \to \pi^*$ transitions involving the electron lone pairs of the carboxylic surface groups. On the other hand, when compared to the α -CDs, silica-Cdots showed a relative increase in UV-Vis absorption from 350 to 600 nm and no shoulder.

The XRD spectra of the SiO₂, a-SiO₂, α -CDs and silica-Cdots nanoparticles (Fig. 16) confirmed their amorphous characteristics. There are only amorphous halos and no XRD reflections typical of crystalline structures were observed. The diffraction patterns of nanoparticles have the following characteristics:

- SiO₂: the amorphous halo of the fumed SiO₂ is observed at around $2\theta = 21.5^{\circ}$.
- α -CD: the amorphous halo observed around $2\theta = 18.5^{\circ}$ could be due to some oxidized graphitic species. In turn, the presence of graphitic species is imperceptible, as only a very smooth tail is observed around $2\theta = 30^{\circ}$. Diffraction patterns for graphite and oxidized graphite are expected as strong reflections at 27° and 16°, respectively.
- a-SiO₂: two amorphous halos are observed around $2\theta = 8.5^{\circ}$ and $2\theta = 21.5^{\circ}$ due to the amino group and SiO₂, respectively.
- silica-Cdots: the amorphous halo of SiO₂ (~ 21.5°) overlaps the α -CD halo (shoulder at ~ 18.5°) and some contribution of the amino group is observed (~ 8.5°).



Figure 12. Micrographs of α-CD primary nanoparticles, with sizes between ~4 nm and ~10 nm: (A) TEM image; (B); (C); and (D): negative stained FEG-TEM images (color inverted to facilitate viewing).



Figure 13. TEM images of a-SiO₂ aggregates and primary particles (magnifications: (A) 63 x 10^3 times; (B) 80 x 10^3 times).



Figure 14. TEM images of silica-Cdots aggregates and primary particles (magnifications: (A) 50 x 10³ times; (B) 32 x 10³ times).



Figure 15. UV-Vis absorption spectra from α-CDs (in red) and from silica-Cdots (blue).



Figure 16. XRD patterns of the SiO₂, a-SiO₂, α -CDs and silica-Cdots nanoparticles.



Figure 17. FTIR spectra collected for fumed silica, amino-functionalized silica, α -CDs, and silica-Cdots.



Figure 18. Comparison between FTIR spectra of SiO₂ and a-SiO₂.



Figure 19. Comparison between FTIR spectra of a-SiO₂ and silica-Cdots.



Figure 20. Comparison between FTIR spectra of α-CDs and silica-Cdots.

The infrared spectra presented on Fig. 17 and Fig. 18 demonstrate the aminofunctionalization of the SiO₂ particles. The spectrum of silica exhibits typical absorption bands at the wavenumbers: 473 cm⁻¹, due to bending motions of Si-O; 1107 and 804 cm⁻¹, assigned to the asymmetric and symmetric stretching of the Si-O-Si bonds, respectively; and there is a 3437 cm⁻¹ broad band due to Si-OH and -OH stretching (SILVERSTEIN; WEBSTER; KIEMLE, 2005; UCHINO et al., 2004). There is also a band around 1630 cm⁻¹, which is due to scissor bending vibration of the -OH groups of adsorbed molecular water (BEGANSKIENĖ et al., 2004).

The FTIR spectrum of the amino-functionalized silica (a-SiO₂) reveals the presence of the C and N groups expected from the reaction between SiO₂ and APTES (Figure 9). Typical amine vibrational absorption bands are observed at: 690 cm⁻¹ (N-H wagging); 1044 cm⁻¹ (C-N stretching); 1445 and 1600 cm⁻¹ (N-H bending); and at 2881-2932 cm⁻¹ (C-H stretching). Again, the presence of molecular water originates an -OH bending band around 1630 cm⁻¹ (BEGANSKIENĖ et al., 2004; SILVERSTEIN; WEBSTER; KIEMLE, 2005; UCHINO et al., 2004).

The carbon nanodots' spectrum, in its turn, displays typical carboxylic acids vibrational absorption bands. There is a very broad and intense O-H stretching absorption in the region of $3300-2500 \text{ cm}^{-1}$ with a long-wavenumber side of the O-H band due to overtone of fundamental bands at high wavenumbers. The intense stretching vibrations bands of C=O are located in the region 1767-1718 cm⁻¹. The absorption band at 1409 cm⁻¹ is referred to the bending vibration of C-O-H; the band at 1278-1197 cm⁻¹ is due to the stretching vibrations of C-O; the band at 925 cm⁻¹ is due to the out-of-plane bending vibration of O-H; and the -OH bending of water is present at ~1630 cm⁻¹ (BEGANSKIENĖ et al., 2004; SILVERSTEIN; WEBSTER; KIEMLE, 2005; UCHINO et al., 2004).

Once the hybrids are expected to show both the groups from the amino-functionalized silica and from the carbon dots, the silica-Cdots FTIR spectrum was compared with the data collected for the a-SiO₂ (Fig. 19) and for the α -CDs (Fig. 20). Indeed, the characteristic absorption bands of the amino-silica and of the carboxylic acids are observed in the Silica-Cdots spectrum (Fig. 17, Fig. 19 and Fig. 20): Si-O and Si-O-Si (473 and 804 cm⁻¹); C-O at 1222 cm⁻¹ overlapped with the Si-O-Si at 1107 cm⁻¹; C-O-H, C=O and C-H at 1386 cm⁻¹, 1715 cm⁻¹ and 2930 cm⁻¹, respectively. Besides, the intense band of the Si-O-Si (1107 cm⁻¹) has a shoulder at 1044 cm⁻¹ due to the C-N stretching (BEGANSKIENĖ et al., 2004; SILVERSTEIN; WEBSTER; KIEMLE, 2005; UCHINO et al., 2004). When comparing Fig. 17 and Fig. 19 to Fig. 20, the OH stretching band (around 3400 cm⁻¹) appears to be more intense and broader after the coupling reaction.

Raman spectra of α -CDs and silica-Cdots nanoparticles (Fig. 21) did not show any scattering signal and only fluorescence effects were observed. The broad luminescence arises from the strong photoluminescent (PL) emission of carbon nanodots excited at the wavelength of 532 nm. The same behavior was observed at 633 nm and at 785 nm (laser lines also used in this study), covering any likely very weak Raman band. In turns, the non-noticeable D or G bands in the Raman spectra indicate disordered carbon atoms, another evidence of the amorphous morphology of the α -CDs and of the silica-Cdots nanoparticles.



Figure 21. Raman spectra (@ 532 nm) of the α-CDs and silica-Cdots nanoparticles.

TGA analysis is shown in Fig. 22. It detected almost no mass variation for SiO₂. This was expected, since the applied thermal range is inferior than the temperatures required for silica phase transitions; and also because there are no organic groups to degrade (GÖTZE; MÖCKEL, 2012; ILER, 1979).

On the other hand, TGA assessed the significant organic content of the silica after the amino-functionalization (a-SiO₂) and after the coupling reaction with the carbon nanodots (silica-Cdots). The TGA profile of silica-Cdots shows an event between ~140 and 350 °C, which is due to the thermal degradation of amorphous α -CDs (BOOBALAN et al., 2020; ĐORĐEVIĆ; ARCUDI; PRATO, 2019). Both the a-SiO₂ and the silica-Cdots show mass losses between ~350 and 560 °C that are related to the decomposition of alkyl-amino groups. No additional mass variations were found after 650 °C.

The percent residual masses at 750 °C were around: 97%, 60%, and 40% for the SiO₂, a-SiO₂, and silica-Cdots nanoparticles, respectively. The relative amounts of SiO₂ and α -CDs in the hybrid nanoparticles were around 40% and 25%, respectively. Thus, the α -CDs/SiO₂ mass ratio was estimated at ~60%.



Figure 22. TGA of nanoparticles of fumed silica, amino-functionalized silica, and silica-Cdots hybrids.

In addition, X-ray photoelectron spectroscopy (XPS) analysis was employed to provide the chemical compositions of a-SiO₂ and α -CDs, and thus to evidence the formation of silica-Cdots. The XPS spectra and atomic quantification of a-SiO₂, α -CDs, and silica-Cdots are shown in Figures 23-25 and Table 1, respectively.

The spectra of the nanoparticles are characterized by the chemical moieties: C-C, C-O, C-N, C-NH₂⁺ and Si-O for a-SiO₂ (Fig. 23b to 23e); C-C, C=C, C-O, and C=O, for α -CDs (Fig. 24b to 24e); and C-C, C=C, C-O, C=O, N-C, N=C, NH-(C=O) and Si-O, for silica-Cdots (Fig. 25b to 25e).

As expected, N (4.3%) and Si atoms (1.5%) were detected in the hybrid sample silica-Cdots. There is a significant increase in the C/Si ratio on the surface of the hybrids (49.5) when compared to the a-SiO₂ (1.6), which is 30 times lower. This indicates that the number of siliconbased particles is lower in the hybrids when compared to the a-SiO₂; and/or that the silicon particles are located at the core of the hybrid system. In addition, the deconvolution of Si2p core level showed two peaks at 101.9 and 102.3 eV, which correspond to the Si-O bond in the SiO₂ structure (Fig. 25e) (CASAMASSIMA et al., 1991).

Besides, the deconvoluted N1s core level exhibited an intensive peak at 399.5 eV, which can be assigned to the amide bond NH-(C=O) between the amino-functionalized silica with the carboxylic acid surface groups of the carbon nanodots (Fig. 25c) (EDERER et al., 2017). So, the XPS analysis confirmed the coupling reaction between $a-SiO_2$ and α -CDs resulting in the silica-Cdots hybrids.

Tougaard (TOUGAARD, 2018) revisited an issue in quantitative XPS analysis based solely on measured peak intensities. The intensity attenuation could be consequence of the distance traveled by the photoelectron in the sample, which is an issue for samples where the atomic concentration varies over the outermost ~5 nm. Indeed, this is the depth range for many of the nanostructures such as the primary particles of the silica-Cdots hybrids. Therefore, the combining of these XPS surface results with the bulk information from KBr-FTIR and TGA corroborates the coupling reaction between a-SiO₂ and α -CDs. In short, the hybrids presented both intense Si-O-Si and C=O FTIR bands (typical of α -CDs); and around 40% and 25% of SiO₂ and α -CDs relative mass, respectively.


Figure 23. (A) XPS spectrum for a-SiO₂; and XPS high resolution spectra: (B) C1s; (C) N1s; (D) O1s; (E) Si2p obtained for a-SiO₂.



Figure 24. (A) XPS spectrum for α -CDs; and XPS high resolution spectra: (B) C1s; (C) O1s obtained for α -CDs.



Figure 25. (A) XPS spectrum for silica-Cdots; and XPS high resolution spectra: (B) C1s; (C) N1s; (D) O1s; (E) Si2p obtained for silica-Cdots.

Sample	C / at%	O / at%	N / at%	Si / at%
α-CDs	68.1	31.9	-	_
a-SiO ₂	39.3	27.3	8.2	25.3
Silica-Cdots	74.3	19.9	4.3	1.5

Table 1. Atomic percentages of samples obtained by high-resolution XPS spectra.

2.5.3. Photophysical characterization

The aqueous dispersions of nanoparticles had their photoluminescence (PL) spectra at room temperature observed with a Cary Ellipse-Varian Fluorescence Spectrophotometer (Agilent Technologies) at excitation wavelengths from 300 to 430 nm, 600 nm/min scan speed, and excitation and emission slits of 5 nm.



Figure 26. Fluorescence spectra of (A) α -CD; and (B) silica-Cdots.

The photoluminescence (PL) emission spectra of α -CDs recorded in water (Fig. 26a) show a maximum emission at 465 nm when the sample is irradiated at 360 nm. When the excitation wavelength changed from 360 to 440 nm, an emission dependency with the excitation was observed with a concomitant loss of intensity.

The PL spectra of the silica-Cdots in water (Fig. 26b), in turns, show approximately the same behavior. The emission is dependent on the excitation-wavelength, but the coupling caused an increase on the noise of the intensity signal. The maximum fluorescence intensity is still observed when the sample is excited by 360 nm (and still corresponds to the emission at 465 nm). It indicates that there is no loss of the stability of the excited state of the fluorescent agent caused by the silica coupling (SUPPAN, 1990).

Moreover, the fluorescence emission peak of the hybrids shifts from 465 to 513 nm (green) when the excitation changes from 360 to 430 nm. The peak intensities also decrease as they red-shift, a behavior previously observed for other CDs (MARTINDALE et al., 2015; SOARES et al., 2019a). Again, the organic groups present on the surface of the CDs significantly affect the fluorescence properties (ARCUDI; ĐORĐEVIĆ; PRATO, 2017; MARTINDALE et al., 2015).

2.5.4. Application of aqueous suspensions of hybrids on pH sensing

Due to the presence of carboxylic groups, the possibility of applying the hybrids for pH assessment was evaluated. In this analysis, a dispersion containing 1.2% (m/m) of silica-Cdots (~12 g/L) in deionized (DI) water was progressively alkalinized by the drop-by-drop addition

of NaOH 0.01 M. The initial pH verified just after the dispersion of the hybrids in water was lower than the DI water's: pH = 4.3 was verified for the hybrids suspension.

After each NaOH addition, the sample: had its pH quantified; was introduced into a cuvette (length of 1 cm); and was excited by a 403 nm LED with full width at half-maximum (FWHM) of 12.2 nm. Then, the fluorescence spectrum was recorded with a hand-held spectrometer (HR4000, resolution of 0.3 nm, Ocean Optics) to obtain the wavelength of maximum fluorescence. After raising the pH to ~12, the opposite procedure was performed. The pH was reduced until ~2 by adding HCl 0.01 M to the dispersion (drop-by-drop addition); and the luminescent spectra were collected analogously.

The nanohybrid concentration of 1.2% (m/m) was chosen for providing an adequate balance between the total fluorescence intensity and the LED attenuation by the particles.

When selecting the light source for exciting the hybrid particles, there are 4 main factors that need to be considered: optical power, wavelength, cost, and safety. Taking into account these parameters, a 405 nm nominal wavelength (actual peak wavelength at 403 nm) high power (3 W) LED source with a full-width at half-maximum (FWHM, a measure of the broadness of the emission spectra) of 12 nm was chosen.

With this configuration, most of the optical power being emitted by the LED is in the 390-415 nm range. Moreover, about half of the optical power is in the visible range, providing more safety when handling a relatively high-powered UV source. The bulk of the emission spectrum of the LED is in a range that produces a good fluorescence response (as noticed on Fig. 26) with a strong signal around 390 nm. The high maximum power (up to 3 W), in its turn, ensures that a strong response is observed even when not using a narrowband laser source near the peak excitation wavelength.

Finally, the LED used had an approximate cost of 20 USD, while a narrowband laser would increase the cost by at least 1 to 2 orders of magnitude. Since the objective was to design a sensor for being used in daily laboratory situations, the selection of this source allows the user to perform experiments without the necessity of elevated investments in both a specific source and in the high-performance UV-protection safe glasses necessary to handle it.



Figure 27. (A) Setup for the pH evaluation using the aqueous hybrids dispersions; (B) wavelength of maximum emitted fluorescence as function of pH for the dispersions of hybrids. The inset shows the linear portion of the curve (pH ranging from 6 to 10).

The use of silica-Cdots hybrids instead of simpler carbon dots for pH monitoring tests has advantages, since the powder is easier to handle. It is due to the fact that hybrids are less hygroscopic than α -CDs. Besides, silica-based nanoparticles doped with fluorophores are interesting hybrid nanosystems that intrinsically combine the mechanical properties of silica with the optoelectronic properties of carbon nanodots.

In particular, the use of hybrids can favor the large-scale manufacture of fluorescent agarose waveguides as pH sensors. In turn, the fluorescence intensity measurements of α -CDs are relatively smaller than those of hybrids (Figures 26a and b), a trend observed at other wavelengths used (300 to 430 nm). Considering the excitations in which hybrids fluorescence emissions were slightly more intense, it appears that silica protects α -CDs from some quenching effects related to interactions with water.

The pH-monitoring tests with aqueous dispersions of silica-Cdots (initial pH of 4.30) were performed accordingly to the setup shown in Fig. 27a. Briefly, the dispersions had the pH modified by firstly adding NaOH, and then the pH was reduced with HCl. For each tested pH, the dispersions were introduced into cuvettes and were irradiated with the LED to have the emission spectra analyzed. The wavelengths corresponding to the peaks of maximum emitted intensities were retrieved, and data were correlated to the pHs. Fig. 28 shows photographs from one sample during the test and under daylight.



Figure 28. Assembled system with aqueous dispersions of silica-Cdots under UV-excitation, and under daylight (inset).

The results are shown on Fig. 27b. They were fitted by a cubic polynomial relating the maximum wavelength to the pH (wavelength = $467.23 + 20.17(\text{pH}) - 3.45(\text{pH})^2 + 0.20(\text{pH})^3$, adjusted R² = 0.91), proving that it possible to optically monitor the acidity. It is also interesting to notice that the increase in pH leads to a red-shift of the emitted fluorescence. Besides that, the fluorescence is stable and reversible regarding the pH. Indeed, the wavelength of maximum emitted intensity easily returns to its previous value by simply reversing the pH change.

This red-shift verified when increasing the pH may be interpreted in terms of the interactions between nanoparticles and solvent, which results in modifications of the excited-state stability. According to Sciortino *et al.* (SCIORTINO et al., 2016), CDs emission energies

show a notable and systematic dependence on solvent characteristics, as well as a strong response of the photoexcited particles to the presence of hydrogen bonds. As consequence, CDs may be used as solvent polarity nanoprobes to monitor neighbor ions and molecules.

The authors verified that the CDs' emissions blue-shifts as the solvent polarity is reduced. They observed the lowest emission wavelengths for water, what is related to the stabilization effect of the hydrogen bonds. Their conclusion was that both the nitrogen and the carboxylic acid groups that may be present on the CDs' surfaces act as efficient hydrogen bond acceptors. This is due to their electron lone pairs, and thus the fluorescence mechanism is closely related to the presence of these N and -COOH groups on the sub-nanometric surface shell around the carbon nuclei (SCIORTINO et al., 2016).

In turn, Bano *et al.* (BANO et al., 2019) used latex as raw material for the production of CDs containing carboxylic acid groups on their surfaces. They verified that the increase in the medium's acidity led to the protonation of the dots' carboxylic surface groups. Consequently, the particles' negative charges decreased (or were even neutralized) in lower pHs, leading to the loss of colloidal dispersions' stability. This ultimately resulted on the aggregation of the CDs and on the extinction of the fluorescence. A similar effect was observed by Chandra *et al.* (CHANDRA et al., 2019), but it was analyzed in terms of the UV-Visible absorbance spectrum: in basic media, the deprotonation of the surface acid groups of CDs caused an intense decrease in the radiation absorption.

In the case analyzed in this Section 2.5, the silica-Cdots present chemical and structural differences in relation to the α -CDs that may impact their interactions with the solvent. The most important ones are: the slightly superior dimensions of the particles, a factor that influences the sizes of the formed dynamic cavities/first solvent shells (REICHARDT, 1994, 2005); and the fact that there may be less carboxylic groups, since -COOH reacts with a-SiO₂.

On the other hand, Figure 9 shows the presence of lone pairs on the hybrid surfaces that are not present in α -CDs. There are lone pairs from: the amide group formed between SiO₂ and α -CD; the Si-O- bonds between silica and the α -CD nanoparticle; and the possible presence of other -Si-OH and -Si-O-O-Si- groups, since these are structural defects commonly observed on SiO₂ surfaces (GÖTZE; MÖCKEL, 2012; ILER, 1979).

Therefore, the silica-Cdots hybrids surface groups could selectively detect Na⁺ or Cl⁻ ions present in the controlled pH solutions. Again, the main chemical groups of the hybrids identified by XPS are: -COOH of the carbon nanodots (α -CDs); NH-(C=O) from the amide group (bond between SiO₂ and α -CD); Si-O- bonds between silica and α -CD; and other silicon bonds such as -Si-OH, -Si-O-Si- and Si-O. The wavelength of hybrids fluorescence (measured at the highest emission intensity) is selectively shifted and quenched because of the interactions among these surface groups and ions in the aqueous solution.

At this moment, considering that the pH of the initial aqueous solution is clearly acid (4.30) and that there are still several groups capable of hydrogen bonding (stabilizing the excited states), it is possible to consider that the hybrids behave as the other acid carbon nanodots cited (BANO et al., 2019; CHANDRA et al., 2019; SCIORTINO et al., 2016).

Therefore, analogous conclusions can be made for the results of wavelength shifts with the pH depicted in Fig. 27: as the pH gets more basic, the deprotonation of the carboxylic groups of the hybrids surfaces increases their negative charges and, consequently, enhance the hydrogen bond interactions between the particles and the solvent (water). Since this effect causes the stabilization of the fluorophores, the red-shift is observed (JIANG et al., 2020; SCIORTINO et al., 2016). The possibly lower number of -COOH groups is not necessarily a problem here: it is known that basic pHs (higher than 10) usually deprotonate colloidal nanostructured silica's silanol groups (CANNAS et al., 2019; ILER, 1979; SOARES et al., 2019c), what would create extra negative charges on hybrids' surfaces.

The inset of Fig. 27 shows a portion of the curve between pHs 6 to 10, which can be fitted by a linear polynomial (wavelength = 480.95 + 4.53(pH), adjusted R² = 0.95). This is the region of maximum variation of wavelength with pH. Therefore, the derivative of this linear portion allows the calculus of the sensitivity (i.e., the rate of variation of the signal in relation to the measured parameter) (SALEH; TEICH, 1991) of the liquid-phase silica-Cdots dispersions on detecting pH changes: 4.53 nm/ (pH units).

Moreover, one can notice that, as the pH gets closer to 2, the curve reaches a signal baseline. It leads to a drop in the sensitivity and makes it difficult to perform readings for more acid media. As the pH is raised to 12, in turn, one can observe an increase on both the noise of the observed fluorescence spectra and on the dispersion of data on Fig. 27b.

However, this is not an issue for industrial purposes. That is because only the use of the linear range with highest sensitivity is indicated for these practical situations, since it facilitates the design of the automation system (BAILEY; OLLIS, 1986; STEPHANOPOULOS, 1983). Therefore, considering these results, it was decided not to test pHs lower than 2 or higher than 12 for the agar waveguide doped with hybrids.

2.5.5. Design and fabrication of agarose waveguide doped with hybrids

Two types of cylinders were prepared by gelling precursor solutions containing agarose in DI water. The first solution contained 300.0 mg of agarose (food grade, acquired in a local market) and 31.0 mg of hybrids (silica-Cdots) dispersed in 10 mL of water, resulting in concentrations of 30.0 g/L (agarose) and 3.10 g/L (hybrids). The second solution was fabricated for comparison: it contained the same concentration of agarose in DI water (30.0 g/L), but no nanoparticles.

The solutions were heated close to their boiling points for initiating the agarose thermalcuring process. This process consists in a cold-setting mechanism related to the formation of double-helixes between the polymeric chains. After being heat above ~85 °C, cross-links are observed between the macromolecules, resulting in the gel formation when the system is cooled. Thus, this reticulation is favored by imposing lower cold temperatures during the cooling step (BUREY et al., 2008).

So, immediately after the first signs of boiling (i.e., formation of small bubbles and of visible aqueous vapor above the liquid surface), the precursor dispersions were introduced into 3D-printed cylindrical molds (7 mm of inner diameter) made of glycol-modified polyethylene terephthalate (PETG) filament (3D-printer Ultimaker 2+, Ultimaker BV). The molds were sealed on their end-faces and left overnight in the refrigerator at ~10 °C for curing.

This process forms hydrogels with the same geometry of the internal mold walls, and these hydrogels can be easily demolded by removing the sealing and the two cylinder's bases (the mold caps are pluggable). After removing the sealing, the hydrogel is left to dry under ambient conditions, so the loss of water diminishes its diameter and provides the loss of contact with the inner walls. After being removed, the formed materials are again put in contact with DI water for recovering the original diameter of 6 mm.

The refractive indices (RIs) of both the agar and the agar with occluded hybrids were evaluated with a MISCO PA 202 Refractometer (Palm Abbe), with a 589 nm high precision LED (resolution of 10^{-4} nm). All samples were measured at ~25 °C and room atmosphere. For this, small volumes of the preheated precursor solutions (heated until boiling) were dropped on the sample window. The reading of the RIs was performed after the complete curing and thermal stabilization of the systems at 25 °C.

The obtained refractive indices were both n = 1.3334, which is very close to the DI water's index (n = 1.3330, evaluated using the same equipment). This is due to the high adsorption of H₂O on the hydrophilic polymers and on the hybrids' surfaces. This RI is also higher than the air's ($n \approx 1$), so light may be guided through total internal reflectance as in conventional optical fibers (SALEH; TEICH, 1991). This light guiding mechanism is represented in Fig. 29.



Figure 29. Agarose waveguide doped with the hybrids.

The efficiency on guiding the light may be quantified in terms of an indicator called Numerical Aperture (NA). For a cylindrical waveguide, NA may be calculated using Equation (2), where n_{clad} is the refractive index of the cladding and n_{core} is the waveguide's core RI (SALEH; TEICH, 1991).

$$NA \cong \sqrt{n_{core}^2 - n_{clad}^2} \quad (2)$$

In the case of the waveguide shown in Figure 29, no coating procedure was performed, so the atmospheric air may be considered the cladding. Thus, $n_{clad} = n_{air} = 1.0000$ is the refractive index of the air (considered the cladding); and $n_{core} = n_{hydrogel} = 1.3334$ is the refractive index of the doped hydrogel (considered the core). This simplifies Equation (2) to Equation (3).

$$NA \cong \sqrt{n_{hydrogel}^2 - n_{air}^2}$$
(3)

The substitution of the refractive indices values on Equation (3) results in NA = 0.882, which is fairly high. It indicates that the doped waveguide has an elevated capacity of capturing and guiding the luminescent radiation from the CD-doped hydrogel (SALEH; TEICH, 1991).

If the waveguide is supposed to be used immersed in water, then n_{air} should be substituted by $n_{water} = 1.3330$ in Equation (3). It would lead to NA = 0.054. Even though this value is substantially lower than NA = 0.882, it still shows the capability of guiding the light (i.e., it is still possible to operate the waveguide immersed in water).

The transmission spectra of both waveguides (the doped agarose used as pH sensor and the net agar used as reference) were analyzed by exciting them with a supercontinuum laser (SuperK Compact, NKT Photonics) in one extremity and collecting the light at their end-faces with a spectrometer (Fig. 30). For comparison, the spectrum of the light source is also presented.



Figure 30. (A) Emission spectrum of the light source. (B) Intensity of light transmitted by the waveguides (excitation with the supercontinuum laser). The dashed region corresponds to the fluorescence of the hybrids.

The photographs obtained for the waveguides under daylight and when transmitting the supercontinuum laser are shown in Fig. 31. This last figure shows that the occlusion of the hybrids gives a brown/orange color to the waveguides and reduces their transparency to the visible.

Before analyzing the results, it is interesting to discuss the selection of this particular concentration of hybrids (3.10 g/L of hybrids with 30.0 g/L of agarose in aqueous solution). In fact, different proportions of silica-Cdots, agarose, and water were tested.

Since NA increases with the polymer's refractive index (enhancing the light guiding efficiency, as shown in Equation (3)), the first tests consisted in evaluating whether the agar concentration significantly changed the RI of the mother liquor. For that, the refractive indices of solutions containing different concentrations of agar in DI water were collected.

As shown in Figure 32, very low variations (in the order of only 10^{-4} refractive index units, RIU) were observed when increasing the agar concentration. In addition, the RI of the

precursor solutions did not reach values higher than 1.3334, which is very close to the water's (1.3330). Then, the amount chosen for the fabrication of the doped cylinder (30 mg of agar/mL of water) was the one that not only resulted in the higher RI, but also in a waveguide with mechanical consistency and with sufficient optical transparency. Another requirement was that, after being doped, the waveguide should allow both the stimulation of the hybrids by the external light source and the further collection of the fluorescence by the spectrometer.

However, increasing nanoparticles concentration severely enhances the opacity of the waveguides because of additional mechanisms of absorption and scattering of the light. It was verified that, for agar concentrations higher than 30.0 g/L, there was sufficient transparency only when working with low concentrations of hybrids. These low concentrations, in turn, resulted in low luminescence and difficulty of detection.

So, additions of agar beyond 30 g/L were actually tested, but the opacity of the final materials progressively grown, resulting in significant increase of the light attenuation. On the other hand, the use of these higher concentrations of agar resulted in very low variations of the mother liquor's refractive index, always in the order of only 10^{-4} refractive index units (RIU). In fact, the RI variation associated with the curing process showed to be more significant than the one associated with the increase of the agar concentration in the precursor solution.



Figure 31. (A) General aspect of the agar waveguide; (B) cross-section of the agar waveguide; (C) agar waveguide transmitting the supercontinuum laser; (D) general aspect of the waveguide with occluded silica-Cdots hybrids; (E) cross-section of the waveguide with occluded hybrids; and (F) waveguide with occluded hybrids transmitting the supercontinuum laser.



Figure 32. Refractive index of the waveguide as function of the agar concentration in the liquid precursor. The variation is in the order of only 10⁻⁴ refractive index units (RIU).

The selection of the silica-Cdots concentration was analogue: 3.10 g/L (~10% m/v) was the value that resulted in the highest luminescent signal. Increasing even more the concentration would lead to a result opposite to the desired: the device would get so opaque that no luminescence could be observed. Then, light sources with much higher power would be required. Since this would also impact the selection of the excitation wavelength, it was decided to apply the concentration of 3.10 g/L. Finally, as mentioned before, the solution of Equation (3) resulted in a high NA (0.882) for the RI of the doped agar after curing (RI = 1.3334, air-cladding); and Fig. 31f indeed shows the excitation and guiding of the luminescence.

The intensities of light transmitted by the net agar and by the silica-Cdots doped agar waveguides as function of the excitation wavelength are shown in Fig. 30b. These light intensities were obtained after exciting the waveguides with a supercontinuum laser and then collecting the transmitted light at the waveguides end-faces (Figs. 29, 31c and 31f).

When comparing the transmission profile obtained for the agar containing no nanoparticles with the spectrum of the source (shown separately in Fig. 30a), one can notice that they present essentially the same format, with almost no attenuation. It could be concluded that there is no emission in this situation (as expected, since no fluorescent particles were added). Besides, the interaction between the polymer and the light does not appear to broaden or to distort the transmission profile.

That is not the case for the doped agar, though. Firstly, the maximum intensity peak appears to be shifted from 680 nm (the wavelength of maximum intensity emitted by the source, as shown in Fig. 30a) to 705 nm.

It is also possible to notice that, until \sim 700 nm, the doped-agar waveguide (red curve of Fig. 30b) follows approximately the same pattern of the light source, but with attenuated intensity when compared to the material containing only agar (blue curve of Fig. 30b). This was already expected from the increased opacity. Then, after 700 nm, the curve for the doped waveguide overcomes the agar curve, as evidenced by the pink dashed region on Fig. 30b. From 700 nm, the light spectrum collected at the end-face of the waveguide doped with silica-Cdots

is clearly broader and more intense than both the spectra transmitted by the device containing only agar and by the supercontinuum laser (Fig. 30a).

On the other hand, Fig. 26b already showed that excitations higher than 400 nm resulted in fluorescent emissions extending over 700 nm for the particles dispersed in water. Also, shifts of the spectra were expected when modifying the medium from water to agar.

If the excited particles were better stabilized in the new medium, then the red-shift of the spectra would result in emissions at even higher wavelengths (BANO et al., 2019; CHANDRA et al., 2019; JIANG et al., 2020; REICHARDT, 1994, 2005; SCIORTINO et al., 2016). Moreover, the intensity profile collected at the end-face of the waveguide is actually a resultant from the combination of the luminescence with the light interactions with all the chemical species present in the system (JIANG et al., 2020; LAKOWICZ, 2006; SALEH; TEICH, 1991; SKOOG et al., 2014).

Therefore, it is possible to conclude that the occlusion of silica-Cdots in the polymeric matrix modifies the agarose's transmission profile. Additionally, the new spectrum is broader and more intense after 700 nm. This new spectrum is resultant from the balance between the light source excitation, the fluorescence emitted by the nanohybrids, and the absorption, scattering, and other attenuation mechanisms by the polymer, adsorbed water molecules, and hybrids themselves (JIANG et al., 2020; LAKOWICZ, 2006; SALEH; TEICH, 1991).

2.5.6. Application of the doped agarose waveguide on pH sensing

The waveguides containing occluded silica-Cdots were submitted to the same pH tests previously performed with the aqueous dispersions of nanoparticles (i.e., the irradiation with a 403 nm LED followed by the analysis of the fluorescence spectra).

The experimental setup remained basically the same (only the cuvette was removed) and took advantage of the material's very high affinity with water. Firstly, the waveguide was kept in the aqueous medium under stirring and in a given pH. Due to the high hydrophilicity of both the agar and the hybrids, the intumescence degree (and, consequently, the solution's pH) took no longer than 30 s to stabilize after each pH modification. At this moment, no more variation of the waveguide's diameter could be observed under naked eye.

After the pH reading got stable, the agar waveguide was rapidly removed from the aqueous medium. It was put into the same place previously occupied by the cuvette and was stimulated by the LED. The light emerging from both the end-face and from the air-agar side interface were collected and analyzed. After each measurement, the waveguide was returned to the aqueous medium for repeating the process under a different pH. Again, the pH was firstly raised to ~12 by adding NaOH 0.01 M, and then it was reduced by dropping HCl 0.01 M.

The pH limits (from 2 to 12) applied to both the tests with the aqueous dispersion and with the doped waveguide were chosen to include the range commonly observed on living organisms and biochemical systems (generally from 4 to 8). In addition, these pHs do not present security risks for the experimenters; and mitigate the risks of damaging either the agarose matrices or the optical instruments (BAILEY; OLLIS, 1986). All of the pH experiments were performed at room temperature (constant, ~25 °C) and air atmosphere. The collected results are shown in Fig. 33.



Figure 33. (A) Comparison between the fluorescence spectrum collected for silica-Cdots dispersed in water and the spectrum obtained for particles occluded into agarose (excitation of 403 nm and pH 4.3). A clear red-shift of the peak's wavelength is observed. (B) Wavelength of maximum emitted fluorescence as function of pH observed for the agar waveguide. The inset shows the linear portion of the curve (pHs from 6 to 10).

As discussed, the pH of the dispersion of hybrids in DI water was acid (4.30) before the first addition of NaOH because of the presence of the carboxylic groups (Fig. 27). The pH of the DI water used to keep the doped waveguides swollen (i.e., the water maintained in equilibrium with the waveguides prior to the sensing tests), in its turn, is less acid (pH = 5.59).

The agarose molecular structure does not contain groups that directly change the pH (only C-OH and C-O-C groups) (BUREY et al., 2008). Thus, this pH variation was not expected from the polymer's chemical structure. It is probably a consequence of the lower concentration of hybrids used for the fabrication of a waveguide with suitable transparency (3.10 g/L) and of the influence of the hydrogel matrix on the acidic equilibrium of the nanohybrids. Since this equilibrium analysis is beyond the scope of this study (which aimed to fabricate and to test the performance of the waveguide on the pH assessment), this investigation is a topic suggested for future research.

Once both the agarose and the hybrids are very hygroscopic, the waveguides' intumescence degree and the aqueous phase pH readings take no longer than 30 s to stabilize when base or acid are added. Then, the waveguides were kept immersed and under stirring (25 °C) to ensure the homogeneity of the aqueous medium. Again, the pH was firstly raised to ~12 (addition of NaOH 0.01 M) and then reduced to ~2 (dropping of HCl 0.01 M). When the pH reading got stable after a given addition, the waveguide was rapidly excited with the LED to have its fluorescence spectrum collected (as in Fig. 29).

It is important to mention here that the wavelength interrogation is independent from the total amount of fluorophores, an important advantage of this approach when compared to intensity-based sensing techniques (LAKOWICZ, 2006; SALEH; TEICH, 1991; WOLFBEIS, 2008). Therefore, as the signals obtained for all of the tested pH ranges (Fig. 27b and Fig. 33b) were sufficient for retrieving the wavelength of the peaks of maximum fluorescence, it was not necessary to correlate the measurements with the added volume of acid or base. The evaluation of quenching mechanisms due to the presence of metal ions (LAKOWICZ, 2006) was also beyond the scope of this study. Thus, since all the tested media allowed the data collection, different concentrations of cations were not deliberately added. All experiments shown in Fig. 33b were conducted under the same temperature and atmospheric air conditions. Then, the modifications of the spectra could be correlated to the changes in solvent polarity, as in the other mentioned reports (BANO et al., 2019; CHANDRA et al., 2019; JIANG et al., 2020; REICHARDT, 1994, 2005; SCIORTINO et al., 2016).

Interesting conclusions are also obtained when comparing (for a same pH) the fluorescence spectrum collected for the doped waveguide with the one obtained for the aqueous dispersion of silica-Cdots (i.e., when comparing the spectra used for obtaining the information shown on Figure 27b with those used on Fig. 33b). An example of the general observed behavior is shown in Fig. 33a, where the spectra collected for the pH 4.30 are compared (both systems excited by the 403 nm LED).

Fig. 33a shows that the peak (maximum intensity of fluorescence) of the hybrids occluded into the hydrogel matrix is red-shifted when compared to the one observed for the aqueous dispersion of silica-Cdots. This indicates an increase in the stability of the excited states (JIANG et al., 2020; LAKOWICZ, 2006; SUPPAN, 1990) - this same shift was observed for all the other pHs. It is also possible to verify on Fig. 33a that the signals collected for the doped waveguide present higher noises (here, the noise is taken as the difference between the signals and the average fitted curves of the figure) (SALEH; TEICH, 1991).

The solvatochromic shifts resulting from the enclosure of fluorescent species into rigid media are complex phenomena, as extensively discussed by other researchers (BANO et al., 2019; CHANDRA et al., 2019; JIANG et al., 2020; LAKOWICZ, 2006; REICHARDT, 1994, 2005; SCIORTINO et al., 2016; SUPPAN, 1990). The observed shifts depend, for example, on the method used for preparing the matrix and on the particular technique applied to the incorporation of the fluorophores (SUPPAN, 1990). For soluble polymers, in particular, an increase on the medium's polarity or on the intensity of the solute-matrix hydrogen bond interactions may result in the reduction of the energy difference between the ground and the excited states, red-shifting the emission (JIANG et al., 2020; SCIORTINO et al., 2016; SUPPAN, 1990).

So, the red-shift observed on Fig. 33a may be explained analogously as performed by other authors who analyzed the increase on the nanoparticles' excited state stability when the CDs are incorporated into hydrogel matrices with plenty of oxygen and hydroxyl groups. For polyvinyl alcohol (PVA), for example, the matrix networks form many hydrogen bonds with the polar groups of CDs, stabilizing the emissive states (JIANG et al., 2020).

Therefore, van der Waals forces and hydrogen bonds between the agarose's C-OH and C-O-C groups (WANG et al., 2018) and the silica-Cdots' oxygen and nitrogen groups (Figs. 17-20) are expected to lead to increased stabilization of the excited states. According to Jiang *et al.* (JIANG et al., 2020), some hydrogels may show interactions between matrices and CDs so intense that they even result in composites with phosphorescence or delayed fluorescence.

Fig. 33b summarizes the correlation between the wavelengths of maximum emitted intensity (the peaks) and the pHs of the aqueous media where the doped waveguides were immersed. Contrary to what was observed for the aqueous dispersions (Fig. 27b), the agar waveguides show a critical point for the results, which is again probably due to the interactions between the hybrids and the hydrogel matrix (BUREY et al., 2008; JIANG et al., 2020).

The critical point corresponds to the initial situation: it is the pH (5.59) of the water initially in equilibrium with the agar (i.e., the water that was used to keep the device swollen before adding NaOH or HCl).

Once the wavelengths of maximum emitted fluorescence have been obtained as function of a given pH (Fig. 33b) by firstly raising and then reducing the pH, it is shown that the measurements present reversibility regarding the pH: they easily return to previous values after adding HCl (return the lower pHs); or NaOH (return to higher pHs).

Then, results were quite repeatable. Again, they were fitted by a 3^{rd} -degree polynomial correlating the maximum wavelength to the pH. This polynomial was given by: wavelength = $474.21 + 48.50(pH) - 7.03(pH)^2 + 0.30(pH)^3$, adjusted R² = 0.83. Despite the fact that no clear baseline was reached, the light intensity signals suffer substantial decreases as pH gets closer to 2 or 12, indicating that the sensor is not adequate for monitoring pHs beyond these values.

This pH range (2-12), however, is wider than the one obtained by Zhang *et al.* (ZHANG et al., 2019): only pHs from 2 to 7 could be assessed in their study. It is also wider than the range achieved by Chen *et al.* (CHEN et al., 2020): as mentioned, they obtained a system able to detect pHs from 3.0 to 11.0, but using a more complicated sensing strategy (ratiometric analysis). In their study, dispersions combining CdTe QDs and CDs in aqueous phase and under different pHs were introduced into a fluorometer, where the data were collected. Each tested pH resulted in two different curves correlating the emitted intensity to the emission wavelength: one curve for the QDs, and other for the CDs. The two peaks of maximum intensities were obtained by the fluorometer, and the ratio between these peaks was calculated. Finally, a calibration curve correlated this peaks' ratio to the pH.

As in Fig. 27b, Fig. 33b shows a linear portion with maximum rate of variation (inset of Fig. 33b). This region corresponds to the pH range from 6 to 10 and may be fitted by a 1^{st} -degree polynomial (wavelength = 610.35 - 5.61(pH), adjusted $R^2 = 0.84$). The derivative of this polynomial is negative, contrary to the observed for the aqueous dispersions (inset of Fig. 27b). The modulus of the derivative was took as the sensitivity (SALEH; TEICH, 1991) of the silica-Cdots/agarose sensor in relation to the pH, and it was calculated as 5.61 nm/ (pH units).

It is interesting to notice that the applied setup (Fig. 29) could be easily adapted to perform the online evaluation of the pH directly on the liquid medium. This would be done by transporting the light with external optical fibers (CHOI et al., 2013): one fiber would guide the light from the LED to one extremity of the agar waveguide; and a second one would collect the light at the end-face of the waveguide to guide it to the optical analyzer.

The clear drawback is that this adaptation would lower the NA and, consequently, the guiding efficiency: as calculated for Equation (3), NA decreases to 0.054 in water. On the other hand, the small lengths of the agarose waveguides used in this study (until ~70 mm) lead to low power losses, as discussed when analyzing Fig. 30. Then, the reduced NA is not expected to be an impeditive factor to this setup modification (SALEH; TEICH, 1991).

However, it was decided not to proceed with this adaptation because it would not allow the evaluation of the sensor capability in retaining information even when it is removed from the assessed medium. This last feature is particularly important, since there are several practical applications where a waveguide capable of retaining the medium information is required. In a biomedical environment, for example, it may be necessary to remove the sensor from the medium to analyze other parameters besides pH. This situation has been reported and analyzed in studies where hydrogel matrices are simultaneously used as waveguides and as scaffolds for growing cells (CHOI et al., 2013, 2015), with need for posterior cell counting.

In the standard cell counting procedure, samples are periodically collected from the analyzed biosystem to be observed and counted on the microscope using specific devices, such

as the Neubauer chamber (SOARES et al., 2019e). If the waveguides can be removed and their volumes are known, the chambers may be substituted by the waveguide itself. Then, the cellular environment would not be disturbed, reducing the risk of causing cell death during counting (CHOI et al., 2013, 2015).

As Fig. 33 shows, the pH information is actually retrieved by the silica-Cdots/agarose waveguide when it is removed from the aqueous medium. Therefore, since the waveguide can be removed and analyzed off-line, this novel device has potential for monitoring other important biochemical parameters in addition to pH (e.g., the number of cells, previously cited, or the morphological characteristics of the doped agar).

A final important comparison to be performed is with the commercial pH-meters. As mentioned, a decrease of the detected fluorescence intensity was noticed as the pHs got closer to 12, preventing the detection beyond this condition.

However, many commercial pH-meters also show loss of signal intensity or other difficulties when evaluating very alkaline media. Indeed, it is widely known that the traditional devices may lose precision when submitted to such conditions (ASTM E70-19, 2019; METHROHM, [s.d.]; SCIENTIFIC; THERMO SCIENTIFIC, 1991; SKOOG et al., 2014).

That is because these devices commonly show substantial interference caused by the presence of Na⁺ ions on pHs > 12, erroneously interpreting Na⁺ as H⁺ ions (SCIENTIFIC; THERMO SCIENTIFIC, 1991; SKOOG et al., 2014). For minimizing this problem, many manufacturers provide tables that correlate the detected pH to the ionic concentrations, allowing the analyst to estimate reading corrections (SCIENTIFIC; THERMO SCIENTIFIC, 1991). Alternatively, some manufacturers indicate devices specifically designed for operation under higher pH ranges or under more drastic conditions (ASTM E70-19, 2019; METHROHM, [s.d.]; SCIENTIFIC; THERMO SCIENTIFIC, 1991).

Lastly, the recovery of fluorescent silica-Cdots hybrids embedded into the agarose after the device discard is technically feasible. Since the agarose is biodegradable, it can be solubilized in water and the hybrids separated by centrifugation. It would be interesting to carry out a study to verify the technical-economic feasibility of the hybrids recovery, considering that they are low-cost and environmentally friendly materials.

2.5.7. Conclusions from this study

This study resulted in an efficient methodology for the fabrication of biodegradable, biocompatible, and fluorescent cylindrical waveguides doped with hybrid amorphous nanoparticles (silica-Cdots).

The fluorescence spectra of the amorphous α -CDs and of the hybrids dispersed in water were analyzed, and it was verified that the coupling caused a red-shift of the wavelength corresponding to the maximum emitted intensity. The hybrids are easier to handle than noncoupled carbon nanodots since they are less hygroscopic. Therefore, they are more adequate for the fabrication of large volumes of agarose waveguides.

The aqueous dispersion of silica-Cdots showed sensitivity regarding the pH, 4.53 nm/(pH units). Then, agarose was doped with these particles for the fabrication of the pH sensor.

The obtained hydrogel-based waveguide showed stable and reversible behavior regarding pH, and maximum sensitivity of 5.61 nm/ (pH units) when excited by a 403 nm UV LED (sensitivity calculated for the pH range from 6 to 11).

Since the pH information is retrieved when the waveguide is removed from the aqueous medium, the system offers a low-cost, disposable, and simplified pH sensor that can be used on multi-parameter biomedical analysis. Moreover, commercial pH-meters present the practical disadvantage of being commonly made of high-fragile glass (ASTM E70-19, 2019; METHROHM, [s.d.]; SCIENTIFIC; THERMO SCIENTIFIC, 1991; SKOOG et al., 2014).

In fact, there are already crystal and polymer pH-meter membranes available, but most of the commercial electrodes used on general applications (including biological, pharmaceutical, and petroleum emulsions applications) still rely on glass membranes. These membranes, in turn, must be maintained under strict temperature conditions and have to be stored immersed in appropriate saline solutions, usually KCl 3M in water (ASTM E70-19, 2019; METHROHM, [s.d.]; SCIENTIFIC; THERMO SCIENTIFIC, 1991).

Since the proposed sensor is made of an elastomeric material (the hydrogel), it presents higher tenacity than the commercial glass devices, with lower risks of mechanical fracture (BUREY et al., 2008; OMENETTO; KAPLAN, 2008; SKOOG et al., 2014).

The verification of the solvatochromic shifts related to pH variations and to the occlusion of the silica-Cdots into agarose is also of particular importance. That is because these data provide insights regarding the interaction mechanisms between fluorescent nanoparticles and their media. As mentioned by Sciortino *et al.*, there is still a lack of research analyzing (or even verifying) the effects of the incorporation of carbon nanodots into different solid media on the luminescent emission mechanisms (SCIORTINO et al., 2016).

Finally, the synthesized amorphous hybrids could also be very interesting as new materials for applications in optoelectronic devices, optical fibers sensors, and solar cells.

Suggestions for forthcoming studies include the exploration of the direct coupling between carboxylic acid terminated carbon nanodots and the amino functionalized silica surface of no-core optical fibers (basically, a silica cylinder) for the fabrication of a fluorescent cladding with sensing applications on media of different polarities.

2.5.8. Contributions and acknowledgements

- Financial support from São Paulo Research Foundation (FAPESP) under grant 2019/22554-4.
- Espaço da Escrita Pró-Reitoria de Pesquisa UNICAMP and FAEPEX/UNICAMP, for the language services provided as support for this research.

- Financial support to other contributors of this work: Coordenação de Aperfeiçoamento de Pessoal de Nivel Superior-Brazil (CAPES), finance code 001; National Council for Scientific and Technological Development (CNPq), finance code 001; The University of Trieste, INSTM; Italian Ministry of Education, MIUR (cofin Prot. 2017PBXPN4); The Spanish Ministry of Science, Innovation and Universities, MICIU (project PID2019-108523RB-I00). Part of this research was performed under the Maria de Maeztu Units of Excellence Program from the Spanish State Research Agency, Grant No. MDM-2017-0720. Prof. Maurizio Prato is the AXA Chair for Bionanotechnology (2016-2023).
- Prof. Maurizio Prato support staff, comprised of Prof. S. Bosi, Dr. F. Arcudi, Dr. G. Filippini, Dr. M. Cacioppo and Dr. P. Bertoncin for technical support.
- Prof. Carlos K. Suzuki from the Laboratory of Photonic Materials and Devices, School of Mechanical Engineering, University of Campinas, SP, Brazil (FEM/UNICAMP); and Prof. Marcelo Carreño and Prof. Inés Pereyra from the Laboratory of Microelectronics, Polytechnic School, University of São Paulo, SP, Brazil (LME/EPUSP) for the technical support and for scientific discussions and insights.
- Dr. Francesco Amato and Prof. Maurizio Prato from the Carbon Nanotechnology Group, Dept. of Chemical and Pharmaceutical Sciences, University of Trieste (Italy); and Prof. Alejandro Criado from the Center for Cooperative Research in Biomaterials (CIC biomaGUNE), Basque Research and Technology Alliance (BRTA), Donostia San Sebastián (Spain) for the chemical synthesis of the hybrid nanoparticles, materials characterization equipment (TEM and FEG-TEM, XRD, FTIR, XPS, Raman, TGA and PL/fluorescence), and support and insights on data interpretation.
- Dr. Thiago D. Cabral and Prof. Cristiano M. B. Cordeiro from the Laboratory of Specialty Fibers and Photonic Materials, "Gleb Wataghin" Institute of Physics, University of Campinas, SP, Brazil (IFGW/UNICAMP) for the physics theory, contextualization and interpretation support, fabrication of the double-clad mPOF, and optical characterization equipment (RI, OSA and Supercontinuum Laser).
- Gildo S. Rodrigues and Prof. Cristiano M. B. Cordeiro from the Laboratory of Specialty Fibers and Photonic Materials, "Gleb Wataghin" Institute of Physics, University of Campinas, SP, Brazil (IFGW/UNICAMP) for the 3D-printing of the molds.
- Prof. Julio Roberto Bartoli from the School of Chemical Engineering, University of Campinas, SP, Brazil (FEQ/UNICAMP); and Prof. Maurizio Prato from the Carbon Nanotechnology Group, Dept. of Chemical and Pharmaceutical Sciences, University of Trieste (Italy) for the support on both the development of the synthetic carbon nanodots methodology and on the project idealization.

2.6. Fabrication of fluorescent PMMA-Carbon Nanodots nanocomposites: improving the efficiency of solar cells through sustainable low-cost materials

This section presents the manufacturing of fluorescent acrylic-based carbon nanodots nanocomposites, a research published by IEEE (SOARES et al., 2023a) and by the Brazilian Journal of Chemical Engineering from Springer Nature (SOARES et al., 2023b). Suggestions and perspectives are given for future works, which may explore the unique properties of these materials on optoelectronics.

Nitrogen-doped carbon nanodots synthesized from L-arginine and ethylenediamine (NCNDs); citric acid-derived carbon nanodots with carboxylic surface groups (α -CDs); and Silica-Cdots hybrids produced through coupling α -CDs to SiO₂ nanoparticles were used for the fabrication of fluorescent PMMA-CDs optical films. PMMA naturally emits luminescence when irradiated by 300-320 nm and the nanoparticles occlusion allows the conversion of a broader UV bandwidth to the visible: emissions around 450 nm are observed for excitations from 330-360 nm.

Since this photoluminescence could increase the efficiency of solar energy concentrators and generators, photovoltaic cells were coated with films obtained with the blueemitting NCNDs. Even using a setup with low contact of the optical polymer film with the silicon surface, a promising increase from 4.24% to 4.72% of the energy conversion efficiency was observed. It could be translated into enormous potential gains on large-scale solar (renewable) energy systems, showing the potential of these environmentally friendly materials.

2.6.1. Introduction

Carbon Nanodots (CDs) are fluorescent nanoparticles characterized by various surface functional groups and sizes below 10 nm (KANG; LEE, 2019; WANG; HU, 2014). The conversion of organic precursors containing carboxylic acids (or nitrogen as doping element) results in the formation of CDs rich in carboxylic (or amine) surface groups with enhanced luminescence (ĐORĐEVIĆ et al., 2022).

Beyond the low-cost, CDs are environmentally safe materials (BOAKYE-YIADOM et al., 2019; ĐORĐEVIĆ et al., 2022) with good biological and biocompatibility properties, being excreted in urine (HUANG et al., 2013; WANG; HU, 2014). The emission properties of CDs are altered by tuning their bandgaps, resulting a plethora of applications, such as: imaging and sensing; fabrication of optoelectronic devices, perovskite solar cells, and graphene phototransistors; photocatalytic splitting of water; CO₂ reduction reactions; drug delivery; and gene transfer (ĐORĐEVIĆ et al., 2022; TUERHONG; XU; YIN, 2017; WANG; LU, 2022).

Energy applications also include the use of CDs to increase the efficiency of energy conversion in solar cells; to photosensitize or photocatalyze the conversion of solar energy into fuels; or to employ their fluorescence to prepare light-emitting diodes (ĐORĐEVIĆ et al., 2022). Their fluorescence properties also find use in light converters for photovoltaic cells and solar concentrators, and may replace dye sensitizers (TUERHONG; XU; YIN, 2017; WANG; LU, 2022). Moreover, they can be combined with polymeric materials to obtain luminescent nanocomposites containing CDs (AMATO et al., 2019, 2021; BOUKNAITIR et al., 2019; GONG et al., 2018, 2022; LI et al., 2023; PERLI et al., 2022). Such polymer nanocomposites, in turns, may be produced through several techniques, including *in-situ* polymerization, cross-linking, solution blending, immersion precipitation and melt intercalation or exfoliation (AFFONSO NETTO et al., 2022; ALEXANDRE; DUBOIS, 2000; BRESSANIN; ASSIS JÚNIOR; BARTOLI, 2018; FISCHER, 2003; MAZZUCCO et al., 2016; PRADO; BARTOLI, 2018; REMANAN et al., 2020). When nanoparticles dimensions are within the molecular levels of polymer chains, these nanocomposites may exhibit enhanced physical properties.

For optical devices applications, poly(methyl methacrylate), PMMA, is a particularly interesting polymer for designing transparent nanocomposite matrices (AFFONSO NETTO et al., 2022; BRESSANIN; ASSIS JÚNIOR; BARTOLI, 2018; PRADO; BARTOLI, 2018). PMMA is a highly transparent thermoplastic and an amorphous polymer in an intermediate

position between commodities and engineering thermoplastics. It presents relative low cost, good mechanical strength and high optical transmittance (ALI; KARIM; BUANG, 2015; CORSARO et al., 2021). Thus, PMMA-CDs nanocomposites with fluorescence properties have potential applications in Light-Emitting Diodes (LEDs) (STEPANIDENKO et al., 2021), Luminescent Solar Concentrators (LSCs) (MA et al., 2019), Dye-Sensitized Solar Cells (DSCs) (MOHAN; BORA; DOLUI, 2018) and Organic Solar Cells (OSCs) (BOUKNAITIR et al., 2019; KWON et al., 2013; LIN et al., 2016; MAXIM et al., 2020; WANG; HU, 2014; ZHAO et al., 2022). In such cases, the polymer matrix is not only responsible for the device's mechanical support, but also for the dispersion of the nanodots and prevention of the solid-state quenching (KWON et al., 2013).

In competition with CDs, organic dyes or inorganic quantum dots have been much more used as PMMA doping substances (HUANG et al., 2023; WALDRON et al., 2017; ZHOU; WANG; ZHAO, 2015). However, the stability of organic dyes and toxicity of inorganic elements (CdTe, PbSe) (ALBALADEJO-SIGUAN et al., 2021; BOTTRILL; GREEN, 2011; MANSHIAN et al., 2017; MOON et al., 2019; WU; TANG, 2014) pose significant concerns. Furthermore, investigations on improving the luminescence quantum yield (QY) of CDs (ratio of emitted to absorbed photons) is currently a very active field of study in modern chemical science, through specialized synthesis routes to produce new doped carbon dots and to obtain unconventional luminescence profiles (AMATO et al., 2019; ARCUDI; ĐORĐEVIĆ; PRATO, 2016, 2017; CACIOPPO et al., 2020; CADRANEL et al., 2018; ĐORĐEVIĆ et al., 2020; ĐORĐEVIĆ et al., 2022; ĐORĐEVIĆ; ARCUDI; PRATO, 2019; GHOSH et al., 2022; XIA et al., 2019; YAN et al., 2023).

Recently, advanced approaches like the use of mechanochemistry, flow chemistry and laser synthesis in the liquid phase are widening the range of properties and applications of these promising nanomaterials. Besides, these novel synthesis methodologies present the advantage of being scalable. Finally, machine learning could be also applied to go beyond the trial-anderror approach commonly used to explore the chemistry of CDs (BARTOLOMEI; DOSSO; PRATO, 2021).

Therefore, improvements in the energy conversion efficiency of solar cells can be achieved with LSCs or Luminescent Down Shifting (LDS) devices using low-cost and environmentally friendly fluorescent carbon dots instead of organic dyes or inorganic quantum dots (CHOI et al., 2017; GONG et al., 2018; LI et al., 2017; ZHAO, 2019). Considering these aspects, this work investigates the fabrication of PMMA optical films doped with fluorescent carbon nanodots. CDs exhibit a good solubility in polar solvents like methanol, whereas PMMA is very soluble in chloroform. As it was previously demonstrated that 2:1 (v/v) is the best ratio between chloroform and methanol to dissolve CDs chloroform (AMATO et al., 2019; SOARES et al., 2023a), this proportion was applied to the solutions of PMMA to produce functionalized films by drop-casting. Three different kinds of CDs were synthesized and tested regarding the fluorescent emissions. Finally, solar cells were coated with these nanocomposite films for proof-of-concept experiments on increasing their energy conversion efficiency.

2.6.2. Nitrogen-doped carbon nanodots synthesis

Blue-emitting nitrogen-doped carbon nanodots (NCNDs) from L-arginine (Fluorochem; \geq 98%) and ethylenediamine (EDA, Sigma-Aldrich; \geq 99.5%) are obtained through the bottomup procedure previously described in literature (ARCUDI; ĐORĐEVIĆ; PRATO, 2016). Two organic precursors at 1:1 (mol/mol) ratio are mixed to ultrapure water (>18 M Ω Milli-Q, Millipore): 87.0 mg of arginine are mixed to 33.0 µL EDA in 100.0 µL Milli-Q water and this solution is introduced into a CEM Discover-SP microwave oven with controlled conditions (240 °C, 26 bar and 200 W) for 180 seconds (reaction represented in Figure 34a). The microwave treatment converts the transparent medium into a brown-colored solution (Figure 34b), which is then diluted in water and filtered through a 0.1 µm microporous membrane for separating a deep yellow liquid (Figure 34c). As shown in Figure 34d, this filtered solution emits a strong blue fluorescence when irradiated with 365 nm ultraviolet (UV) light (ĐORĐEVIĆ; ARCUDI; PRATO, 2019). Finally, the yellow solution is dialyzed against pure water through a dialysis membrane with molecular weight cut-off of 0.5-1 kDa (Spectrum Labs) for 2 days (water refreshed every 6 hours; membranes previously activated with a solution of 0.2 L of ethanol in 1.8 L of water for 8 min) (AMATO et al., 2019).

The dialyzed solution of NCNDs is lyophilized using a bench-top freeze-dryer (LaboGene ScanVac CoolSafe; -49 °C; 72 h of vacuum). Each synthesis results in 23.0 mg of a brownish solid, so eleven batches are run to obtain 250 mg of NCNDs. It is demonstrated that this procedure is quite reproducible, and previous characterizations reveal that the obtained fluorescent NCNDs present relative quantum yield (QY) of 0.17 (ARCUDI; ĐORĐEVIĆ; PRATO, 2016); narrow distribution of diameters (1.0-4.5 nm); and plenty of surface traps and functional groups that allow tuning the luminescent emissions. Besides, nitrogen doping has been reported to give excellent optical properties and usually blue-shifted fluorescence (ARCUDI; ĐORĐEVIĆ; PRATO, 2016). The NCNDs fluorescence shows a broad emission peak at 356 nm when excited at 300 nm and a bathochromic shift from 356 to 474 nm as the excitation changes from 300 to 420 nm (ARCUDI; ĐORĐEVIĆ; PRATO, 2017; ĐORĐEVIĆ; ARCUDI; PRATO, 2019).

It is worth noticing that these NCNDs were previously submitted to the Photoelectron Spectroscopy (XPS) characterization by Arcudi et al. to provide their chemical composition (part of the characterization protocol applied to each CD synthesized in the laboratories of the Carbon Nanotechnology Group) (ARCUDI; ĐORĐEVIĆ; PRATO, 2016). It was reported the detection of C (68.0%), N (16.1%) and O (15.9%) with peaks at 286.8 eV (C1s), 400.33 eV (N1s) and 532.34 eV (O1s), respectively. The chemical moieties of C and N were further analyzed by deconvoluting their spectrum. C1s was deconvoluted into five surface components: sp² (C=C) at 274.5 eV; sp³ (C-C and C-H) at 285.5 eV; C-O/C-N at 286.2 eV; C=O/C=N at 288.3 eV; as well as COOH at 290.5 eV. In turn, N1s spectrum was deconvoluted into four peaks centered at 398.3; 399.6; 400.5; and 401.9 eV, corresponding to C=N; NH₂; C-N-C; and N-C₃, respectively. The presence of primary amino groups was confirmed by a positive Kaiser test (ARCUDI; ĐORĐEVIĆ; PRATO, 2016).

2.6.3. α-CDs and Silica-Cdots hybrids production

Citric acid-derived carbon nanodots (α -CDs) and the nanocomposites formed by combining them with SiO₂ nanoparticles (Silica-Cdots) are used as produced and characterized in a previous (open access) report (AMATO et al., 2021).

Briefly, α -CDs with sizes from 4 to 10 nm (mostly around 6 nm) are synthetized from the thermolysis of citric acid (200 g, Fluka, 99.5%) in a muffle furnace under air atmosphere at 180 °C for 40 h. In turns, commercial fumed silica nanoparticles (206 mg Aerosil 300, primary particle size ca. 7 nm, Evonik) are dispersed in ethanol (5 mL) and treated with 3-

aminopropyltriethoxysilane (APTES, 5 mL). This dispersion is stirred overnight at room temperature (r.t.) before being purified by centrifugation; dispersed in ethanol (three times); and lyophilized for obtaining amino-functionalized silica nanoparticles (a-SiO₂).

Finally, a-SiO₂ (50 mg) is mixed to the α -CDs (223 mg) dispersed in dry dimethylformamide (DMF, 10 mL) in the presence of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (200 mg, EDC·HCl Alfa Aesar) and N-hydroxysuccinimide (120 mg NHS, Sigma Aldrich). This mixture is stirred at 70 °C for 2 days under inert atmosphere (Ar), and DMF is removed through azeotropic distillation with toluene. Milli-Q water is added, and the system is purified by centrifugation (two cycles of 20 min at 3000 rpm) for obtaining Silica-Cdots nanohybrids with sizes on the order of 50 nm, nitrogen and oxygenated surface groups, and excitation-dependent fluorescence (Figure 9). The maximum intensity is observed for the 360 nm-excitation (emission at 465 nm), and the emission shifts from 465 to 513 nm (green) as the excitation changes from 360 to 430 nm. FTIR, TGA, XPS, XRD analysis and Raman spectra of the α -CDs and Silica-Cdots nanoparticles are readily available in the Supporting Information document accompanying the reference (AMATO et al., 2021).



Figure 34. (a) Scheme of formation of blue-emitting NCNDs; (b) brown-colored solution obtained after microwave-assisted synthesis; (c) yellow solution obtained after filtering; and (d) emission of blue fluorescence by the filtered solution when it is irradiated at 365 nm UV light.

2.6.4. Preparation of doped-PMMA optical films

The synthesized carbon nanodots are used to prepare nanocomposites with PMMA by solution blending: PMMA pellets are dissolved in chloroform, whereas previously lyophilized nanodots are dispersed in a solution of methanol and chloroform. The solutions are mixed, and thin films of nanocomposites are finally prepared by drop-casting on a glass substrate (Petri dishes).

PMMA pellets (Plexiglas V0 52, Arkema) are dried in an oven for 4 h at 80 °C and subsequently cooled to room temperature in a vacuum chamber with drier agent. For the preparation of a PMMA optical film by casting, a ratio of (21.5):1 (mL/g) of chloroform (Sigma-Aldrich) to PMMA is used. For instance, an optical film with diameter of 50 mm and thickness of ~100 μ m is obtained with 232 mg of PMMA. Then, 5 mL of chloroform are added to the PMMA pellets, and the system is left under magnetic stirring for 2 h at room temperature, followed by 20 s of ultrasound bath.

Lyophilized carbon nanodots are dispersed in a mixture of chloroform and methanol 2:1 (v/v) (best ratio previously demonstrated (AMATO et al., 2019)) and subsequently kept in an ultrasound bath for 10 min. One example of dispersion prepared with this procedure is shown on Figure 35, where α -CDs (5 wt%) are observed under daylight and under 365 nm UV light.



Figure 35. Lyophilized α -CDs (5 wt%) dispersed in a mixture comprised of chloroform and methanol (proportion of 2:1 (v/v)) observed under: (a) daylight; (b) UV light ($\lambda = 365$ nm).



Figure 36. PMMA-NCNDs (5 wt%) solution (before casting) observed under: (a) daylight; (b) UV light ($\lambda = 365$ nm).

After that, the CDs dispersion is added to the PMMA-chloroform suspension and mixed in an ultrasound bath for 10 min. Different CDs-PMMA systems are prepared according to the desired concentration of CDs, from 0.1% to 5% in mass (for instance, Figure 36 shows the aspect of the solution obtained for the system PMMA-NCNDs (5 wt%)).

Next, the optical films are produced by solution casting onto Petri dishes, slowly pouring (drop-by-drop) the CDs-PMMA solution with a pipette. For this step, the dishes are kept at level to evenly maintain the thickness of the casted volume. Finally, the Petri dishes are left to dry in an atmosphere saturated with chloroform vapor (room temperature) for 48-72 h to avoid formation of microvoids due to rapid volatilization. The saturated atmosphere is created by placing several vials containing chloroform close to the Petri dishes, keeping the set covered to ensure isolation from the room. A PMMA casting film with no carbon nanodots (pristine sample) is also prepared through this same procedure. The optical films formed on the Petri dishes are weighed after 24 h, 48 h and 72 h, until the mass losses due to the evaporation of chloroform are stabilized. Figure 37 shows the aspect and the blue fluorescence observed ($\lambda = 365$ nm irradiation) from a PMMA-NCNDs (5 wt%) film formed in the Petri dish.



Figure 37. PMMA-NCNDs (5 wt%) films on the Petri dishes after drop casting: (a) frontal aspect, under daylight; (b) side aspect, under daylight; (c) frontal aspect, under UV light ($\lambda = 365$ nm); (d) side aspect, under UV light ($\lambda = 365$ nm).

2.6.5. Films' fluorescence and photovoltaic characterizations

The PMMA-CDs film is cut with a scalpel from the bottom of the Petri dish in the shape of a 45 mm \times 13.5 mm rectangle. Then, the dish is taken to the freezer for 1 to 2 min to allow the polymeric film to be released from the dish (a spatula may be used to remove the film). Thus, the film's mass and thickness are measured before the fluorescence evaluation. Figure 38 shows the aspect of one film formed with PMMA and NCNDs (0.5 wt%) when the material is observed under daylight and under 365 nm-UV light.



Figure 38. PMMA-NCNDs films (0.5 wt%) observed under: (a) daylight; (b) UV light ($\lambda = 365$ nm).

PMMA films had their photoluminescence (PL) spectra analyzed at room temperature with a Cary Ellipse-Varian Fluorescence Spectrophotometer (Agilent Technologies) at excitation wavelengths from 300 to 360 nm, 600 nm/min scan speed, and excitation and emission slits of 5 nm. For that, quartz cuvettes (High Precision Cell Suprasil, light path 10×10 mm, Hellma Analytics) were adapted for solid analysis, allowing rectangular films to be inserted into the cuvettes' diagonal positions (13.5 mm). Since the films are thin and flexible, they may show a curvature after their insertion into a cuvette. Thus, it is necessary to verify if the modification of the curvature direction (concave or convex) has any effect on the PL spectra for a given film. A Fluorolog 3 Fluorescence Spectrophotometer (Horiba) equipped with sample holders for thin films was also used in the characterization of the produced optical films.

Photovoltaic measurements were performed with in-house silicon-based solar cells (laboratory scale, usually destined to didactic purposes) with dimensions of 25 mm × 25 mm and maximum efficiency of 5%. The tests were conducted by positioning and holding the pristine PMMA and doped PMMA-CDs optical films on the surface of the solar cells. The cells were tested on a bench designed for photovoltaic measurements (STEM, 2007) equipped with a solar simulator where the light source is a xenon XPS 300 (Solar Light) adjusted for an incident intensity of 1000 W/m². A thermostatic bath keeps the cells temperature constant at 25 °C, and the I × V curves of the photovoltaic devices are measured with a digital multimeter HP 34401A (Hewlett Packard) and Lab Tracer 2.0 (Keithley) software. Also, the measurement system uses a standard solar cell with short-circuit current $I_{sc} = 66.40$ mA for reference purposes. The solar cells and the testing bench are shown on Figure 39.



Figure 39. (a) Silicon solar cell; (b) bench for photovoltaic measurements; (c) PMMA-NCNDs (0.5 wt%) optical film positioned on the solar cell; (d) Measurements of I × V curve and obtention of photovoltaic parameters with Lab Tracer 2.0 software.

2.6.6. Characterization of films fluorescence emission

The pristine PMMA film exhibits a natural fluorescence emission when irradiated from 300-320 nm (broad emission peak around 450 nm), but there is no luminescence for irradiations at longer wavelengths (Figure 40a). If compared to the pristine material, the PMMA-NCNDs films reveal additional emission bands for excitations longer than 320 nm (Figures 40b-d). From the films produced using chloroform/methanol 2:1, it is possible to discern the PMMA typical bands without spectral shifts along with the CDs ones with lower intensities. The lower intensity of CDs emissions can be explained by several phenomena: (i) low number of light emitters in the matrix (GONG et al., 2018; JIANG et al., 2020; LAKOWICZ, 2006; PERLI et al., 2022); (ii) low fluorescence quantum yield of the emitters (related to the type of carbon dots used) (LAKOWICZ, 2006); (iii) matrix-related effects and the quality of nanoparticles dispersions (modification of the emissive domains on each dot) (JIANG et al., 2020); and (iv) solvatochromic effects (BANO et al., 2019; CHANDRA et al., 2019; REICHARDT, 2005). In addition, quenching phenomena can occur, as carbon dots can act as electron donors or acceptors in their excited states (CACIOPPO et al., 2020; ĐORĐEVIĆ et al., 2020). The composition of the solvent mixture (type of CD and its concentration) is a major factor in modulating the fluorescence emission of the film (Figures 40c-d). This is illustrated by the matrices obtained for chloroform/methanol ratios of 3.3:1 and 4:1 showing PMMA emissions alongside broader NCNDs emission bands with undistinguishable maximum (~400-450 nm). From this data, the solvent mixture ratio 2:1 resulted in the best compromise in terms of NCNDs emission for this study.

To verify the hypotheses that the intensities could be related to the concentration and nature of the occluded carbon nanodots, higher concentrations of NCNDs (5 wt%) were tested and compared against the same concentrations of α -CDs and Silica-Cdots. The PMMA- α -CDs solution used in this study (before casting) is shown on Figure 41, whereas the PL results are presented in Figure 42.



Figure 40. PL spectra: (a) PMMA pristine film; and different volumetric proportions of chloroform to methanol for producing PMMA-NCNDs nanocomposites (0.1 wt% of CDs). Proportions of: (b) 2:1 (selected as standard); (c) (3.3):1; and (d) 4:1 (v/v).



Figure 41. PMMA- α -CDs (5 wt%) solution (before casting) observed under: (a) daylight; (b) UV light ($\lambda = 365$ nm).

Increasing NCNDs nanoparticles concentration resulted in more well-defined and intense emission bands for the dots emissions, even reaching levels slightly higher than the PMMA matrix. Now, the maxima for emissions from 330-360 nm excitations are clearly centered at 450 nm. Thus, the presence of fluorescent nanoparticles extends the range of UV-to-Visible conversion in PMMA (here, it was verified for excitation wavelengths up to 360 nm).

Superior spectral energy conversion was obtained when testing α -CDs and Silica-Cdots hybrids in relation to NCNDs, with several emission peaks showing higher intensities than the emissions from the matrix. The peaks are still centered at 450 nm, and Figure 42b (α -CDs) presents all CDs emissions above the PMMA's (peaks increasing with the excitation wavelength). Emissions observed for 350 and 360 nm excitations overcame 1000 a.u. (arbitrary units) and saturated the detector, so they were omitted from Figure 42b. Lastly, Figure 42c shows lower intensities for the hybrids when compared to α -CDs. This is most likely related to the very larger dimensions of the hybrids and to the modification of the surface functional groups originated from the coupling reaction between the α -CDs carboxylic acids and the SiO₂ nanoparticles, which removes some of the free -COOH. Such structural differences modify the interactions between the dispersed phase and the acrylate matrix and can lead to changes in the quenching mechanisms and emissive domains on each nanodot (AMATO et al., 2021; BANO et al., 2019; CADRANEL et al., 2018; JIANG et al., 2020).



Figure 42. PL spectra of films produced by doping PMMA with different amounts of nanoparticles (concentration in mass): (a) 5 wt% of NCNDs; (b) 5 wt% of α-CDs (emissions for 350 and 360 nm were omitted, since intensities overcame 1000 a.u. and saturated the detector); and (c) 5 wt% of Silica-Cdots hybrids.

To avoid further detector saturation issues, the previous analysis was repeated, but the excitation and emission slits were reduced from 5 to 2.5 nm. As shown on Figure 43, the slits

reduction results in spectra with much lower intensities. As a matter of fact, only the PMMA- α -CDs system could be analyzed, showing intensities that increase with the excitations from 340 to 370 nm; and a clear emission maximum at 425 nm, which corresponds to the excitation at 370 nm. This increase of the intensity with the excitation wavelength was not observed on the other systems.



Figure 43. Photoluminescence spectra obtained for PMMA-α-CDs (5 wt%) optical films when reducing the excitation and emission slits from 5 to 2.5 nm. The collected intensities considerably decreased, allowing the observation of the spectra with no saturation.

The films observed under daylight and under UV radiation ($\lambda = 365$ nm) are shown in Figure 44. Their absorption and transmittance properties, in turn (obtained with the spectrophotometer), are compared in Figure 45. In Figure 45a, the UV-Visible absorption spectra collected for the nanodots nanocomposites show maximum absorbance at 250 nm, corresponding to the $\pi \rightarrow \pi^*$ transition of the sp² carbons of the CDs cores. Shoulders at 275 -300 nm with tails extending to the visible range are present, assigned to the $n \rightarrow \pi^*$ transitions involving the electron lone pairs of the carboxylic and nitrogen surface groups (AMATO et al., 2021; PERLI et al., 2022). The pristine sample presents almost no absorbance on the analyzed range, whereas the PMMA- α -CDs is the nanocomposite with highest capability of absorbing ultraviolet light. This behavior is approximately opposite to the observed for the transmittances (Figure 45b): until 300 nm, pristine has a transmittance considerably higher than the nanocomposites, whereas the PMMA- α -CDs shows a slower sigmoidal increase of the transmittance, reaching a value close to 100% only for wavelengths longer than 500 nm. The Silica-Cdots nanocomposite has the highest transmittance on the visible, which may be related to inherent optical properties of silicates (SALEH; TEICH, 1991; SANTOS et al., 2011).



Figure 44. Different optical films observed under: (a) daylight; (b) UV light ($\lambda = 365$ nm).



Figure 45. (a) Absorbances; and (b) transmittances obtained for the different optical films.

2.6.7. Screening of the photovoltaic properties

Carbon nanodots show interesting applications in photocatalysis and renewable energies and can be used in solar concentrators (LSC) or converter (LDS) devices. These devices are designed to collect solar light by absorbing incident photons and reemitting them through an optical waveguide (STEPANIDENKO et al., 2021; WANG; HU, 2014; ZHAO et al., 2022).

In general, the LSC collector is comprised of thin plates or sheets of a transparent material doped with luminescent species. Incident sunlight excites these species, and then their reemissions are collected with a waveguide and directed to the photovoltaic cells, improving the energy conversion efficiency (BARIK; PRADHAN, 2021; LIU et al., 2020; REISFELD et al., 1988). In turn, solar converters (LDS) are films or photoluminescent layers deposited and adhered on the surface of solar cells or photodiodes. LDSs have the same function of shifting the solar spectrum to longer wavelengths (down shifting), converting UV radiation to visible light (AHMED et al., 2012; CHOI et al., 2017).

Due to its great optical properties, PMMA is one of the most applied materials for manufacturing LSCs (REISFELD et al., 1988) and LDSs (CHOI et al., 2017). In general, these LSCs use organic dyes or inorganic quantum dots as fluorescent species, showing

disadvantages such as the photodegradation of the organic dyes or the toxicity of the inorganic nanoparticles (AHMED et al., 2012; WALDRON et al., 2017; ZHOU; WANG; ZHAO, 2015). Thus, the photoluminescent behavior of the PMMA-CDs matrices could be exploited to improve the External Quantum Efficiency (EQE) of photovoltaic cells, considering the large-scale systems' production costs (REISFELD et al., 1988).

Carbon nanodots-based nanocomposites have already been leveraged on solar energy applications (CHOI et al., 2017; GONG et al., 2018; LI et al., 2017). In these studies, PMMA-doped films were used as luminescent solar collectors and cells' top-layers, converting UV to visible light. That is because silicon-based solar cells show poor light harvesting performance under UV-irradiation, leading to poor quantum efficiencies in the UV region (AMATO et al., 2019; TSAI et al., 2016).

Most of the incident UV photons produce photogenerated carriers (electron-hole pairs) close to the surface, which could easily recombine with defect sites in the depletion region, the intermediary zone of the solar cell's p-n junction where the electric current is generated. In this context, NCNDs could facilitate the down-conversion effect on silicon cells: photons with longer wavelengths (in the visible range) could be absorbed and excite carriers in the depletion region for immediate photogenerated carrier separation due to the built-in electric field, leading to increased photovoltaic effect (AMATO et al., 2019; CHOI et al., 2017; TSAI et al., 2016).

Therefore, as PMMA-CDs nanocomposites are promising candidates for solar cells applications, NCNDs-doped optical films were used in proof-of-concept experiments on the improvement of cell efficiency by positioning the doped films on the external surfaces of silicon-based solar cells with dimensions of $25 \text{ mm} \times 25 \text{ mm}$. Figure 46 shows a representation of this setup for the blue-emitting NCNDs-PMMA, indicating that part of the visible range from the solar radiation is directly converted by the cell. The UV is not converted, though, and could even degrade the device. So, by converting part of the UV to visible, the NCNDs not only increase the bandwidth from the solar light that can be used for electricity generation, but also protect the cell from UV-degradation. It ultimately leads to economic gains related to the improvement of both the efficiency and the total cells' life cycles (WANG; HU, 2014).

The photovoltaic results (current I versus voltage V for a given incident irradiance power P_{in}) obtained for the cell with pristine are compared to the NCNDs-doped (0.5 wt%) optical film in Figure 47, and the experimental parameters obtained are shown in Table 2. Here, I_{sc} is the short-circuit current, which is the maximum current that may occur on the cell (zero-voltage condition). This current is due to the generation and collection of light-generated carriers. For an ideal solar cell at moderate resistive loss mechanisms, it is identical to the light-generated current (HONSBERG; BOWDEN, 2019a). The open-circuit voltage V_{oc}, in its turn, is the maximum voltage available for a solar cell, occurring at zero current. It corresponds to the amount of forward bias on the solar cell due to the bias of the cell junction with the light-generated current (HONSBERG; BOWDEN, 2019b).

 V_{oc} presents a complex non-linear relation with temperature. Another important characteristic of V_{oc} is that it increases with the bandgap, while I_{sc} decreases with this gap. In an ideal device, V_{oc} is limited by radiative recombination (electron-hole) (HONSBERG; BOWDEN, 2019b). I_{sc} , on the other hand, depends on a series of factors, including: (i) the area of the solar cell; (ii) the number of incident photons or the power of the incident light source P_{in} ; (iii) the spectrum of the incident light; (iv) the optical properties (absorption, transmittance and reflection) of the solar cell; and (v) the minority-carrier collection probability of the solar

cell, which mainly depends on the surface passivation and on the minority carrier lifetime in the cell's base (HONSBERG; BOWDEN, 2019a).

For both I_{sc} and V_{oc} conditions, the power produced by the cell is zero. So, to determine the efficiency of the cell, a third parameter called fill factor (FF) is analyzed in conjunction with I_{sc} and V_{oc} . It is given by the relation between the maximum power P_{max} of the cell and the product between I_{sc} and V_{oc} , as in Equation (4) (HONSBERG; BOWDEN, 2019c).



Figure 46. Scheme of solar cell coated with doped-PMMA: CDs convert part of the UV to visible, enhancing the solar radiation bandwidth that may be used for electricity generation; and protecting the cell from UV-degradation.

$$FF = \frac{P_{max}}{(V_{OC} \times I_{SC})}$$
(4)

FF may be understood as a measurement of the "squareness" of the solar cell's I × V curve and is also the area of the largest rectangle which may be inscribed within this plot. The FF from a solar cell can be determined by differentiating its power with respect to the voltage and then finding the maximum P_{max} (dP/dV = 0): the rectangle area is obtained by multiplying the V of maximum power by the correspondent current value retrieved from I curve (HONSBERG; BOWDEN, 2019c). From these parameters, the efficiency of the solar cell η may be finally calculated as Equation (5) or, in percentage, as Equation (6) (GONG et al., 2018).

$$\eta = \frac{(J_{SC} \times V_{OC} \times FF)}{P_{in}}$$
(5)
$$\eta = \frac{(J_{SC} \times V_{OC} \times FF)}{P_{in}} \times 100\%$$
(6)

The short-circuit current density J_{sc} is related to the cell's transmission and to the amount of excited photoelectrons in the device, presenting a great influence on the overall efficiency of the system (CHUNG et al., 2012). Moreover, previous studies with carbon nanodots-doped light solar concentrators indicate that both J_{sc} and V_{oc} should increase with the concentration of nanoparticles. Since the total of excited photoelectrons is associated with the doping concentration, the intensity of the emitted fluorescence increases with CDs' concentration. Gong *et al.* (2018) argue that such an increase is not indefinite, though, so the concentration of nanoparticles has an optimal value. This comes from overlaps between the absorption spectra and the fluorescence emission spectra of carbon nanodots leading to reabsorption of emitted photons by the CDs themselves. Finally, as the fluorescence intensity is necessarily smaller than 1 (LAKOWICZ, 2006), the final emitted fluorescence intensity is necessarily smaller than the absorbed intensity, resulting in a loss of energy in the conversion process. Therefore, if the doping concentration exceeds the optimum value (a condition that must be determined empirically), the fluorescence intensity and the solar cell's efficiency will start decreasing (GONG et al., 2018).

In Figure 47 and Table 2, the I \times V curve and the photovoltaic parameters are presented for a PMMA-0.5 wt% NCNDs and pristine optical films of ~35 µm thicknesses. An increase in the solar cell efficiency is observed for the NCNDs-doped matrix, from 4.24% to 4.72%.

Even though at first glance this 11.3% increase might seem of low significance, it can be translated into substantial savings of economic and environmental resources on commercial systems. For instance, a typical panel has an efficiency of 15% and a surface area of 1 m², producing about 150 W of electrical energy (VOURVOULIAS, 2023). Employing such panels, the National Renewable Energy Laboratory (NREL - USA) estimates that 2.8 acres of panels are needed to supply 1000 households with electricity for a year (1 GWh), what corresponds to the operation of a solar farm with 32 acres of land (BUSINESS, 2013; ONG et al., 2013). Thus, an efficiency increase of 11.3% would bring the net panel efficiency up to 16.7%, reducing the total area of the panels to 2.5 acres (10.7% reduction); and lowering the total land needed for the solar plant to 28.7 acres (10.3% reduction).

Furthermore, the current experimental setup is based on the simple partial superposition of the optical films on the cell's surfaces. It is an assembly strategy that limits the efficiency gain due to factors like the poor interface contact conditions and the possible formation of an intermediate air layer (dielectric). Light reflections may be observed on a setup like this, as the PMMA layer is not adhered on the cell surface and the film thickness is not optimized for interferometric anti-reflexive properties. Spurious reflections reduce the conversion efficiency by partially rejecting light back to the external medium. Therefore, the reduction of the film's reflectance could be a strategy for improving the energy conversion (SALEH; TEICH, 1991; TAYLOR, 2002). Naturally, the use of the most-efficient carbon nanodots (α -CDs) is also

106



expected to lead to better results, since they present the most intense emissions.

Figure 47. Curves of current versus voltage for the solar cells covered with: pristine (black); and PMMA-NCNDs (pink) optical films.

	Pristine	PMMA-NCNDs
Isc (mA)	23.87	26.55
V _{oc} (V)	0.6069	0.6098
J _{sc} (mA/cm ²)	9.95	11.06
P _{max} (mW)	10.18	11.32
FF	0.703	0.699
η (%)	4.24	4.72

 Table 2. Photovoltaic data obtained for the two tested solar cells covered with pristine and PMMA-NCNDs optical films.

2.6.8. Conclusions from this study

Three typologies of carbon nanodots (NCNDs, α -CDs and Silica-Cdots hybrids) were applied to the fabrication of fluorescent PMMA optical films. The films significantly enhance the PMMA's natural fluorescence and allow the conversion of a wider UV window to visible, increasing solar cells' efficiencies.

Initial testing showed an 11.3% increase in efficiency by employing fluorescent films, even considering their use in non-optimized conditions. When compared to the power obtained with regular panels, this gain would be translated in up to 10.3% of land use reduction. It is a result that clearly demonstrates the feasibility and potential application of these low-cost sustainable materials.

Upcoming works will focus on optimizing the usage of α -CDs (that present the highest UV-to-Visible conversion) as the standard for fluorescent film fabrication, further enhancing the efficiency gains. Since these nanoparticles are formed by thermolysis in simple muffles, they are particularly adequate for large-scale manufacturing due to requiring simpler, cheaper, and easily scalable equipment. In addition, as very high UV absorbances are observed for α -CDs (Figure 45a), doped PMMA films will help protect the cell against UV-induced degradation on the passivation layers, increasing the lifespan of panels and leading to reduced maintenance costs. Methodologies for direct coating the cells with doped films will also be investigated to eliminate the extra dielectric layer (air gaps) and to minimize reflection losses. Potential avenues to accomplish this are drop-casting the PMMA-CDs chloroform solutions directly on the cell's surface and spin-coating.

2.6.9. Contributions and acknowledgements

- Financial support from São Paulo Research Foundation (FAPESP) under grant 2019/22554-4.
- Financial support to other contributors of this work: FAPESP grant 2018/08782-1; Coordenação de Aperfeiçoamento de Pessoal de Nivel Superior–Brazil (CAPES), finance code 001; National Council for Scientific and Technological Development (CNPq), finance code 001; The University of Trieste, INSTM; Italian Ministry of Education, MIUR (cofin Prot. 2017PBXPN4); Prof. Maurizio Prato is the AXA Chair for Bionanotechnology (2016-2023).
- Dr. Thiago D. Cabral from the Laboratory of Specialty Fibers and Photonic Materials, "Gleb Wataghin" Institute of Physics, University of Campinas, SP, Brazil (IFGW/UNICAMP) for the physics theory and interpretation support.
- Dr. Francesco Amato, Dr. Francesca Arcudi, Dr. Michele Cacioppo, Dr. Giacomo Filippini, Beatrice Bartolomei and Prof. Maurizio Prato from the Carbon Nanotechnology Group, Department of Chemical and Pharmaceutical Sciences, University of Trieste (Italy) for the chemical synthesis of the nanoparticles and support and insights on data interpretation.
- Prof. Marcelo Carreño, Prof. Inés Pereyra, Carlos A. S. Ramos, Prof. Manuel Cid Sánchez and Igor Abbe from the Laboratory of Microelectronics, Polytechnic School, University of São Paulo, SP, Brazil (LME/EPUSP); and Gilson Schaberle Goveia and Prof. José Fernando Diniz Chubaci from the Institute of Physics, University of São Paulo, SP, Brazil for the technical support, providing the solar cells, bench for photovoltaic characterization, and also helping with scientific discussions and insights.
- Prof. Julio Roberto Bartoli from the School of Chemical Engineering, University of Campinas, SP, Brazil (FEQ/UNICAMP); and Prof. Maurizio Prato from the Carbon Nanotechnology Group, Dept. of Chemical and Pharmaceutical Sciences, University of Trieste (Italy) for the support on both the development of the synthetic carbon nanodots methodology and on the project idealization.
3. Design and Application of Fiber Optic Chemical and Biochemical Sensors

3.1. Motivation

Optical fibers are cylindrical waveguides formed by dielectric materials with low loss of light power. They have a central core (where the light is guided) surrounded by a cladding with refractive index slightly lower than the core's. Light rays incident on the core-cladding interface with angles greater than a certain critical value suffer total internal reflection, being guided through the core without suffering refraction. Rays that do not follow this critical angle condition are transmitted through the cladding: they suffer high loss of power and are not effectively guided (SALEH; TEICH, 1991). This is the idea previously explored on Fig. 29.

The principles of light transmission in optical fibers are essentially the same as those applied to planar waveguides, except for the cylindrical geometry. Moreover, light propagates in the form of modes throughout the fibers. It is worth noting that it was exactly the development of these light guidance techniques that allowed the conduction of light to positions inaccessible to traditional instruments (lenses and mirrors). It also allowed the confinement of light in optoelectronic devices of reduced dimensions, enabling the miniaturization of such systems (SALEH; TEICH, 1991).

The discovery of the laser in the early 1960s, in turn, motivated the application of the light spectrum in communications (i.e., motivated its use as an extension of the radio and microwave spectra), what allowed the transmission of information at much higher rates than hitherto used. Thus, there was a stimulus to the development of optical fiber-based communication systems in which transmitted or reflected light is captured by a photodetector (KEISER, 2013). The detector, then, converts the optical stimulus to an electrical signal that is electronically or computationally processed (GHATAK; THYAGARAJAN, 2000).

The most common configuration of optical fiber is the so-called "step-index fiber": it consists of a central dielectric core (index of refraction n_1) covered by a cladding of material with index of refraction n_2 , where $n_2 < n_1$. In addition, other fiber configurations are possible (GHATAK; THYAGARAJAN, 2000; SALEH; TEICH, 1991): fibers may present refractive indices that vary continuously with the distance from their central axis ("graded-index fibers"); or they may even show complex microstructures that contain cavities filled with air, vapors or liquids (LI et al., 2018c; OLIVEIRA et al., 2016; PETERS, 2011; YANG et al., 2018).

The growth of optoelectronic and telecommunication industries led to the advent of the fiber optic sensor technology, which was the alternative found by these industries so that they could produce themselves the monitoring and control components for their manufacturing processes (UDD, 2002). The great technical progress observed in these sectors from the 1980s, on the other hand, made miniaturized and low-cost light sources and photodetectors commercially available. Finally, the production of high-quality optical fibers allowed the development and use of the fiber optic sensors in applications beyond communications, such as biomedicine (WENCEL; ABEL; MCDONAGH, 2014).

So, as component prices were reduced and quality improvements were achieved, fiber optic sensors started replacing traditional instruments used for various types of measurements, like: rotation, acceleration, temperature, pressure, mechanical deformation, voltage and electric current (UDD, 2002). Also, technical advantages inherent to the use of optical fibers were observed, including: typically reduced mass of the devices; small dimensions of the sensors; low energy consumption by the equipment; resistance to electromagnetic interference presented by optical devices; and biocompatibility. Other interesting optical fiber sensors properties noticed were high: sensitivity; stability; measurement resolution; bandwidth; and resistance to the environment, both from the chemical and from the thermal point of view, with possibility of remote operation and under aggressive conditions (LI et al., 2018c; UDD, 2002).

Sensors with such characteristics show several potential applications in chemical and biochemical monitoring: detection of gases and vapors; chemical and biomedical analysis; molecular biotechnology; environmental analysis (from the analysis of agricultural pesticides to the monitoring of marine environments); industrial production monitoring; bioprocess control; monitoring of the production of catalysts and other components in automotive industry (WANG; WOLFBEIS, 2020; WOLFBEIS, 2008); and even monitoring of cell proliferation in microfermentors (SOARES et al., 2019b, 2019e).

Traditionally, the set of optical fiber chemical sensing systems is divided into two main classes: direct sensing schemes (called "label-free" sensors); and indirect ones, based on the addition of indicators (e.g., a dye with fluorescence dependent on the presence of a target analyte). In the first case, intrinsic optical properties of the analyte (e.g., its refractive index, its absorption, or its emission) are assessed. In the second one, either the fluorescence or the color of an immobilized indicator agent (the "label") is evaluated; or another optical property of the "probe" is selected for being monitored (WANG; WOLFBEIS, 2020; WOLFBEIS, 2008).

Some authors also consider that there is a subclass of chemical sensors called biosensors. There is no consensual definition for biosensors, though, and different and even mutually exclusive concepts regarding this subject are found in literature. For instance, one useful definition of fiber optic biosensors is a set of devices derived from optical fibers that use the optical field for the detection of biological molecules (including proteins, antibodies, nucleic acids, and even cells). Such devices are commonly modified with biological species to improve their selectivity (LEUNG; SHANKAR; MUTHARASAN, 2007; WANG; WOLFBEIS, 2020; WOLFBEIS, 2008). Ideally, biosensors should not only respond to low analyte concentrations, but also be capable of differentiating species according to the recognition molecules attached to their surfaces. They have several applications in the health area, including the detection of biological markers for clinical diagnosis and the detection of pathogens and toxins in water and food (LEUNG; SHANKAR; MUTHARASAN, 2007).

So, the objective of this work was the design and the application of fiber optic sensors to important chemical and biochemical systems. The sensors were validated for the assessment of biphasic systems (common in petrochemistry); fermentation monitoring; and simultaneous detection of nanoparticles suspensions' velocity and concentration. Such suspensions are present in several sectors, from the traditional chemical, petrochemical and mining facilities to biochemical and food industries, with a range of control and monitoring use-cases.

3.2. Monitoring of biphasic flow with tilted fiber Bragg grating optical sensor

The work published by the IEEE Sensors Journal (ARISTILDE et al., 2021) and protected by a patent (CORDEIRO et al., 2019) is presented here. In this system, a 3D-printed

millifluidic device with an inserted tilted fiber Bragg grating sensor is used for assessing velocity and refractive index on biphasic systems (air-in-oil, water-in-oil and water-in-air suspensions). So, it has important applications in the monitoring of petrochemical facilities.

Moreover, the test of suspensions formed by water, air, and vegetable oils is indeed a methodology typically applied to gas-water and oil-water studies (ANGELI; HEWITT, 2000).

3.2.1. Introduction

Multiphase flows are characterized by the simultaneous transport of immiscible substances, the dispersed and continuous phases. They are observed in the oil and gas industries during the extraction of light and heavy oils containing dispersed components like minerals, gases, and water (ANGELI; HEWITT, 2000); in nuclear reactors (COLOMBO; FAIRWEATHER, 2015); and in biomedical applications (YAO; TAKEI, 2017).

On the other hand, milli- and microfluidic devices can be used for precisely generating and manipulating such multiphase systems, once they allow the formation of droplets flowing through a continuous phase. These devices present, then, important applications in microreactors and clinical analyses (JOANICOT; AJDARI, 2005; YAGER et al., 2006).

The assessment of the multiphasic systems is usually based on quantifying flow rates, fluid velocity, temperature, and dispersed phase concentration (SNOEK, 1990). Nowadays, several methods are available for that, including: imaging and computer vision-based systems; use of ultrasonic, capacitive, and electronic sensors; and spectroscopy analyses (SNOEK, 1990; WU; GU, 2011; YAN et al., 2018; ZHU; FANG, 2013).

Limitations remain in terms of processing time, portability, robustness, and implementation costs of such methods, though (WU; GU, 2011; ZHU; FANG, 2013). In this context, optical fiber sensors emerge as suitable alternatives due to their intrinsic advantages, like compact size, high sensitivity, and immunity to electromagnetic interference. Besides, silica fibers are inert to several chemical and biological agents (LEE, 2003; WANG; WOLFBEIS, 2020).

For the particular case of biphasic media, different setups of optical fiber sensors were described, like reflection-type sensors for estimative of velocity and geometry of dispersed slugs. They were based on the reflected light intensity, using either standard or specialty fibers. Despite their simplicity, these devices showed limited sensitivity to refractive index changes and were vulnerable to bending due to flowing fluid tangential and inertial forces (LIM et al., 2008; VEJRAŽKA et al., 2010). In other studies, velocity and concentration of droplets interacting with the evanescent field were monitored by microfibers. The fibers were positioned transversely to the flow direction, and the detection was based on a complex interrogation setup (HSIEH et al., 2016). Photonic crystal fibers were also explored by trapping volumes of liquids and sensing their characteristics as the droplets flowed through air holes. However, it was difficult to clean clogged fibers in this case (EUSER et al., 2009; NIELSEN et al., 2005).

Another interesting approach used for the detection of biphasic systems was the use of a grid comprised of multiple fiber Bragg gratings (FBGs) to track the passage of dispersed volumes. This strategy is based on mechanical stimulation, but it does not provide chemical characterization (ZAMARRENO et al., 2015). This limitation can be overcome for the particular case of detection of surrounding droplets by using exposed FBGs (DAVID; DJILALI; WILD, 2012); or long-period gratings (LPGs) (CHIN et al., 2008), but such strategies require additional fiber processing and only periodic flows can be analyzed.

A feasible alternative to FBG and LPG sensors is the application of tilted fiber Bragg gratings (TFBGs), which exhibits high sensitivity to external RI changes and intrinsic temperature compensation capability (ALBERT; SHAO; CAUCHETEUR, 2013; GUO et al., 2016). As a matter of fact, the monitoring of biphasic systems with TFBGs was successful in detecting surface tension (LIU et al., 2018); and flow rates and directions (SHEN et al., 2018, 2020), but the sensors relied on the use of metallic coatings and spectral analysis. So, despite the fact that current fiber interrogation hardware is usually capable of providing fast wavelength scanning and peak/dip detection, these devices present relatively high-costs and complexity.

As a solution to such difficulties, this study developed a TFBG-based biphasic flow sensor with single-wavelength detection (ARISTILDE et al., 2018). A millifluidic device was used here to produce controlled droplets that stimulate the TFBG, allowing the assessment of the flow characteristics from the output light intensity signals.

The advantage of this device when compared to other approaches is that it employs a simplified interrogation system based on a single photodetector. Then, the response time only depends on the sampling rate of the data acquisition hardware. The sensor was validated for water, oil, and air slugs, providing reliable results with a straightforward, easy-to-implement setup.

3.2.2. Droplets formation on biphasic milli- and microfluidic devices

Some milli- and microfluidic devices are designed for promoting the controlled formation of drops. For that, they independently drive a dispersed phase and an immiscible carrier fluid through different channels, providing their encounter in a junction (BAROUD; GALLAIRE; DANGLA, 2010).

The most important physical parameters that determine the formation of the droplets are: the geometry of the junction; the flow rates of the components; the intrinsic properties of the components (specially their viscosities and surface tensions); and the ratio q between the components, where $q = Q_D/Q_C$. Here, Q_D and Q_C represent the flow rates of the dispersed and the continuous phases, respectively (BAROUD; GALLAIRE; DANGLA, 2010).

The sizes of the formed droplets, in their turn, are dependent on the force resultant from the competition between: the pressure related to the flow movement (flow inertial forces); and the viscous shear stresses and capillary pressure. Importantly, the capillary pressure represents the resistance of the channel to deformation (BAROUD; GALLAIRE; DANGLA, 2010).

Several authors reported the application of T-junctions as reliable alternatives for the drop formation, but with the disadvantage of a complex flow dynamics (BAROUD; GALLAIRE; DANGLA, 2010). These junctions were used for forming water droplets from the flow of two-phases (water dispersed in different oils) through orthogonal and coplanar channels (THORSEN et al., 2001). Then, considering the easier fabrication and flow control, as well as the fact that water-oil systems would be tested here, the T-junctions were selected for this study.

After being formed in the junctions, the drops are transported as bubbly flows if their diameters are smaller than the channel size. In this situation, drops flow with the external velocity of the carrier (continuous phase) and follow its streamlines. Alternatively, they may

be transported as slug flows, occupying most of the cross section of the channel. In this last case, the flow is affected by capillary effects and by the deformability of the interface between the phases (BAROUD; GALLAIRE; DANGLA, 2010).

It is simpler to monitor the slug flow due to the higher contrast between phases' physical properties and to the increase on the interrogation area. Therefore, the ratio q must be optimized for guaranteeing the slug flow and, consequently, that every droplet is properly detected by the sensor. If q is very low, very small bubbles that are not capable of stimulating the TFBG sensor are formed. On the other hand, the use of critically high values of q could result on the dripping and jetting of the fluids, a situation in which no droplets could be distinguished (ANNA, 2016; BAROUD; GALLAIRE; DANGLA, 2010).

3.2.3. TFBG detection principles

The standard fiber Bragg grating is fabricated by exposing a short section of a singlemode optical fiber to an intense ultraviolet radiation. A fiber core with periodically varying refractive index (essentially, a pattern of interference fringes) is thus obtained. When a broadband light is launched through the fiber, the FBG allows the coupling between the forward-propagating and the backward-propagating core modes, creating a reflection response. The constructive interference of the reflected light waves occurs for a specific wavelength λ_B (Bragg wavelength). It is given by Equation (7), where n_{co} is the effective RI of the core's fundamental mode and Λ is the grating period (LEE; JEONG, 2002; ZHANG; ZHANG; BENNION, 2002).

$$\lambda_B = (2n_{co})\Lambda(7)$$

The phenomenon observed for the tilted fiber Bragg grating is slightly different, though: the index modulation of the core forms planes (the interference fringes) that are tilted by an angle θ in relation to the normal plane of the fiber (plane perpendicular to the cross section and containing the fiber's axis). These tilted fringes couple the core mode to several cladding modes, which are, in turn, sensitive to the external medium's RI (ALBERT; SHAO; CAUCHETEUR, 2013; ARISTILDE; CORDEIRO; OSÓRIO, 2019; SHEN et al., 2018).

A medium with low refractive index allows all cladding modes to be guided, and each of them appears as an individual valley on the fiber's transmission spectrum. However, if the fiber is submitted to a higher RI, the cladding modes with lower RIs will leak away, with consequent decrease of the signal amplitude. In this case, the cladding modes with higher refractive indices are still guided, but shift to higher wavelengths (ALBERT; SHAO; CAUCHETEUR, 2013; ARISTILDE; CORDEIRO; OSÓRIO, 2019; SHEN et al., 2018).

In summary, tilted fiber Bragg gratings are comprised of periodic RI changes along the core length wherein the diffraction template is slanted with respect to the fiber axis. The TFBG enhances the coupling between core-propagating modes and a set of cladding high-order modes, creating resonances in the transmission spectrum toward shorter wavelengths. Since the evanescent field of cladding modes interacts with the external medium, resonance dips are red-shifted as the surrounding RI (index n) approaches the cladding effective index. It makes the

TFBG sensors suitable for chemical measurements (ALBERT; SHAO; CAUCHETEUR, 2013; GUO et al., 2016).

Equation (8) provides the phase-matching condition for the TFBG. In this equation, the matching condition is given by the resonance wavelength λ_i of the *i*th-cladding mode; Λ is the grating period; θ is the tilt angle; and n_{co} and n^i_{cl} are the effective refractive indices of the fiber core and of the *i*th-cladding mode, respectively (ALBERT; SHAO; CAUCHETEUR, 2013).

$$\lambda_i = \left(n_{co} + n^i{}_{cl}\right) \frac{\Lambda}{\cos\theta} \tag{8}$$

When a TFBG is subjected to a longitudinal two-phase flow formed by: a phase with RI n_D (dispersed phase); and a (continuous) phase with index n_C , the index of the surroundings of the fiber varies with time, as the dispersed phase passes along the grating. Since typical methods assess the output spectrum for quantifying shifts in the resonance wavelengths (GUO et al., 2016), velocity measurements in flowing droplets are restricted by the scanning frequency of the optical spectrum analyzer (OSA) or by the interrogation hardware.



Figure 48. Variation of surrounding refractive index as a function of time: the output spectra of TFBG shifts with the dispersed phase transport, allowing the evaluation of flow speed and substances estimative. (A)-(D): flow of colored-water droplets (lower RI, in gray) in oil (higher RI, in yellow) in different time instants (t₁ to t₄). The TFBG is represented by the tilted lines on the fiber core: when the grating is in contact with the gray droplets, a higher signal intensity is detected, and a profile like (E) is obtained.

So, an alternative is to select a fixed transmission wavelength λ , making the TFBG works as a tunable notch filter. In this case, variations on the output light intensity I(t) arising

from modifications of the instant refractive index n(t) of the medium in contact with the grating can be measured in real-time with a photodetector connected to an oscilloscope or with a data acquisition card. Consequently, for a grating with length L_G, the average flow speed V can be evaluated from the temporal features of I(t), and each phase can be identified from its RI value (KRAUS et al., 2004). This is represented in Fig. 48: assuming I(t) has an average time period given by T, the flow velocity V can be estimated as the relation $V = L_G/T$.

3.2.4. Sensor design and measurement setup

The general measurement setup is represented in Figure 49. Basically, a light source in one extremity of the setup is responsible for exciting a single-mode optical fiber, whereas a detector positioned at the opposite extremity measures the output light filtered by the TFBG.

A section of the optical fiber is inserted into a transparent T-junction millifluidic device, so the waveguide is placed in a direction parallel to the flow movement. Two input flows are generated and controlled by syringe pumps. One of them transports the continuous phase (sunflower oil in food grade; or air), and the other transports the dispersed phase (colored water; or air). Then, a controlled biphasic flow profile (e.g., water droplets in oil) is formed in the interior of the device after the T-junction. Furthermore, a transverse static camera performs optical tracking measurements for comparative and validation analyses of the obtained results.

The TFBG was fabricated by phase-mask technique, by exposing a hydrogen-loaded fiber to UV light (Quantel Q-Smart 450 laser, 266 nm). It resulted on the following Equation (8) parameters: $\Lambda = 535.6$ nm; $L_G = 4$ mm; and $\theta = 6^{\circ}$ (ARISTILDE; CORDEIRO; OSÓRIO, 2019). The fabrication of the millifluidic device, on the other hand, was performed with stereolithography with a 3D-printer (Formlabs, Somerville, MA, USA) and transparent photopolymer (Clear resin). This manufactured device showed channel length and cross-section area of 30 mm and 1 mm², respectively (Fig. 50 shows the project used for the 3D-printing). Lastly, the optical fiber was stretched and centered inside the channel before the device's lateral accesses get sealed with a photocurable resin.

In order to determine the best wavelength for stimulating the sensor, the system's response to the surrounding refractive index was firstly characterized outside of the millifluidic device. For that, a TFBG was immersed in water; in oil; and in several glycerin aqueous solutions obtained by progressively adding different masses of glycerin to deionized water. Each tested medium had its refractive index evaluated with a MISCO PA 202 Refractometer (Palm Abbe) with a 589 nm high precision LED (resolution of 10^{-4} nm) at ~25 °C and room atmosphere. The solutions showed indices *n* in the range $1.33 \le n \le 1.47$, where n = 1.33 was the RI assessed for the water; n = 1.47 was the index obtained for the sunflower oil; and n = 1.00 was the index for the air (refractometer with no sample positioned on its crystal).

For each tested solution, the waveguide was excited with a superluminescent diode source and the transmitted light spectrum was measured with an optical spectrum analyzer (OSA). Based on the output transmission range (Fig. 51), it is possible to choose a particular λ value for the implementation of the single-wavelength interrogation scheme.

When analyzing Fig. 51a, it is possible to notice that the intensities of the dips on the light transmission spectra decrease as the refractive index of the tested solution increases. On the other hand, for a given spectrum, the intensities of the dips vary with the excitation wavelength.



Figure 49. Optical fiber sensor: water-in-oil biphasic flow passes through the millifluidic device and changes the refractive index surrounding the TFBG, resulting in different intensities detected by the oscilloscope.



Figure 50. Sketch and blueprint of the 3D-printed device (quotes in millimeters). The full device presents horizontal length of 30 mm. Its upper face is plane-polished with isopropyl alcohol for 15 min for allowing the visual observation of the droplets.

The conclusion, then, is that the highest sensitivity of the sensor (the situation where the assessment of different RIs results in the maximum possible differences of signal intensities) is obtained when selecting the wavelength where the dips show the highest intensities for a same refractive index. Naturally, the maximum difference allowed for the system is observed when comparing a dip collected for RI = 1.33 (most intense dip) with the one obtained for RI = 1.47 (no visible dip), as shown in Fig. 51a.

Fig. 51b shows the spectra on a narrower wavelength range, the region where the most intense peaks are observed for each RI. This window was used for selecting the wavelength λ = 1531.36 nm for the operation of the laser. Fig. 52, in turns, was obtained by plotting the individual values of the transmission losses (values collected on Fig. 51b for λ = 1531.36 nm) against the correspondent RIs of the tested solutions. A linear correlation was obtained from this plot: transmission (dB) = -18.4*n* + 24.6. The derivative of this correlation gives the TFBG sensitivity: -18.4 dB/RIU, where RIU stands for refractive index unit.



Figure 51. TFBG sensor responses to the surrounding refractive index *n*: (A) transmission spectra; (B) resonance dips around 1531.5 nm. The vertical line indicates $\lambda = 1531.36$ nm, whereas the legend indicates *n* values. Transmission data were normalized for the sake of visualization.



Figure 52. Transmission as a function of n (solid line is a linear curve fitting that excludes outliers). Transmission data were normalized for the sake of visualization.

After the wavelength selection, the fiber sensor can be applied to the assessment of biphasic flows using a tunable laser source set in 1531.36 nm and a photodetector connected to an oscilloscope (Fig. 49). The syringe pumps connected to the millifluidic device were empirically adjusted to establish a periodical slug flow. For that, the effect of ratio q on the droplets lengths must be analyzed, as discussed (BAROUD; GALLAIRE; DANGLA, 2010).

The ratio q ranged from 0.10 to 1.00 for the analysis of the droplets' lengths (Fig. 53). The pumping was performed with a computer-controlled step motor which pushes syringe plungers with rates from 2 to 30 μ m/s, corresponding to velocities ranging from 0.16 to 2.45 mm/s in the entrance of the channels. Results of droplets lengths' L for different q ratios are summarized in Table 3. For improving the visualization, the water slugs were marked using small volumes of dye, since prior measurements indicated that deviations in the sample refractive index caused by the dye were negligible.

Ratios superior to the range shown in Fig. 53 and Table 3 were ignored. As q grows, the distance between successive droplets reduces, making it more difficult to distinguish between successive drops both by the signal analysis and by visual observation. It was observed that ratios q > 1.00 were critically high, so the dripping and jetting of the fluids prevented the distinguish of droplets (ANNA, 2016; BAROUD; GALLAIRE; DANGLA, 2010).



Figure 53. Evaluation of water-in-oil droplets' lengths L for different flow ratios q.

q	L (mm)
0.10	1.00
0.20	2.37
0.30	2.41
0.40	2.77
0.50	3.03
0.60	3.36
0.70	3.36
1.00	3.36

 Table 3. Droplets lengths' L verified for each q ratio.

For the ratios shown in Figure 53, the length L rises with q and reaches a maximum value when q = 0.60 (ratio correspondent to the velocities of 0.49 and 0.82 mm/s for the water and for the oil, respectively). For this q ratio, the drops are completely in the slug regime and the maximum L is adequate for the TFBG detection. Also, as q grows from 0.60 to 1.00, a reduction of the distances between successive droplets is observed, making the detection more difficult as discussed. So, the ratio q = 0.60 was selected for performing the experiments where the sensing of different multiphasic systems (oil-in-water and oil-in-air systems) are compared.

When using the full setup shown on Fig. 49, the intensity signals collected by the photodetector are acquired by an oscilloscope at 100 Hz sampling rate and are processed in a computer for evaluating the flow characteristics. In this study, all experiments were conducted at room temperature and the collected data were validated by comparison with the concomitant optical tracking measurements. The fiber and the millifluidic device were carefully cleaned between measurements with isopropyl alcohol to avoid contamination of samples.

3.2.5. Multiphase flow assessment

In addition to Fig. 53 and Table 3, Fig. 54 compares the effect of different q ratios (q = 0.6 and q = 0.5) on the optical signals ($\lambda = 1531.36$ nm) collected for water-in-oil flows (i.e., flows of water dispersed in oil). The light intensity I(t) fluctuates over time and achieves maximum values when a water slug passes by the grating. The RI of water (n_D = 1.33) increases the transmission signal, in contrast to the obtained for the sunflower oil (n_C = 1.47).

The reduction of $q = Q_D/Q_C$ corresponds to the increase of the relative importance of the continuous phase flow rate (and of its velocity, as the channels have constant diameter) over the dispersed phase flow rate. Once the drops are dragged by the continuous phase, the reduction of q implies on an increase of the frequency of the periodical signal I(t) resultant from the passage of the water droplets on the TFBG. When the carrier flows faster, more droplets are transported, so a higher number of signal peaks are observed during a given time interval.

For the temporal analysis of Fig. 54, it is useful to recall that the TFBG length is given by $L_G = 4$ mm. Each peak width on Figs. 54a-b corresponds to the time interval Δt between the instant when a drop start stimulating the TFBG (instant when it reaches the beginning of the grating) and the time when it stops stimulating the sensing region (instant when it completely left the grating). As shown on Figure 55, the physical distance (total length) corresponding to the width of each detected peak is then the interval needed for one drop to go through the distance ($L_G + L$), the sum of the TFBG length with the leaving droplet length. Now, the actual droplet velocity can be directly calculated from the collected signals as $V = (L_G + L)/(\Delta t)$.

Also, a simpler procedure can be performed if resolved peaks with a single maximum point (such as the ones in Fig. 54) are present; and if one droplet reaches the TFBG just as the previous one leaves the sensing region. The maxima correspond to the instants of highest stimulation of the TFBG, when the drops are perfectly centered on the sensing region. So, the time T between successive maxima is the period of the flow; and the travelled distance is simply the length of the sensing area itself (one drop leaves the center before the next droplet reaches this same point). The velocity, then, can be calculated as $V = L_G/T$.



Figure 54. Measurement of water-in-oil flows: normalized intensity for (a) q = 0.6; and (b) q = 0.5. Peaks and dips indicate the passage of water and oil slugs, respectively, along the TFBG. Flow profiles for (c) q = 0.6; and (d) q = 0.5. Water slugs are colored with black dye for facilitating their observation.

For q = 0.6 (Fig. 54a), thus, the signal period T = 7.16 s resulted in the droplet velocity V = 0.56 mm/s. The ratio q = 0.5 (Fig. 54b), in turn, resulted in T = 5.64 s and V = 0.71 mm/s.

These values corroborate with the optical tracking measurements, in which V = 0.55 mm/s and 0.68 mm/s were obtained for q = 0.6 and 0.5, respectively. The comparison between the optical fiber and the visual analysis resulted, therefore, in a maximum relative error of 4.4%.

Fig. 54 shows that the transitions in I(t) are not abrupt (even though the substances are immiscible and with discrepant refractive indices). That is because the resonance dip shifts depend on the relative proportion of water and oil surrounding the grating for a given time, as

shown by the model depicted in Fig. 49. On the other hand, the signal intensity profile is expected to change depending on the flow velocity and on the detector sampling rate.



Figure 55. Out-of-scale representation of a droplet reaching and completely leaving the TFBG sensing region from the optical fiber. The time comprised between the beginning and end of each sensing peak (peak width) is the interval needed for one droplet to go through the distance $L_G + L$. This distance should be used when there is no clear (resolved) signal maximum.

The replacement of the syringe containing water by an air-filled syringe (keeping q = 0.60) can be used to create a flow of air droplets in oil. The results collected when assessing this situation are shown in Figure 56a. In this case, deviations in the output intensities are more subtle in amplitude than the observed for the water-in-oil system. That is because the RIs of the dispersed (air) and continuous (oil) phases produce an almost coincident transmission level at 1531.36 nm. The difference observed in Fig. 51b for the transmissions in air and transmissions in oil is of only ~0.25 dB, making the sensor less sensitive to the passage of the air drops.



Figure 56. Normalized intensity signals for (a) air-in-oil (dips indicate the passage of air slugs along the TFBG); and (b) water-in-air flows (peaks represent transport of water slugs). All results were collected for the ratio q = 0.60.

Indeed, one could obtain a higher sensitivity for air droplets by changing the reference wavelength: as noticed on Fig. 51b, the selection of the wavelength $\lambda = 1531.5$ nm would result in a difference between the transmissions for n = 1.00 and n = 1.47 of approximately 4.4 dB.

Nevertheless, the TBFG is capable of distinguishing both phases: a period T = 11.83 s is obtained from the signals, resulting in an average flow velocity V = 0.34 mm/s. The peaks observed during phases transitions are due to the non-monotonic characteristic of the sensor calibration curve for $n \le 1.33$; and due to small air bubbles formed during the droplet transport (BAROUD; GALLAIRE; DANGLA, 2010).

A similar analysis can be performed for the water-in-air system. This system is obtained through the substitution of the oil syringe by an air-filled syringe while keeping q = 0.60 (Fig. 56b). As for the water-in-oil droplets, the water slugs (dispersed phase) in air (continuous phase) are detected as intensity peaks. It is due to the distinct transmission levels observed in Fig. 51b, even though the RI of air extrapolates the calibration curve shown in Fig. 52.

For the data in Fig. 56b, the average period and velocity obtained were T = 17.96 s and 0.22 mm/s, respectively. Despite the I(t) signals in Fig. 51b indicating that the continuous phase may be confused with oil due to the similar intensity values, it must be stressed that the sensor could be calibrated for other RI ranges by simply adjusting the interrogation wavelength λ .

Therefore, it is possible to track the temporal evolution of liquid or gas/vapor slugs flowing through a continuous phase by using the TFBG and a single-wavelength detection scheme. The response time for the sensor depends only on the sampling frequency of the data acquisition hardware.

Although a tunable laser source was employed for the sake of convenience, a simpler approach would consist in using a single-mode longitudinal distributed feedback laser diode for exciting the fiber at a specific wavelength. In this case, a resonance dip could be adjusted by tailoring the TFBG tilt angle to match the laser emission. It would allow the interrogation system to be realized with low-cost, ordinary telecom components.

The evaluation of flow velocity is also similar to the well-established optical tracking methods, but the proposed system does not require transparent tubes or colored fluids and is simpler to compute than image processing approaches (ZHU; FANG, 2013).

The fiber sensor is also capable of identifying each flowing phase based on their refractive index values. Cleaning the fiber may be necessary in case of measuring substances like oil, though. That is because it is important to eliminate films that may be formed in the cladding surface. The presence of such films could lead to systematic changes in n_{cl}^i .

Furthermore, it is worth noticing that the sensor response is affected by the environmental temperature, since the tested fluids and the fiber material present characteristic thermo-optic coefficients (their RIs are dependent on the temperature). Therefore, changes in n_{co} and n_{cl}^{i} would shift the resonance wavelengths and affect the output intensity range.

Nevertheless, thermal fluctuations in this single-TFBG sensor could be compensated by monitoring the Bragg reflection peak λ_B of the core mode. That is because λ_B is insensitive to the surrounding RI, in contrast to the cladding modes resonances (GUO et al., 2016).

Therefore, one may implement a dual-wavelength scheme to simultaneously assess λ and λ_B . It would correct the calibration curve in real-time, so no extra reference fibers would be needed.

3.2.6. Conclusions from this study

This study resulted in the design and fabrication of a TFBG-based optical fiber sensor for measuring the flow velocity in biphasic flows. The sensor successfully assessed samples comprised of water, oil, and air transported through a millifluidic device.

By using a single-wavelength interrogation scheme, it is possible to assess the velocity of the dispersed phase in real-time, yielding maximum relative error of 4.4% in comparison to a concomitant optical tracking measurement. So, the response time is limited by the frequency of the data acquisition hardware. Moreover, the refractive indices from both phases can be estimated from the transmission intensity values using the calibration curve (Fig. 52). Finally, the sensor characteristics (including its sensitivity to a particular RI) are adjustable by properly setting a reference wavelength.

Despite the promising results, further investigation should be conducted regarding nonperiodic and other flow regimes which may produce complex intensity patterns. In such cases, time frequency analysis and machine learning algorithms are techniques that can be used to retrieve the flow characteristics. Besides, tracing systems formed by more than two phases is theoretically viable by employing additional wavelengths and detectors. There would be an increase in the system's complexity, but it would still be simpler than the application of spectral scanning methods.

3.2.7. Contributions and acknowledgements

- Financial support from São Paulo Research Foundation (FAPESP) under grant 2019/22554-4.
- Financial support to other contributors of this work: FAPESP grants 2017/25666-2, 2018/10409-7; Coordenação de Aperfeiçoamento de Pessoal de Nivel Superior–Brazil (CAPES), finance code 001; National Council for Scientific and Technological Development (CNPq), finance code 001.
- Gildo S. Rodrigues and Prof. Cristiano M. B. Cordeiro from the Laboratory of Specialty Fibers and Photonic Materials, "Gleb Wataghin" Institute of Physics, University of Campinas, SP, Brazil (IFGW/UNICAMP) for the 3D-printing of the devices.
- Stenio Aristilde and Prof. Cristiano M. B. Cordeiro from the Laboratory of Specialty Fibers and Photonic Materials, "Gleb Wataghin" Institute of Physics, University of Campinas, SP, Brazil (IFGW/UNICAMP) for the TFBGs fabrication and operation.
- Dr. Thiago D. Cabral and Prof. Cristiano M. B. Cordeiro from the Laboratory of Specialty Fibers and Photonic Materials, "Gleb Wataghin" Institute of Physics, University of Campinas, SP, Brazil (IFGW/UNICAMP) for the physics theory, contextualization and interpretation support, and characterization equipment (RI, OSA, tunable laser, photodetector and oscilloscope).
- Cristiano M. B. Cordeiro from the Laboratory of Specialty Fibers and Photonic Materials, "Gleb Wataghin" Institute of Physics, University of Campinas, SP, Brazil (IFGW/UNICAMP); and Prof. Fabiano Fruett from the School of Electrical and Computer Engineering, University of Campinas, SP, Brazil (FEEC/UNICAMP) for the support on both the development of the sensing setup and methodology and on the project idealization.

3.3. Portable smartphone-based optical fiber sensor for fermentation monitoring

The development of a portable smartphone-based optical fiber sensing platform for the online assessment of fed-batch fermentation systems is presented here as published in the openaccess journal Engineering Proceedings from MDPI (SOARES et al., 2020b).

In this setup specifically designed for field monitoring and on-site fast fabrication, a smartphone is equipped with a 3D-printed case that couples optical fibers to its camera and its LED, guaranteeing the correct positioning of the fibers and light isolation. A Java application is then responsible for collecting images from the camera and analyzing their pixel intensities. Finally, the obtained intensities are correlated to the broth refraction index, which is a function of the sucrose concentration (the ethanol formation is too low to significantly disturb the RI).

3.3.1. Introduction

Contemporary industry is in a period of great expansion. The so-called "*Industry 4.0*" applies novel mathematical and computer-based methods for the optimization and monitoring of systems, with social, economic, and environmental repercussions on many human activities (PAN et al., 2015). This new period relies on the development of new sensor technologies capable of collecting, distributing, and delivering information by themselves.

In chemical and biochemical industries, the increase on the data availability and on the portability of the monitoring devices has potential for enhancing safety; productivity; energy-use efficiency; environmental sustainability; product quality; and general process performance (REIS; KENETT, 2018). However, the analysis and evaluation of many chemical and biochemical agents (from pesticides to pharmacological drugs) is still based on high-performance liquid chromatography (HPLC); gas chromatography (GC); combined techniques like GC coupled to mass spectrometry (GC-MS); and enzyme-linked immunosorbent assay (ELISA). Such methods are sensitive, reliable, and precise, but demand expensive and bulky instrumentation; highly trained technicians; and procedures with long times of analysis. The use of compact and real-time sensors, on the other hand, allows the monitoring, control, and screening of the best process conditions (JU; KANDIMALLA, 2008; REIS; KENETT, 2018; SOARES et al., 2019e).

Optical fiber sensors, in particular, are very attractive for chemical assessment. They present biocompatibility; immunity to electromagnetic interference; and the fibers demonstrate chemical and thermal stability (LI et al., 2018c); as well as reduced manufacturing costs, making the devices suitable for mass-fabrication (GONG et al., 2017; SOARES et al., 2019e).

In this work, then, a smartphone-based optical fiber sensor was designed for the monitoring of fed-batch fermentation systems. The fed-batch mode was chosen for the study because most of the alcoholic fermentation industries in Brazil operate with this methodology (CARLOS; OLITTA; NITSCHE, 2011). The results were validated through comparison with a handheld refractometer and with the Monod mathematical model.

It is worth mentioning that this platform is essentially different from other chemical and biochemical smartphone-based analytical tools already reported. Most of the previous works are based on electrochemical setups where the USB port of the phone is explored for the evaluation of the current in an external circuit (GUO, 2016; HASENFRATZ et al., 2012).

The optical monitoring smartphone systems, in turn, are generally of high costs and complexity, and their interrogation is usually based on colorimetric analysis of the images captured by the camera (DUTTA; SARMA; NATH, 2015). For instance: a smartphone was coupled to a commercial enzymatic chromogenic-kit for detecting coliforms and bacteria in water (KUMAR GUNDA et al., 2014); and a colorimetric sensor was projected to analyze fluorescent emissions from perfectly positioned spheroids of cells, but these spheroids had to be genetically modified for emitting visible light (MICHELINI et al., 2019).

3.3.2. Fermentation process modelling and monitoring

The monitoring and control of a fermentation process is focused on the maintenance of the adequate conditions for the microorganisms, being based on the evaluation of the cells' concentration X. Many of the traditional measurements (e.g., cell counting with Neubauer chamber; dry mass evaluation; and the surface plating method to estimate the number of viable cells) rely on manual time-consuming procedures (SOARES et al., 2019e).

Therefore, in most of the practical and industrial cases, the assessment and control of the bioprocesses depend on the quantification of a specific property from the medium, which may be either physical (e.g., variation of the medium's refractive index, viscosity, or electrical conductivity); or biochemical (concentration of: proteins, carbohydrates, DNA, or RNA, for example) (BAILEY; OLLIS, 1986; DORAN, 2013; SOARES et al., 2019e).

These quantified properties are posteriorly correlated to the concentration of cells by an appropriate model derived from the general fermentation reaction, Equation (9). In this equation, a microorganism (concentration X) consumes a substrate (concentration S) to produce both a product (concentration P) and an increase in the cellular concentration ΔX that represents the cellular reproduction (it is an autocatalytic process). The substrate is the "reactant" of cellular reactions: a common choice is to use sucrose as S. For yeast fermentation, in particular, the product is usually ethanol (BAILEY; OLLIS, 1986; DORAN, 2013; SOARES et al., 2019e).

$$X + S \to P + (X + \Delta X) (9)$$

The cellular growth mathematical models are based on the definition of the specific cell growth rate μ , given by: $\mu = (1/X)(dX/dt)$. One of the most applied models is the Monod equation, given by: $\mu = \mu_m S/(K_M + S)$, where μ_m is the maximum specific growth rate and K_M is the Monod constant (SOARES et al., 2019e).

The estimative of rates of product formation and substrate uptake can be performed with two supporting definitions, which are: the specific rate of product formation: $q_p = Y_{P/X}\mu + m_p$, where m_p is the product formation rate not associated to the cellular growth, and $Y_{P/X}$ is the theoretical yield of product formation per cell reproduction (i.e., $\Delta P/\Delta X$, where ΔX is the increase of cell biomass); and the specific rate of substrate consumption: $\mu_s = (1/Y_{X/S})\mu + m_s$, where m_s is the substrate consumption rate associated to the metabolic activities, and $Y_{X/S}$ is the theoretical yield of cell reproduction per substrate uptake (SOARES et al., 2018a, 2019e).

On fed-batch operation mode, the reaction is started with initial concentrations: X_0 , P_0 and S_0 (P_0 is usually zero) and an initial volume of fermentation broth V_0 . A constant feed flow

F supplies the reactor with an aqueous solution of fresh substrate (feed solution concentration $= S_F$). The expressions that correlate the instant volume of fermentation broth *V* and the instant concentrations *X*, *P* and *S* with the time *t* from the beginning of the process are given by Equations (10)–(13) (SOARES et al., 2018a). If *F* = 0, the equations are still applicable and represent the fermentation batch mode. That is because these equations are derived directly from the mass balance of the biochemical process (BAILEY; OLLIS, 1986; DORAN, 2013; SOARES et al., 2018a, 2019e).

$$\frac{dV}{dt} = F \Rightarrow V = V_0 + Ft (10)$$
$$\frac{dX}{dt} = \mu X - \frac{F}{V} X (11)$$
$$\frac{dP}{dt} = q_p X - \frac{F}{V} P (12)$$
$$\frac{dS}{dt} = -\mu_s X + \frac{F}{V} (S_F - S) (13)$$

In this work, *Saccharomyces cerevisiae* ATCC 7754 cells were cultivated in yeastpeptone-dextrose (YPD) medium (composed of yeast extract, peptone and dextrose with concentrations in proportions of 1:2:2) and pH of 6.5 ± 0.2 . These conditions are adequate for yeast growth and provide all the necessary macro- and micronutrients (SOARES et al., 2019e).

The cells were inoculated into a bioreactor with a total volume of 2 L. The operational parameters were based on the conditions previously applied to a total volume of 10 L (SOARES et al., 2018a). They were obtained by simply keeping a constant proportion in relation to the previous conditions (i.e., reduction factors of 2 L/10 L = 1/5 were applied to each parameter).

Then, sucrose dissolved in deionized (DI) water ($S_F = 30.0 \text{ g} \cdot \text{L}^{-1}$, a condition of excess of substrate that prevents the growth inhibition associated to the lack of *S*) was fed with a flow rate of $6.67 \times 10^{-2} \text{ L.h}^{-1}$ using a peristaltic pump (MPS 380, Marte Científica, São Paulo, SP, Brazil). The reactor initial conditions were $V_0 = 0.1 \text{ L}$, $X_0 = 1.5 \text{ g} \cdot \text{L}^{-1}$, $S_0 = 10.0 \text{ g} \cdot \text{L}^{-1}$, and P_0 = 0. The temperature was kept constant at 33 °C during all the fermentation, once this is the condition that maximizes the *S. cerevisiae* fermentation yield (SOARES et al., 2019e).

The reactor design was chosen for obtaining a high ratio of surface area per liquid column height. Its surface was kept free to the atmospheric air and under magnetic stirring, guaranteeing the saturation of the liquid medium with air. In aerobic conditions, the cell reproduction is favored over the ethanol production (ethanol is mostly formed in anaerobioses). Therefore, such conditions prevent the variation of the refractive index due to the sucrose uptake by cells to be confused with the RI variation that could be caused by a large ethanol formation (BAILEY; OLLIS, 1986; DORAN, 2013; SOARES et al., 2019e).

Equations (10)–(13) were numerically solved (Euler method; step 0.1 h; all differential equations simultaneously integrated) with the μ_m and K_M values previously obtained when this same strain of microorganism cultivated in YPD was inoculated into a perfusion fermentor that operated under sucrose flow at 33 °C: $\mu_m = 0.49$ h⁻¹ and $K_M = 4.1$ g·L⁻¹ (SOARES et al., 2019e). The other adjustable parameters from these equations were defined as the ones obtained

in a previous work where a different strain of *S. cerevisiae* was cultivated in a complex medium similar to YPD for being used in fed-batch fermentation under 33 °C: $Y_{P/X} = 2.660 \text{ g.g}^{-1}$, $Y_{X/S} = 0.2880 \text{ g.g}^{-1}$, $m_p = 0.010 \text{ h}^{-1}$, and $m_s = 0.290 \text{ h}^{-1}$ (SOARES et al., 2018a).

3.3.3. Smartphone optical fiber sensor design and fabrication

The optical fiber sensor used in this work is based on the modulation of the power reflectance caused by differences in the refractive index of the liquid medium. These differences are originated from the consumption of sucrose by the cells (SOARES et al., 2019e).

Light is emitted from a LED source (that may be either the smartphone camera's LED or an external source) through a multi-mode silica optical fiber (MMF), and the light is directed by a 2×1 coupler to the liquid medium. When light reaches the fiber-liquid interface, part of it is transmitted and part is reflected back, with power given by the Fresnel law, Equation (14). In this equation, I(t) and I_R are the reflected and the reference light intensities, respectively; c is a coupling coefficient that accounts for power losses; and n_c and n_s are the refractive indices of the fiber core and of the sample, respectively (SALEH; TEICH, 1991; SOARES et al., 2019e).

$$I(t) = cI_R \left(\frac{n_c - n_s}{n_c + n_s}\right)^2$$
(14)

So, I(t) signals are modulated by the medium's refractive index n_s . The reflected light is finally redirected by the coupler to the smartphone's camera; and a developed application acquires and processes the data. The correct positioning of the optical fibers in relation to the phone's camera and the isolation from the environmental light are crucial for a reliable reading.

Thus, a smartphone case was developed with dimensions for fitting a Samsung Galaxy 9 Plus smartphone (76 mm \times 83 mm \times 14 mm, hardware setup: Snapdragon 845 2.8 GHz, 6 GB RAM, 12 MP resolution camera). The case contains ports for connecting optical fibers to the camera and to the LED, guaranteeing the correct fixed position of the fibers, as well as the adequate light isolation. It was manufactured using a 3D-printer Ultimaker 2+ Extended (Ultimaker BV, Utrecht, The Netherlands) using poly(ethyleneglycol) filament. The full setup for the operation and analysis of the fed-batch fermentation system is shown in Fig. 57a, whereas the 3D-printed case is presented in Figure 57b. A detailed blueprint of the case's project is provided as Appendix 1.

The application for processing the intensity signals was developed in the Android Studio Integrated Development Environment (IDE) and implemented in Java language. The operation is based on three steps: (i) setting of the image processing parameters in the main menu; (ii) acquisition of the fiber output light; and (iii) analysis of intensity on each video frame. The user-defined parameters that must be input in the main menu are the total duration of the measurement (in seconds); the interval between frames to be analyzed (in ms); and the dimensions (resolution) of the window where the user wants to effectively analyze the image (it determines the total number of pixels that will be evaluated). Fig. 58a shows a screenshot obtained from this menu.

The application presents two operation modes (screenshot in Fig. 58b): the first one evaluates the light intensity (pixels intensity) for a single image received from the camera. This

mode is used for calibration and fiber alignment. The second mode, in its turn, performs the effective acquisition of data by recording a video (in "mp4" file extension) which is further analyzed frame-by-frame.

Briefly, the software discretizes the frames from the recorded video and then reads the obtained figures. These images collected by the camera consist of dark backgrounds with an illuminated spot referent to the optical fiber termination.

The application calculates the average pixel luminous intensity I_m for each image on the region previously selected by the user in the main menu. For that, it evaluates Equation (15), where N is the total number of pixels present on the region of interest; and $I_w(x_i, y_i)$ is the intensity level for the pixel in the coordinate (x_i, y_i) . This intensity is given by the average calculated for each one of the three RGB channels in this (x_i, y_i) coordinate, Equation (16).

$$I_{m} = \frac{\sum_{i=1}^{N} I_{w}(x_{i}, y_{i})}{N}$$
(15)
$$I_{w}(x_{i}, y_{i}) = \left| \frac{I_{Red}(x_{i}, y_{i}) + I_{Green}(x_{i}, y_{i}) + I_{Blue}(x_{i}, y_{i})}{3} \right|$$
(16)



Figure 57. (A) Setup of the fed-batch fermentation reactor with the monitoring system; (B) 3D-printed smartphone case. MMF refers to the multi-mode silica optical fiber.



Figure 58. Screenshots representing the (A) main menu; and (B) video-recording mode for capturing the MMF light intensity signals with the application.

When evaluating Equations (15) and (16), the dark region should not be considered for the calculus, and the condition $|[0,0,0]| \le I_w(x_i, y_i) = |[R, G, B]| \le |[255,255,255]|$ must be observed. Here, [R,G,B] represents the color of a pixel in the coordinate (x_i, y_i) using the RGB-System: [0,0,0] is a black-colored pixel; [255,255,255] is a white-colored pixel; and $I_{Red}(x_i, y_i)$, $I_{Green}(x_i, y_i)$, and $I_{Blue}(x_i, y_i)$ are the intensities of the pixel in the coordinate (x_i, y_i) for the Red, Green, and Blue channels from the RGB system, respectively.

After evaluating the images, the application allows the user to export the processed light intensities as a text file. When monitoring a chemical or biochemical medium, the normalized data should be also compared to a calibration curve (previously obtained) for allowing the real-time assessment of the process.

3.3.4. Obtention of calibration curve and fed-batch fermentation monitoring

For obtaining a calibration curve for the analyzed fermentation system, solutions of sucrose in deionized water with concentrations ranging from 2.5 to $100 \text{ g} \cdot \text{L}^{-1}$ (the concentration range commonly applied to industrial and laboratory fermentation processes (SOARES et al., 2019e)) had their refractive indices evaluated with a MISCO PA 202 Refractometer (Palm Abbe, Cleveland, OH, U.S.A.). They were also tested with the fiber sensor for evaluating the sensor sensitivity regarding *S* (sucrose) and RI. The collected results are shown in Fig. 59a.

Finally, the fed-batch reaction was online assessed over 3.5 h with the smartphone and the results were compared with the refractometer's and with the model predictions (Equations (10)-(13)). The refractometer's results for the substrate instant concentrations were obtained by taking small samples of the fermentation broth for off-line analysis of RI. All experiments and microbial cultures were performed in accordance with the Bioethical Committee of the

University of Campinas and with the declaration to Brazilian's Genetic Heritage Database (Register number: AD886EA). The fermentation results are shown in Fig. 59b.

Figure 59a shows the correlation between RI and the sucrose concentrations ranging from 0 to 100 g·L⁻¹. A linear increase in the refractive index *n* with sucrose concentration was observed: $n = 1.3330 + (1.4432 \times 10^{-4})S$, where S is the sucrose concentration in g·L⁻¹, adjusted R² = 0.9971. Also, this figure shows the data collected for the average intensities I_m detected by the smartphone-based optical fiber sensor for the same solutions. From these, a linear correlation between I_m and S (decrease on the intensity with sucrose concentration) was retrieved: (normalized I_m) = 1.01016 – (9.08 × 10⁻³)S, adjusted R² = 0.9193.

Then, a correlation between normalized pixel average intensity and RI could be also obtained: (normalized I_m) = 85.8354 – (63.6342) n, adjusted R² = 0.9345 (correlation obtained for the range $1.3330 \le n \le 1.3475$). From this correlation, the sensitivity of the fiber sensor was calculated as the ratio of variation of the intensity with the refractive index, leading to a sensitivity of (-63.6342) RIU⁻¹ (refractive index units). Alternatively, the sensitivity could be obtained as the derivative from the correlation between intensity and concentration as (-9.08 × 10^{-3}) g⁻¹·L (SALEH; TEICH, 1991; SOARES et al., 2019e).

The signal-to-noise ratios (SNRs) were evaluated for each point retrieved by the fiber sensor as the relation I_m^2/σ^2 , where σ is the signal standard deviation (SALEH; TEICH, 1991). So, SNRs ranging from 2.25 × 10² to 2.4 × 10⁵ were obtained.

The fed-batch fermentation assessment is shown in Figure 59b, where the mathematical model predictions are represented by a solid black line. Results obtained by the smartphone sensor corroborate with the refractometer and with the theoretical model analyses.

The comparison between the model predictions and the results for each measurement strategy are summarized in Table 4. The refractometer showed deviations from Monod model (taken as the error) from 0.00 to 9.36% (3.15%, in average), whereas the smartphone sensor present deviations from 2.79 to 31.16% (12.83% in average). The smartphone sensor measurements in Fig. 59b were obtained from the average intensities evaluated for the different collected images, resulting in errors from 0.64 to 7.24% in relation to the mean observed signal.



Figure 59. (A) Correlation between sucrose concentration S (red) and refractive indices (RI) of the solution, and calibration of pixels intensity in relation to the RI (blue); (B) fed-batch fermentation results.

t (h)	S from model (g/L)	S from refractometer (g/L)	Refractometer error (%)	S from smartphone sensor (g/L)	Sensor error (%)
0.0	10.0	10.0	0.00	12.7	27.00
0.5	14.3	12.9	9.36	12.7	11.05
1.0	16.6	15.9	4.16	11.4	31.16
1.5	17.9	17.6	1.34	15.2	15.02
2.0	18.6	18.7	0.25	18.1	2.79
2.5	19.0	19.7	3.73	18.0	5.06
3.0	19.0	19.7	3.50	18.3	3.59
3.5	18.8	19.3	2.86	20.1	6.94

Table 4. Comparison between Monod predictions and S values calculated from each methodology.

In fermentation systems, relatively high deviations from the models are usually expected. It is due to the uncertainties involved in representing different cells as a homogeneous population and to other different aspects inherent to bioprocesses. These aspects may include: temporal evolution of the microorganisms; adaptation to differences on substrate composition and nutritional content; oscillations of temperature throughout the experiment; differences in shear stresses, etc. Therefore, the constant recalculation of the adjusted parameters is highly suggested (BAILEY; OLLIS, 1986; DORAN, 2013; SOARES et al., 2018a, 2019e).

The refractometer presents a high resolution of 1×10^{-4} RIU, but it is a high-cost device and requires sample collecting throughout the experiment. In contrast, the smartphone-based fiber sensor is available for online monitoring directly on the fermentation broth.

Finally, it is important to notice that the solution of Equation (12) for 3.5 h of experiment (the *P* curve, which is not shown in Fig. 59) resulted in a final concentration of *P* (ethanol) of only 3.51 g·L⁻¹. This value is 5.36 times lower than the one predicted for the sucrose concentration *S* (18.80 g·L⁻¹).

Considering that the solution has approximately the same density as the water at 33 °C (994.8 kg.m⁻³), this concentration *P* corresponds to a mass percent of approximately 0.35% of ethanol. On the other hand, it is known that a mass fraction of 0.50% of ethanol in water (a concentration value considerably higher than the estimated *P*) results in a hydro-alcoholic solution with refractive index of only 1.3334 (RUMBLE, 2019).

This RI = 1.3334 is the same value that was obtained for an aqueous solution containing concentrations as low as $2.5 \text{ g} \cdot \text{L}^{-1}$ of sucrose (Fig. 59a). Thus, a concentration 7.52 times lower than the value predicted for *S* would already be sufficient for overcoming the ethanol effect on the refraction. Therefore, the ethanol effect on the RI can indeed be neglected in these analyzed situations, since the high concentrations of sucrose make this one the dominant component. So, the sucrose concentration is the factor that determines the RI.

3.3.5. Conclusions from this study

This study resulted in the design and fabrication of a portable and low-cost smartphonebased optical fiber sensor for the monitoring of bioreactors, which provides a sensitivity of - 63.6342 RIU^{-1} and a reliable assessment of the fermentation process.

Due to the limited frequency of data collection by the camera, the system is not capable of performing a quasi-elastic light scattering analysis. This analysis could provide the direct evaluation of the biomass concentration, as demonstrated (SOARES et al., 2019e). On the other hand, the smartphone sensor's production costs are considerably low, and the sensor can be manufactured on-site by 3D-printing. So, it can be easily integrated into an industrial line.

Naturally, the approach used in this present study (the introduction of the sensor on the process by simply dipping the fiber tip on the broth) would not be possible neither for microfluidic systems nor for the traditional bioprocess assessment methods discussed in the beginning of this Section 3.3. As mentioned, the integration to the line is of major importance for the "*Industry 4.0*" concept, making the smartphone setup more interesting for field and manufacturing applications. Thus, suggestions for future works include the enhancement of the sensitivity of the sensor and the testing of its performance under higher fermentation scales and in more complex systems. The smartphone processing could be also applied to the interrogation of specialty fibers and other chemical sensors.

3.3.6. Contributions and acknowledgements

- Financial support from São Paulo Research Foundation (FAPESP) under grants 2017/20445-8 and 2019/22554-4.
- Financial support to other contributors of this work: Coordenação de Aperfeiçoamento de Pessoal de Nivel Superior–Brazil (CAPES), finance code 001; National Council for Scientific and Technological Development (CNPq), finance code 001.
- Dr. Franciele F. Vit and Prof. Lucimara Gaziola de la Torre from the Laboratory of Advanced Development of Nano and Biotechnology, School of Chemical Engineering, University of Campinas, SP, Brazil (FEQ/UNICAMP) for the yeast strain (*S. cerevisiae* ATCC 7754).
- Gildo S. Rodrigues and Prof. Cristiano M. B. Cordeiro from the Laboratory of Specialty Fibers and Photonic Materials, "Gleb Wataghin" Institute of Physics, University of Campinas, SP, Brazil (IFGW/UNICAMP) for the 3D-printing of the smartphone cases.
- Pedro M. Lazari and Matheus S. Rodrigues from the Laboratory of Photonic Materials and Devices, School of Mechanical Engineering, and from the Laboratory of Specialty Fibers and Photonic Materials, "Gleb Wataghin" Institute of Physics, University of Campinas, SP, Brazil (UNICAMP) for the design and test of the application and support on experiments conduction.
- Dr. Thiago D. Cabral and Prof. Cristiano M. B. Cordeiro from the Laboratory of Specialty Fibers and Photonic Materials, "Gleb Wataghin" Institute of Physics, University of Campinas, SP, Brazil (IFGW/UNICAMP) for the physics theory, contextualization and interpretation support, and characterization equipment (RI).

3.4. Dynamic light scattering optical fiber sensor for monitoring nanofluids in static and dynamic conditions

This work demonstrates the design of a dynamic light scattering sensor. It applies artificial neural networks for simultaneously assessing concentration and flow speed of nanofluids through a simplified all-optic Fresnel reflectance setup. This work was published by the open-access journal Sensors from MDPI (CÉSAR PRADO SOARES et al., 2020).

The sensor was validated for suspensions of *in-house* synthesized silica nanoparticles (diameter of 195 nm) in water, yielding a sensitivity of 0.78288×10^3 s⁻¹ for static conditions. Then, it was submitted to situations that simulate spatial concentration changes, offering better results than those obtained from traditional mathematical models. Finally, in flow tests, the light backscattered by the nanoparticles was collected by a fiber probe placed parallel to the streamline. The intensity values were processed by artificial neural networks, obtaining mean absolute errors of 0.09 wt% and 0.26 cm/s for concentration and velocity measurements, respectively.

From traditional chemical, petrochemical, and mining to food and advanced biotechnology, several industries must deal with nanofluids and colloidal suspensions. So, this system has a range of important practical applications on facilities control and monitoring.

3.4.1. Introduction

Nanofluids are stable suspensions of nanoparticles in a base-fluid, and their physical and chemical properties can be tailored according to the characteristics of both the dispersed and the continuous phases (LI et al., 2009). In particular, the use of silica particles presents advantages in terms of sphericity and surface properties. Therefore, silica-based nanofluids have been developed for use in thermal conductivity enhancement (CHEN et al., 2008); *in-vivo* fluorescence imaging (KOBAYASHI et al., 2013); and tunable optical filters (TAYLOR et al., 2013).

In this sense, the assessment of micro- and nanoparticles subjected to flow and other dynamic conditions (e.g., concentration gradients and disturbances) is essential not only for silica nanofluids applications, but also for several other biochemical, biomedical, and food engineering uses. Examples include the monitoring of red cells in blood streams (NILSSON; TENLAND; OBERG, 1980); the flow of polymeric particles (e.g., polystyrene) obtained by chemical emulsion processes (CHEN et al., 1997); and the fabrication of food emulsions based on the nanoencapsulation of nutrients (QUINTANILLA-CARVAJAL et al., 2010).

Currently, different techniques are available to measure the properties of nanoparticle suspensions, such as laser Doppler velocimetry (LDV) (CHEN et al., 1997) and particle dynamic analysis (PDA) (FAN et al., 2010). However, these approaches rely on bulky and expensive instrumentation and the detection capabilities are limited to concentrations ranging from 10³ to 10⁴ particles/mL (LEUNG; SUH; ANSARI, 2006). There are also electromechanical approaches for the evaluation of the flow of particulate systems, like the sensors for ultrasonic flow assessment and the Coriolis sensor. The ultrasonic sensors are generally based on the use of piezoelectric materials, relying on transducers for transforming an electric signal into an acoustic wave and vice-versa. The acoustic wave must be transmitted across the flow and will carry information about the whole system. Therefore, it is not invasive,

but may be impaired by geometric flaws in the tube and provides only average information (in general, the flow velocity) (WANG; WOLFBEIS, 2013).

In Coriolis sensors, part of the fluid is flown through an U-tube, generating Coriolis forces. Then, the forces excite an angular motion that is electromagnetically evaluated (i.e., it does not present immunity to electromagnetic interference). These devices are quite expensive and large, thus making it difficult to evaluate mass flows below ~0.5 g/s (LEE, 2003). Even though such sensors are capable of assessing mass flows and fluid densities (proportional to the total of dispersed particles), they are unable to perform colloidal stability analyses. The stability evaluation is possible, though, when applying light scattering sensors: when the hydrodynamic diameters of the aggregates get too high due to reduction of stability, particles stop scattering light and no more optical signal is detected (SOARES et al., 2019c; WIESE; HORN, 1991).

In this context, optical fiber sensors (OFSs) are promising alternatives for the aforementioned technologies owing to their intrinsic characteristics, such as compact size, remote operation and, especially in the case of silica waveguides, immunity to a variety of biochemical reagents (ELLIOTT et al., 2003; SADASIVAN; RASMUSSEN, 1997). For instance, the design of OFSs based on the dynamic light scattering (DLS) phenomenon for analyzing particles' sizes and static concentration profiles of nanoparticles dispersions has been reported in the literature (ENOKSSON; STEMME; STEMME, 1997; HAUPTMANN et al., 1998; SOARES et al., 2019c; WIESE; HORN, 1991).

On the other hand, few studies have addressed the measurement of suspensions under a flow regime by using all-optical fiber schemes. Leung et al. (2006) designed a DLS system in which the fiber probe is inserted perpendicularly to the streamline. The information regarding the particle diffusion coefficient is retrieved from the scattered light intensity and is then correlated to the velocity (LEUNG; SUH; ANSARI, 2006). The sensor was evaluated for different particles sizes, but the system is not capable of resolving the light scattering due to overlaid effects of concentration and velocity. Nilsson et al. (1980), in turn, explored a setup in which optical fibers are used to launch and collect the light scattered by moving red cells. Therefore, it is possible to compare the reference (static) and backscattered signals to detect the Doppler frequency shift, which is related to the flow velocity (NILSSON; TENLAND; OBERG, 1980). However, this technique demands a complex interrogation system to properly retrieve Doppler shift information.

Thus, this research proposes an optical fiber DLS sensor for the evaluation of silica nanofluids' static and dynamic conditions. Firstly, the sedimentation of colloidal silica in test tubes was done to create environments with different concentration zones. The sensor response was evaluated in this case by varying the position of the optical fiber probe along the test tube. Once each zone shows an approximately homogeneous concentration (MCCABE; SMITH; HARRIOTT, 1993), this allows the evaluation of the dynamic response of the sensor in relation to concentration disturbances. The actual concentrations in each zone were calculated by comparing the signals with a calibration curve obtained when assessing static suspensions with known silica concentrations. These tests also allowed the obtention of the sensor sensitivity.

Finally, the OFS was applied to the detection of velocity of nanofluids with different concentrations and flow conditions. Contrary to previous works, the present system is capable of simultaneously estimating the sample concentration and flow velocity by using artificial neural networks, providing a simple, minimally invasive, and nondestructive approach to assess particle dispersions.

3.4.2. DLS and mass transfer fundamentals

The DLS phenomenon takes place when light interacts with particles whose dimensions are comparable to the radiation wavelength, what results in absorption and secondary emission in a different direction. In the case of suspensions of nanoparticles in a base fluid, the Brownian motion enhances the variation of the collected data. Thus, it is possible to obtain information about the sample by analyzing the characteristics of the scattered waves (FINSY, 1994).

Moreover, if the nanoparticles are subjected to flow conditions, there is a competition between: the fluid translational movement, which exerts drag forces on the particles (viscous action of the fluid that tends to align the particles with the direction of the flow); and the Brownian diffusivity (random motion in all directions) (WELTY et al., 2008). This competition is represented out of scale in Fig. 60, where a silica nanoparticle flowing in water with velocity u is shown.

For independent and non-interacting particles, the homodyne backscattered light intensity I(t) measured by the photodetector at an instant t is function: of the total concentration of particles dispersed in the base fluid; and of the particles' diffusion coefficient, D_{AB} . If there is a relative translational movement between the nanofluid and the light source, the Doppler shift may also introduce the dependence of I(t) with the flow velocity u and with the beam radius of the source w, where the relation w/u is the beam transit time (CHOWDHURY et al., 1984; LEUNG; SUH; ANSARI, 2006).



Figure 60. Out of scale representation of the competition between the flow drag forces (blue arrows) and the Brownian random motion (red arrows) from a SiO₂ nanoparticle in water. The water flows with velocity "u", and the nanoparticle has diameter "a" and diffusivity D_{AB}.

One may evaluate the autocorrelation function $G_2(\tau)$ of I(t) by Equation (17) (BERNE; PECORA, 1976; SALEH; TEICH, 1991).

$$G_2(\tau) = \lim_{T \to \infty} \frac{1}{T} \int_0^T I(t) \cdot I(t+\tau) dt$$
(17)

In Equation (17), τ is an arbitrary delay time; and G₂ is a statistical measurement which takes in account the previous history of the system and that is influenced by the total number of dispersed particles (BERNE; PECORA, 1976; HUNTER, 2004; SALEH; TEICH, 1991). Since the light scattering induced by the Brownian motion is influenced by previous particles positions, the phenomenon will become completely independent and neglect its past history after a sufficiently long time. So, G₂ decreases as τ rises (SALEH; TEICH, 1991).

 G_2 can be approximated by the exponential Siegert relation, Equation (18), where the approximation presents better results for spherical particles (FINSY, 1994; KOPPEL, 1972).

$$G_2(\tau) = \alpha + \beta \cdot exp(-2\Gamma_m \tau) (18)$$

In Equation (18), α and β are instrumental factors, and Γ_m is the average decay rate (FINSY, 1994). Γ_m is correlated to the light scattering vector by Equation (19).

$$\Gamma_m = D_{AB} q^2 (19)$$

In Equation (19), the parameter q is the magnitude of the scattering vector and D_{AB} is the diffusion coefficient (diffusivity) of a particle A in a solvent B. For spherical particles dispersed in low concentrations (such as the one represented in Fig. 60), D_{AB} can be estimated through the Stokes-Einstein model, Equation (20) (FINSY, 1994; WELTY et al., 2008).

$$D_{AB} = \frac{kT}{3\pi a\mu_B} (20)$$

In Equation (20), $k = 1.38 \times 10^{-23} \text{ m}^2 \cdot \text{kg} \cdot \text{s}^{-2} \cdot \text{K}^{-1}$ is the Boltzmann constant; T is the system's temperature (in K); a is the average diameter of the particles; and μ_B is the dynamic viscosity of the fluid.

In the presence of a translational movement, Equation (18) must be corrected as Equation (21) (LEUNG; SUH; ANSARI, 2006), where w is the light source beam radius and u is the flow velocity.

$$G_{2}(\tau) = \alpha + \beta \cdot exp(-2\Gamma_{m}\tau) \cdot exp\left(-\frac{u^{2}\tau^{2}}{w^{2}}\right)$$
(21)

Finally, the decay rate is determined from the field autocorrelation function $G_1 = G_2 - \alpha$. For that, the expansion on Equation (22) is evaluated (FINSY, 1994).

$$\ln G_1(\tau) = \ln \sqrt{\beta} - \Gamma_m \tau + K_2 \frac{\tau^2}{2} + K_3 \frac{\tau^3}{6} + \cdots (22)$$

The expansion parameters K_2 , K_3 , ... on Equation (22) are the moments of distribution of the decay rates. Thus, information about the particles can be retrieved by determining the coefficients of the polynomial (by fitting a 6th-order polynomial, for example).

Furthermore, the competition between the diffusion and the translation effects can be analyzed in terms of the dimensionless Peclet number, Pe. It is given by Equation (23), where L is the tube characteristic dimension (WELTY et al., 2008).

$$Pe = \frac{uL}{D_{AB}}$$
(23)

Since Pe is a relation between the translation and the diffusivity, high Pe values imply the predomination of the translation over the diffusivity, i.e., the modulation of the Brownian motion by the flow movement (WELTY et al., 2008).

It is interesting to analyze the physical interpretation of the above-mentioned equations. It is possible to demonstrate that the light scattering vector (Equation (19)) is directly proportional to the total number of particles dispersing the light; and that the relation between the decay rate and the particles concentration C is linear for small concentration ranges (BERNE; PECORA, 1976; FINSY, 1994; HUNTER, 2004). Several works have also empirically observed this linearity (LEUNG; SUH; ANSARI, 2006; SOARES et al., 2019c; WIESE; HORN, 1991), so it is possible to obtain a calibration curve correlating Γ_m to C.

The diffusion coefficient may be interpreted as the frequency of the random Brownian motion (FINSY, 1994; WELTY et al., 2008). Therefore, it is expected that particles in a base fluid show increased decay rates when their diameters are reduced. Indeed, Equation (20) shows that reductions of the diameter result in the increase of the diffusivity.

On the other hand, Equation (23) shows that Pe grows with the flow velocity, i.e., the presence of flow leads to Pe increases, what corresponds to a modulation of the apparent diffusivity. That is because the fluid inertial forces get predominant over the random motion as the velocity rises, giving orientation to the particles. Then, as the velocity increases, one may notice an apparent reduction on Equation (19) (WELTY et al., 2008).

3.4.3. Silica nanoparticles synthesis and characterization

Silica nanoparticles were synthesized by the Vapor-phase Axial Deposition (VAD) method (MURATA, 1986), in which a high-temperature O₂-H₂ flame promotes the hydrolysis and oxidation of the SiCl₄ precursor according to Equation (24).

$$SiCl_{4(g)} + 2H_{2(g)} + O_{2(g)} \rightarrow SiO_{2(s)} + 4HCl_{(g)}$$
 (24)

The formed particles are deposited on the surface of a rotating target. They present high purity, spherical shape, and amorphous structure. Finally, the material is mechanically detached from the target and ground in a quartz mortar to obtain silica powder (SOARES et al., 2018c).

The VAD system is designed for the fabrication of completely amorphous silica glass of high transparency destined to the production of optical fiber preforms and other photonic components (MURATA, 1986; SANTOS et al., 2011). Therefore, considering the high purity and morphological control of the silica, as well as the wide availability of characterization data (SANTOS et al., 2011; SOARES et al., 2018c; WIESE; HORN, 1991), the use of the *in-situ* synthesized nanoparticles was preferred over commercially available materials.

Moreover, the morphological control reduces the width of the size distribution and, consequently, the effect of the introduction of a particle diameter distribution when performing sedimentation tests. It is also known that a nanofluid system obtained with these particles presents the advantage of not requiring the use of tensoactives to be kept stable; and that the silica nanoparticles present high chemical and thermal inertia (SOARES et al., 2019c; WIESE; HORN, 1991). An important disadvantage that must be cited, though, is that the high stability of the nanostructured SiO₂ dispersions results in a very slow sedimentation process when compared to systems like CaCO₃, which require only a few hours to be completely sedimented (MCCABE; SMITH; HARRIOTT, 1993).

The nanoparticles were analyzed with a scanning electron microscope (SEM, EVO MA 15, Zeiss, Oberkochen, Germany) equipped with LaB₆ thermoionic cannon for obtaining secondary electron images. The samples were prepared by dispersing SiO₂ powder in deionized (DI) water; dropping this suspension on stubs; and drying the stubs under environmental conditions. The stubs were then gold-coated using a Bal-Tec SCD 050 Sputter Coater to obtain images under high-vacuum conditions. The particles size distribution was also measured with a Malvern Zetasizer Nano Zn-Zen 3600 (Malvern Panalytical, Malvern, UK) through LDV.

The SEM images and the size distribution are shown in Figure 61, yielding a diameter $a = (195 \pm 93)$ nm.

Once the statistical distribution obtained with the Zetasizer presents high skewness and kurtosis, it was fitted by the lognormal distribution (adjusted $R^2 = 0.9938$). The most probable diameter (i.e., the point of maximum observed in the probability density function (PDF) shown in Figure 61) was taken as the central value of the interval (195 nm). The PDF was then used to obtain a symmetrical interval (centered in 195 nm) with correspondent accumulated probability of at least 95% (i.e., this interval should contain at least 95% of the total area under the PDF curve). The half-width of this interval was finally taken as the uncertainty: 93 nm.

The detailed statistical analyses, including: the fitting of the lognormal; calculus of statistical and shape parameters; the fitting of the logistic curve; and the verification of the accumulated probabilities are included in Appendix 2. It is worth noticing that, once the particle distribution evaluation provides a hydrodynamic diameter (which includes at least one layer of solvent molecules around the nanoparticles), the average diameter obtained through this technique may be slightly larger than that observed in the SEM image.



Figure 61. (a) SEM images; and (b) size distribution of the silica nanoparticles.

To obtain the SiO₂ aqueous suspensions, nanoparticles were dispersed in DI water according to a mechanically mixing procedure; followed by sonication in a temperature-controlled ultrasound bath (5.9 L Ultrasound Bath, Ultronique Eco-Sonics, Indaiatuba, SP, Brazil) for 180 min to ensure homogenization. The samples present a practically constant dynamic viscosity value of $\mu_B = 0.933 \times 10^{-3} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$ at 25 °C (SOARES et al., 2019c), so the diffusivity calculated from Equation (20) is given by $D_{AB} = 2.40 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ at 25 °C.

3.4.4. Optical fiber sensor setup

The OFS is depicted in Figure 62. Light emitted by a 1310 nm-laser diode is launched into a standard silica single-mode fiber (SMF). The optical signal is divided by a 1×2 90:10 directional coupler: 10% of the light is used as the reference whereas the remaining part is delivered to the sample. The fiber end-face (plane-polished and encapsulated in a zirconia ferrule) works as the probe. Therefore, reflection occurs at the fiber-liquid interface due to the refractive indices difference in accordance with the Fresnel law modulation, Equation (14).

Finally, the reflected light is guided to the photodetector and the signal is processed in a computer. For the nanoparticles suspensions, the backscattered light is also partially coupled to the fiber core, so the DLS effect emerges as a superimposed noise in the reflected light intensity I(t) signals. Consequently, one may evaluate $\ln(G_1)$ to retrieve Γ_m , and then investigate particle concentration and flow velocity. The optical signal is acquired at 1 kHz sampling rate and processed by MATLAB (Mathworks) routines (SOARES et al., 2019e, 2019c).



Figure 62. Optical fiber DLS sensor setup. The probe position 2 (parallel to the flow) was chosen for flow sensing experiments.

Fig. 62 shows two possible probe positions for the sensor setup: a position perpendicular to the flow, and a second one parallel to the flow. Since preliminary experiments showed a better sensitivity when working with the sensor parallelly positioned, this configuration was selected for this study. Indeed, a dependency of the sensor performance with the probe position was expected, since the light source beam radius w is a parameter from Equation (21).

3.4.5. Monitoring of nanofluids concentration disturbances

To create an environment with different particles concentrations (suitable for the simulation of concentration disturbances), two (1000 mL)-test tubes were filled with silica suspensions with 1 wt% of mass concentration. The suspensions were left in rest so that the particles could slowly sediment to create a clarified zone on the top of the flask; a concentrated zone on the bottom; and zones with intermediate concentrations between these two (MCCABE; SMITH; HARRIOTT, 1993). During all of the sedimentation time, the tubes were kept sealed to avoid contamination with external microorganisms, and microscope images were obtained for all of the zones at the end of the experiment.

For the sensing experiments, the optical fiber probe was immersed in each one of the regions to collect 20,000 optical data. Then, it was rapidly moved to another zone, where its response was evaluated again. All experiments were performed at room temperature ($\sim 25^{\circ}$ C).

The height h(t) from the bottom of the tube to the beginning of the clarified zone presents an initial value h_i that progressively decreases with time. If the initial concentration of particles is C_i (mass/volume); and assuming that the concentration in the clarified zone is negligible (so that the particles are all on the most concentrated region), the estimated concentration C(t) in the bottom zone is given by Equation (25), a direct consequence of the mass balance of solid particles (MCCABE; SMITH; HARRIOTT, 1993).

$$C(t) = C_i \frac{h_i}{h(t)}$$
(25)

Figure 63 shows one of the test tubes on the first day of experiment; and after 73 days of sedimentation, when 4 concentration zones are distinguishable. This long time required for the visualization of these zones is a consequence of the above-mentioned low average diameter and size distribution width, as well as of the very high suspension stability of the SiO₂ nanofluid. These properties lead to a very slow introduction of the size distribution on the test tubes.



Figure 63. Test tube containing the colloidal silica: (a) first day of experiment; (b) 73 days after the beginning of sedimentation; (c) 4 different sedimentation zones that could be distinguished on day 73. Each zone presents a different value of particle concentration, creating an environment where it is possible to simulate concentration disturbances (heights expressed in cm).

Usually, particles and aggregates with the highest diameters are the first to sediment. So, higher concentrations of larger particles are expected to be found in the lower sedimentation zones (closer to the bottom of the tube). As Figure 61b shows a population of particles with several possible diameters, one could expect that a modification on the size distribution could be introduced by the sedimentation: particles with lower diameters would get concentrated closer to the top, whereas the larger diameters would appear closer to the bottom of the test tube (FOUST et al., 1980; MCCABE; SMITH; HARRIOTT, 1993). So, once Equation (20) states the dependence of diffusivities with diameters, the introduction of the diameter profile could possibly affect the decay rates and generate errors on the concentration estimates.

This is not a problem here, though. For SiO₂ nanoparticles with diameters on this order of magnitude from 100 to \sim 300 nm (Fig. 61), diameter differences such as the ones that could be created by the sedimentation are only expected to significantly modify the decay rates if the particle concentration is higher than 1.5 wt%. Actually, almost no difference on the signals is expected for concentrations lower than 1.2 wt% (SOARES et al., 2019c; WIESE; HORN, 1991).

This is a consequence of the fact that the autocorrelation function (Equation (17)) is a statistic that takes in account all the intensity measurements performed, and which quality depends on the total number of particles scattering the light. In addition, the small number of particles that are dispersed in solution when the concentrations are lower than 1.2 wt% reduces the sensor sensitivity (SALEH; TEICH, 1991), so no differences regarding the average diameter can be noticed (SOARES et al., 2019c; WIESE; HORN, 1991).

Therefore, concentrations lower than 1.2 wt% must be used on sedimentation tests to prevent diameter differences to significantly interfere on the analysis. Indeed, the application of the heights shown in Fig. 63c to Equation (25) results in an estimated concentration of only \sim 1.16 wt% (Fig. 64a shows the concentrations calculated for each height and day). Thus, the tube was considered adequate for this research, since different decay rates would be correspondent to changes in concentration and would not be confused with diameter effects.

Rapidly moving the fiber probe from one sedimentation zone to another (a zone change) is equivalent to submitting the sensor to a step-disturbance on nanoparticles concentration. Thus, the optical fiber probe was sequentially dislocated from the clarified (Zone 1) to the more concentrated zone (Zone 4, Fig. 63); and then the opposite sequence was performed (Zone 4 to Zone 1). The reflected light intensities I(t) collected for this experiment are shown in Fig. 64b.

According to Equation (25), moving the probe from Zone 1 to Zone 4 corresponds to modifying the detected silica concentration from 0 to 1.16 wt%. Indeed, when using the OFS to evaluate the clarified zone during the experiment, no DLS phenomenon was observed (i.e., no exponential decay was noticed on $G_2(\tau)$), confirming that this region is approximately free of particles (Fig. 64c).

In opposition, the monitoring of Zone 4 (Fig. 64d) showed the clearest exponential decay profile obtained for $G_2(\tau)$. This is the behavior expected from Equations (18) and (21) when observing the dynamic light scattering: when there are dispersed nanoparticles, the autocorrelation function shows an exponential decay followed by a baseline, with rate of decay $dG_2/d\tau$ correlated to the particles concentration. So, when the curve $G_2(\tau)$ actually presents an exponential format, it is fitted by a 6th-degree polynomial to obtain an expression that may be interpreted as the expansion of Equation (22). Finally, considering that this fitting and Equation (22) are equivalent expressions, the polynomial 1st-order coefficient is taken as ($-\Gamma_m$).

However, many DLS experiments may show a deviation from this ideal exponential behavior: a minimum point or an oscillation of the baseline may be observed on $G_2(\tau)$ as consequence of experimental errors and deviations; or of the discretization errors and approximations involved in the mathematical processing of the signal by the algorithm

described by Equations (17) to (22) (SOARES et al., 2019c; WIESE; HORN, 1991). When observing these deviations, one may have to select an appropriate portion of the curve $G_2(\tau)$ for obtaining a satisfactory polynomial fitting.



Figure 64. (a) Average values of the heights verified for the two tubes and concentrations estimated from Equation (13) (secondary vertical axis); (b) sequential step disturbances in the concentration detected by the OFS probe; (c) $G_2(\tau)$ obtained for Zone 1, as function of the arbitrary delays τ applied by the algorithm; (d) $G_2(\tau)$ obtained for Zone 4 (with an exponential decay), as function of the arbitrary delays applied by the algorithm.

To correlate the DLS response with the actual concentration of particles in each zone (which may be different from the sedimentation model predictions), a calibration curve was also obtained. For that, the optical fiber was introduced into nanofluids with different known concentrations ranging from 0 (DI water) to 2.0 wt%. So, the sensor static response and its sensitivity in relation to the concentration were evaluated. The results are shown in Fig. 65a, where the linear regression of the experimental data resulted in $\Gamma_m = 0.78288C + 0.10898$, C in wt% (R² = 0.95942), yielding 0.78288 × 10³ s⁻¹ sensitivity.

By applying the algorithm described on Equations (17) to (22) to data from Fig. 64b, Γ_m was retrieved for each fermentation zone. Then, the calibration curve was used to convert these decay rates to actual silica concentrations (Fig. 65b). In addition, the standard deviations σ were obtained for the I(t) signals collected on each concentration region, as presented in Fig. 65c.



Figure 65. (a) Calibration curve correlating Γ_m to SiO₂ nanoparticles concentration; (b) Γ_m and the correspondent concentrations assessed for each sedimentation zone; and (c) standard deviations of I(t) signals collected for each zone. First sequence represents the probe dislocation from Zone 1 to Zone 4, whereas Second sequence represents the opposite movement, from Zone 4 to Zone 1.

It is possible to notice on Fig. 65b that the sensor detected a concentration of ~ 0.57 wt% for Zone 4, what is quite inferior to the ~ 1.16 wt% prediction obtained from Equation (25). So, the concentration is indeed in the range where diameters differences are not expected to interfere on the decay rate evaluation (SOARES et al., 2019c; WIESE; HORN, 1991).

The difference between the concentration detected by the sensor and the value predicted by the model may be understood as consequence of the tacit hypothesis involved on the deduction of Equation (25). As discussed by important authors specialized on projecting equipment for chemical industries (FOUST et al., 1980; MCCABE; SMITH; HARRIOTT, 1993), concentration zones are formed in the majority of sedimentation vessels, but their positions are highly dependent on different factors inherent to each system, like: the particular phase dispersed; the geometry of the vessel; and pH, ionic strength and temperature conditions (SOARES et al., 2019c). So, for simplifying the engineering project of the sedimentation equipment, they assume that only two zones are present: the clarified and the concentrated bottom zone. This is the reason why Equation (25) calculates C(t) only for the bottom zone: all other regions are considered to be part of the clarified portion (FOUST et al., 1980; MCCABE; SMITH; HARRIOTT, 1993).

Since Figure 63 clearly shows that there are four different concentration zones, a fraction of the particles that Equation (25) predicted to be in Zone 4 are divided between Zones 2 and 3.
So, the actual Zone 4 concentration must be lower than predicted. The sensor solves this problem, since it provides a simple and more accurate instant evaluation of C.

Figs. 65b and 65c show similar behavior for Γ_m and σ : the two sequences of probe dislocations show approximately the same tendencies when comparing these two figures. Also, the intensity I(t) data (Fig. 64b) show small modifications of the average signal when the probe is moved from one zone to another, probably caused by fiber macrocurvature losses. Then, it is possible to evaluate the lowest and highest signal-to-noise ratios (SNRs) as μ^2/σ^2 , where μ is the mean value of the collected signals (SALEH; TEICH, 1991): 2.604 × 10⁴ (Zone 4, second sequence) and 2.869 × 10⁵ (Zone 1, first sequence), respectively. The lowest SNR for Zone 4 is a direct consequence of the increase of nanoparticles concentration, since the DLS phenomenon results in the enhancement of light intensity oscillations (SOARES et al., 2019e).

When analyzing Figs. 65b and 65c, a hysteresis can be also noticed, but this effect is lower for Fig. 65b: differences between signals collected for the same concentration zones are lower when evaluated in terms of decay rates. A probable cause is the difference between the statistical methods applied to each figure. The results obtained with the autocorrelation function take in account not only the whole group of measurements, but also the memory effect of the light intensity oscillations related to the Brownian motion (i.e., it considers that each oscillation of the particles in a given moment affects the immediately following oscillations, but do not affect what occurs after large temporal distances) (FINSY, 1994; SALEH; TEICH, 1991). On the other hand, it is known that decay rate measurements are not dependent on the particular light intensity reference adopted by the photodetection system (FINSY, 1994), what is not necessarily true for the standard deviation quantification. Despite these disadvantages, the computational costs and time required for the calculation of σ are very lower, a fact that can make the use of the standard deviation strategy more attractive when deciding how to assess a given process.

Moreover, the elucidation of the physical causes of the hysteresis requires more investigation. Feasible hypotheses are related to the moment when the probe is pulled back to the surface of the flask: the environment is disturbed, carrying particles from the lower to the upper zones; or a small quantity of particles from the lower zones remains close to the probe surface due to the inertial forces of the optical fiber movement and to the surface attraction between the two silica materials (fiber probe and nanoparticles).

Figure 66a reveals the general aspect of the solid material (silica nanoparticles) deposited on the bottom of the flask, whereas Figs. 66b–66e show microscopic images obtained for particles collected in each sedimentation zone under higher magnification. As predicted, it is difficult to visually observe differences in the average diameters: the nanofluid stability and the time required to visualize the sedimentation zones are both very high, so only a very low sizing distribution is introduced (SOARES et al., 2019c; WIESE; HORN, 1991).

The images also do not show contamination with algae, yeast, or other microorganisms. That is because these cells are usually observed on the microscope as approximately circular or spherical particles with diameters in the order of ~1-5 μ m. Their presence would not be a significant problem for the sensor analysis, though, since the decay rates collected with this type of sensor for yeast cells of *Saccharomyces cerevisiae* are usually much lower than those observed in Figure 65 (LUDOVICO et al., 2001; SOARES et al., 2019e; WARD, 1991).

For concentrations of cells up to 1×10^8 cells/mL, decay rates one order of magnitude lower than those from Fig. 65 are expected for *S. cerevisiae*. Actually, such values of cell concentrations are pretty high, so the microorganisms would be easily detected by microscopes.

Moreover, cellular aggregates would be probably observable to the naked eye as a yellow or green precipitate formed on the bottom of the flask. Lower concentrations of cells, in turn, would lead to even lower Γ_m with negligible interference on the silica assessment (SOARES et al., 2019e).

As a matter of fact, very low Γ_m associated to the microorganisms are expected from Equations (19) and (20): when compared to SiO₂ nanoparticles, the very high cells' diameters (1-5 μ m; against 100-300 nm measured for SiO₂) result in very lower diffusivities and decay rates. So, microorganisms are not expected to interfere in the silica concentration experiments.



Figure 66. (a) General aspect of the most concentrated zone (scale bar: 1 μm; image under lower magnification, useful for the detection of particles like microorganisms, which present diameters much larger than the SiO₂); images collected under higher magnifications (scale bars: 200 nm): (b) detail of particles collected in Zone 1; (c) detail of particles collected in Zone 2; (d) detail of particles collected in Zone 3; (e) detail of particles collected in Zone 4. It is difficult to observe significant differences between the average diameters when comparing the images, and no microorganism is noticeable.

3.4.6. Simultaneous assessment of nanofluids concentrations and velocities

Finally, the nanofluids were evaluated when submitted to the flow regime. In this case, the probe is placed parallel to the nanofluid flow streamline (as shown in Figure 62), so the light scattered by particles is coupled to the fiber and measured with a photodetector. The nanofluids with different concentrations C are moved through a 6-mm inner-diameter silicone tube under hydrostatic pressure gradient at room temperature. The flow speed u is controlled by a microvalve, whereas the optical response is analyzed using the fiber sensor.

The experiments were carried out for SiO₂ suspensions with concentrations C ranging from 0.50 wt% to 2.00 wt% and velocities u ranging from 0 to 9.5 cm/s. Taking the characteristic dimension L as the tube diameter (6 mm); and D_{AB} as the value calculated in the end of Section 3.4.3 ($2.40 \times 10^{-12} \text{ m}^2.\text{s}^{-1}$), Equation (23) shows that Pe is directly proportional to u and is simply given by Pe = (2.50×10^7) u, u in cm/s.

Therefore, u and Pe can be easily exchanged by simple conversion, and all of the conclusions regarding the increase of u can be extended to the increase of Pe (i.e., the increase of the flow inertial forces in relation to the diffusion of the nanoparticles).

It is also important to notice that the velocity of the fluid u is zero in all experiments shown in Section 3.4.5 (the obtention of a calibration curve; and the simulation of concentration disturbances in test tubes - situations in which the probe is dislocated to each zone and is maintained in the same position until the sensor completes 20,000 measurements). Therefore, the second exponential term of Equation (21) is 1. For the experiments with nanofluids flowing, on the other hand, the second exponential increases with the velocity u (LEUNG; SUH; ANSARI, 2006), introducing a non-linearity to the relation between Γ_m , u, and C.

The results collected for the evaluation of flow conditions are shown in Figure 67. The scattering increases for concentrated solutions due to the particles' Brownian motion. In turn, Γ_m decreases with speed, since: diffusion and light intensities are attenuated by longitudinal flow dynamics (as represented on Fig. 60); and I(t) is affected by laser beam depth resolution (WEISS; VAN LEEUWEN; KALKMAN, 2013). This explains the decay rate Γ_m reduction with u, in contrast to what is observed in transverse flows (LEUNG; SUH; ANSARI, 2006).



Figure 67. (a) Normalized autocorrelation function for 2 wt% silica nanofluids at different flow speeds. The inset shows the normalized scattered light intensities; (b) Γ_m as a function of flow speed for different concentrations. The solid lines are guides to the eye.

Indeed, the influence of u in the light scattering can be explained by the competitive effects between the Brownian and translational motions (Fig. 60). As the flow velocity increases (increase of Pe), the translational component of the particles position vector overcomes the diffusive effects and modulates the magnitude of I(t) (HUNTER, 2004; WELTY et al., 2008). This is observed in Fig. 67b: as the inertial forces become dominant with the increase of Pe, an approximate constant decay rate is reached, indicating the decrease of the influence of the Brownian diffusivity. However, the diffusion effect is not completely eliminated, since Fig. 67b shows that the final decay rate is higher for more concentrated nanofluids.

When comparing Fig. 67b with Fig. 65a (static case), it can be noticed that the relation between the light scattering, flow speed, and particle concentration is highly non-linear. It is a consequence of the increase of the second exponential term in Equation (21) with the velocity u, as already mentioned (LEUNG; SUH; ANSARI, 2006).

Therefore, in order to achieve a precise mathematical model instead of using successive linear interpolations, data analysis with Artificial Neural Networks (ANNs) was proposed. The ANNs allow the obtention of more precise results without losing the generality of the phenomenon for the tested range, a characteristic that is highly attractive for the development of new instrumentation (SETIONO, 2001). Furthermore, to simultaneously evaluate the concentration and flow speed of the nanofluids with the sensor, an ANN correlator was implemented in MATLAB by varying the delay step $\Delta \tau$ from 100 to 1000 ms (CIPELLETTI; WEITZ, 1999). Also, the k-fold cross-validation method was applied (KOHAVI; LI, 1995; SETIONO, 2001).

The measurements shown in Fig. 67 were randomly selected without reposition to form k = 10 distinct groups with six measurements (k-value justified by the amount of data and by the fact that the measurements were relatively sparse). After this division, the ANN was trained with k_{i-1} groups and tested with the *i*th-group k_i for all of the 10 groups i = 1, 2, ..., 10 (a process known as "*leave-one-out*"). Despite the fact that the error estimator's variance and the computational effort are proportional to the number of folds, the use of 10 folds results in a low-biased and highly-accurate estimator (in contrast with other traditional training methodologies like the "Bootstrap" method) (KOHAVI; LI, 1995).

The size of the ANN, in turn, was defined to avoid overfitting: the number of layers was fixed to 2 (only one hidden layer) and the number of neurons was progressively increased. The increase was performed until the error achieved a value considered satisfactory (when the increase on the number of neurons no longer produced a significant reduction of the error); and with no evidence of overfitting (what would be observed as a substantial difference between the loss curves obtained for training and validation).

Then, an array of decay rates $\Gamma_m(\Delta \tau)$ was used as the input of 2 dense layers (20 neurons per layer). The tangent sigmoid was set as the activation function and the ANN architecture was designed for returning both C and u (i.e., the neural networks perform the simultaneous regression of these two responses). The networks were trained using backpropagation, but with a scaled conjugate gradient algorithm that uses 10-fold cross-validation (CIPELLETTI; WEITZ, 1999; KOHAVI; LI, 1995). The general architecture of the ANN and the results obtained for these parameters are shown in Figure 68, yielding 0.09 wt% and 0.26 cm/s mean absolute errors (MAE) for concentration and flow speed, respectively.



Figure 68. ANN correlator: (a) an example of a general dense neural network architecture for retrieving C and u simultaneously; and measurement of errors for: (b) concentration; and (c) flow speed.

Fig. 69 shows the results that could be obtained for slightly lower values of neurons. It is easily noticed that the use of less than 20 neurons results in a considerable increase of error: when using 16 neurons, the calculated MAEs were of 0.44 wt% and 1.15 cm/s for concentration and flow speed, respectively. When using an ANN with 18 neurons, in its turn, the obtained MAEs were 0.37 wt% and 0.88 cm/s for concentration and flow speed, respectively.



Figure 69. ANN regressor: calculated errors (MAE) for: (a) concentration (ANN with 16 neurons); and (b) flow speed (16 neurons); (c) concentration (ANN with 18 neurons); and (d) flow speed (18 neurons).

The results collected for the ANN using 20 neurons (Fig. 68) are comparable to those reported for optical coherence tomography (WEISS; VAN LEEUWEN; KALKMAN, 2013), laser Doppler velocimetry (FINSY, 1994), and conventional DLS (CARR, 1990) systems.

The proposed method presents several advantages over these studies: it provides simultaneous measurements; and relies on a simple, low-cost, all-optical fiber instrumentation, which is suitable for inline nanofluids monitoring. The simplicity and low cost of the system, on the other hand, does not allow the evaluation of particle size distribution, since it is not capable of retrieving angular information regarding the optical signals.

3.4.7. Conclusions from this study

This study demonstrated an optical fiber sensor that was successfully applied to the monitoring of a multi-concentrated particulate system (silica nanofluids), an environment that is suitable for simulating step disturbances of particles' concentration. The nanofluids were obtained by VAD-synthesizing SiO₂ spherical nanoparticles with diameters of (195 \pm 93) nm. Then, these particles were dispersed in water under different concentrations.

The information collected with the system were used to retrieve actual concentration values that were considerably different from those estimated by the simple sedimentation model traditionally applied to Chemical Engineering practice (the Equation (25), which is of great practical importance for engineering projects). The reason for this difference is an assumption of the model: for simplifying the project of sedimentation tanks (used in environmental, separation, purification, and waste treatment processes), the model only considers the presence of two sedimentation zones: the clarified and the concentrated bottom zone. This assumption results in empirical differences, once the height of the more concentrated zone is actually lower than the end of the clarified; and the particles are divided between one or more intermediate regions. On the other hand, it is not possible to simply apply the height of the most concentrated zone to Equation (25), since the proportion expressed by this equation is derived from the mass balance between only two different regions (MCCABE; SMITH; HARRIOTT, 1993).

Once this model is used on both the project of industrial equipment, and on their monitoring during operation (MCCABE; SMITH; HARRIOTT, 1993), more precise information such as those provided by the DLS sensor could save fabrication costs and allow the obtention of more efficient facilities.

Finally, a DLS sensor based on an ANN-regressor was demonstrated for the simultaneous evaluation of concentration and flow velocity of nanofluids. Considering the low amount of available data, the process known as *"leave-one-out"* was used with 10 folds for training a low-biased and highly-accurate estimator. Also, the architecture of the ANN was kept very simple (comprised of only 2 dense layers) to prevent overfitting (the memorization effect). Even though artificial neural networks do not generate a model easily explainable (like the ones obtained from linear regressions or decision trees), a powerful model was needed for accounting for the non-linear relation between decay rate, velocity and particles concentration (a non-linearity that is evidenced by the second exponential term in Equation (21)).

As a matter of fact, the algorithm used here is a hybrid model consisting of a physicsinformed neural network: the data fed to the network is not the raw optical data itself, but a preprocessed and transformed information derived from the autocorrelation function and from the physical principles of DLS. It is a strategy that reduces the noise of the training data and makes the algorithm more powerful and based on solid principles, instead of being a simple "*black-box*". That is because each data point used for the training is obtained after pre-processing a set of 20,000 optical intensity values with Equations (17) to (22). Naturally, the use of more precise instrumentation for controlling the flow rate (like the peristaltic pump used for testing the smartphone-based fermentation sensor); and the collection and processing of a larger dataset (containing more data points and wider ranges of concentration and flow speed values) would allow the training with more powerful architectures (like convolutional or recurrent neural networks) without the risk of overfitting the training data. The use of such architectures could show reduced prediction errors (increased precision) because they are designed for capturing important features and memory effects, being more adequate for modelling time-series data.

A final suggestion for future works is the application of this optical system to other nanoparticles and inline processes. Several industries and laboratories that work with particulate liquid systems can leverage these studies for controlling and monitoring their operation. Among them, one may find not only metals, mining, and traditional chemical and petrochemical facilities, but also fancy and advanced biotechnological, biomedical and food industries.

3.4.8. Contributions and acknowledgements

- Financial support from São Paulo Research Foundation (FAPESP) under grants 2017/20445-8 and 2019/22554-4.
- Financial support to other contributors of this work: Coordenação de Aperfeiçoamento de Pessoal de Nivel Superior–Brazil (CAPES), finance code 001; National Council for Scientific and Technological Development (CNPq), finance code 001.
- Brazilian Nanotechnology National Laboratory SP, Brazil (LNNano, CNPEM/MCTI) for the SEM images.
- Willian H. A. Silva from the Laboratory of Photonic Materials and Devices, School of Mechanical Engineering, University of Campinas, SP, Brazil (FEM/UNICAMP) for the support on developing the computational routines for windowing the data collected from disturbance experiments.
- Cláudio Silveira and Prof. Carlos K. Suzuki from the Laboratory of Photonic Materials and Devices, School of Mechanical Engineering, University of Campinas, SP, Brazil (FEM/UNICAMP) for the support on the synthesis of SiO₂ nanoparticles by VAD.
- Dr. Egont A. Schenkel and Prof. Carlos K. Suzuki from the Laboratory of Photonic Materials and Devices, School of Mechanical Engineering, University of Campinas, SP, Brazil (FEM/UNICAMP) for the support on SiO₂ characterization by SEM; and Gabriel Perli from the Institute of Chemistry, University of Campinas, SP, Brazil (IQ/UNICAMP) for the characterization support through LDV/DLS.
- Matheus K. Gomes and Matheus S. Rodrigues from the Laboratory of Photonic Materials and Devices, School of Mechanical Engineering, University of Campinas, SP, Brazil (FEM/UNICAMP) for the preparation of colloidal suspensions, and for the extensive support for the development of the setup, experimental procedure and DLS-process algorithm.
- Prof. Carlos K. Suzuki from the Laboratory of Photonic Materials and Devices, School of Mechanical Engineering, University of Campinas, SP, Brazil (FEM/UNICAMP) for the technical support and for scientific discussions and insights.

4. Conclusions

- This study resulted in sustainable, cheap, scalable, and straightforward methodologies to obtain carbon nanodots with low polydispersity. Sugarcane syrup-derived CDs with 3 nm in average and fluorescent upon irradiation with UV light were obtained.
- A fluorescent hydrogel-CDs nanocomposite was obtained using cheap gelatin polypeptide as the polymeric matrix. The CDs emission spectrum bands broadened towards blue upon incorporation into the hydrogel tridimensional network.
 - The new hydrogel-CDs nanocomposite was incorporated into the cavities of a double-clad polymer optical fiber fabricated with an innovative design.
 - This work demonstrates a potential alternative for the substitution of rare-earths and other inorganic heavy metals for applications in luminescent optical fibers.
- It is possible to extend the methodology used for the synthesis of carbon nanodots from sugarcane syrup to other two widely available natural sources (orange juice and milk), opening the possibility of applying a broad portfolio of natural raw materials.
 - Heating time (the main process parameter) could be optimized for each raw material to obtain lower particle dimensions and a consequent increase on the fluorescence intensity.
 - This optimization would be particularly important for the milk-derived materials, which showed high diameters possibly caused by a heating time excessively large for their total organic content.
- It is not possible to affirm that there is a best solution for obtaining CDs. Each material may be better for a given situation (for instance, there may be differences in the availability of raw materials). On the other hand, since the orange juice derived dots are rich in carboxylic groups and show high intensity of emission, they are promising for use in applications that explore the chemistry of the -COOH groups, like the formation of silica-CDs nanocomposites (the Silica-Cdots synthesis, for example, was based on the bonding between -COOH groups from α -CDs and the amine groups from a-SiO₂).
 - This bounding of CDs to silica can be used to fabricate nanocomposites with applications on sensors and on the fabrication of fluorescent dyes for anti-counterfeiting.
- An efficient methodology for the fabrication of biodegradable, biocompatible, and fluorescent cylindrical waveguides doped with hybrid amorphous nanoparticles (silica-Cdots) was demonstrated. Hybrids are easier to handle than non-coupled carbon nanodots, since they are less hygroscopic. Therefore, they are more adequate for the fabrication of large volumes of agarose waveguides.
 - Both the aqueous dispersion of silica-Cdots and the hydrogel-based waveguide with occluded hybrids showed sensitivity and reversible behavior regarding the pH.
 - Since the pH information is retrieved when the waveguide is removed from the aqueous medium, the system offers a low-cost, disposable, and simplified pH sensor that can be used on multi-parameter biomedical analysis.

- Since the proposed sensor is made of an elastomeric material (the hydrogel), it presents higher tenacity than the commercial glass devices, with lower risks of mechanical fracture.
- The hybrids could be very interesting as new materials for applications in optoelectronic devices, optical fibers sensors, and solar cells. Thus, suggestions for forthcoming studies include the exploration of the direct coupling between carboxylic acid terminated carbon nanodots and the amino functionalized silica surface of no-core optical fibers for the fabrication of a fluorescent cladding with sensing applications on media of different polarities.
- Three typologies of carbon nanodots (NCNDs, α -CDs and Silica-Cdots hybrids) were applied to the fabrication of fluorescent PMMA optical films. The films significantly enhance the PMMA's natural fluorescence and allow the conversion of a wider UV window to visible, increasing solar cells' efficiencies.
 - Initial testing showed an 11.3% increase in efficiency by employing fluorescent films, even in non-optimized conditions. When compared to the power obtained with regular panels, this gain would be translated in up to 10.3% of land use reduction. Also, doped PMMA films will help protect the cell against UV-induced degradation on the passivation layers, increasing the lifespan of panels and leading to reduced maintenance costs.
 - Upcoming works should focus on optimizing the usage of α -CDs (that present the highest UV-to-Visible conversion) as the standard for fluorescent film fabrication.
 - Since these nanoparticles are formed by thermolysis in simple muffles, they are particularly adequate for large-scale manufacturing.
 - Methodologies for direct coating the cells with doped films will also be investigated to eliminate the extra dielectric layer (air gaps) and to minimize reflection losses. Potential avenues to accomplish this are drop-casting the PMMA-CDs chloroform solutions directly on the cell's surface and spin-coating.
- A TFBG-based optical fiber sensor was designed for measuring the flow velocity in biphasic flows. The sensor successfully assessed samples comprised of water, oil, and air transported through a millifluidic device.
 - By using a single-wavelength interrogation scheme, it is possible to assess the velocity of the dispersed phase in real-time, yielding maximum relative error of 4.4% in comparison to a concomitant optical tracking measurement.
 - Depending on the system being assessed, the interrogation wavelength may be adjusted for increasing the sensitivity regarding the specific chemicals flowing through the device.
 - Despite the promising results, further investigation should be conducted regarding non-periodic and other flow regimes which may produce complex intensity patterns. In such cases, time frequency analysis and machine learning algorithms are techniques that can be used to retrieve the flow characteristics.

- A portable and low-cost smartphone-based optical fiber sensor based on Fresnel reflectance was used for the monitoring of bioreactors. Also, an application for processing the images collected through the phone's camera was designed.
 - The smartphone sensor's production costs are considerably low, and the sensor can be manufactured on-site by 3D-printing. So, it can be easily integrated into an industrial line.
 - The integration to the line is of major importance for the "*Industry 4.0*" concept, making the smartphone setup interesting for field and manufacturing applications.
 - Suggestions for future works include the enhancement of the sensitivity of the sensor and the testing of its performance under higher fermentation scales and in more complex systems. The smartphone processing could be also applied to the interrogation of specialty fibers and other chemical sensors.
- Finally, an optical fiber sensor based on DLS and Fresnel reflectance was successfully applied to the monitoring of a multi-concentrated particulate system (silica nanofluids).
 - The information collected with the system were used to retrieve actual concentration values that were considerably different from those estimated by the simple sedimentation model traditionally applied to Chemical Engineering practice. The more precise information could save fabrication costs and allow the obtention of more efficient facilities.
- A DLS sensor based on an ANN-regressor was demonstrated for the simultaneous evaluation of concentration and flow velocity of nanofluids.
 - Considering the low amount of available data, the process known as "*leave-one-out*" was used with 10 folds for training a low-biased and highly-accurate estimator. Also, the architecture of the ANN was kept very simple to prevent overfitting.
 - A powerful model was needed for accounting for the non-linear relation between decay rate, velocity and particles concentration.
 - So, the algorithm used here is a hybrid model consisting of a physics-informed neural network: the data fed to the network is not the raw optical data itself, but a pre-processed and transformed information derived from the autocorrelation function and from the physical principles of DLS.
 - The use of more precise instrumentation for controlling the flow rate (with consequent noise reduction) and the collection and processing of a larger dataset (containing more data points and wider ranges of concentration and flow speed values) would allow the training with more powerful architectures like convolutional or recurrent neural networks. Such architectures are more adequate for modelling time-series data.
 - A final suggestion for future works is the application of this optical system to other nanoparticles and inline processes. Metals, mining, traditional chemical and petrochemical facilities and advanced biotechnological, biomedical and food industries could leverage the sensor for controlling and monitoring their operation.

5. References

ABEDIN, Kazi S.; FINI, John M.; THIERRY, Taunay F.; ZHU, Benyuan; YAN, Man F.; BANSAL, Lalit; DIMARCELLO, Frank V.; MONBERG, Eric M.; DIGIOVANNI, David J. Seven-core erbium-doped double-clad fiber amplifier pumped simultaneously by side-coupled multimode fiber. **Optics Letters**, *[S. l.]*, v. 39, n. 4, p. 993, 2014. DOI: 10.1364/OL.39.000993. Disponível em: https://opg.optica.org/abstract.cfm?URI=ol-39-4-993.

Aerosil 300 Technical Datasheet. [s.d.]. Disponível em: https://www.productcenter.coatingadditives.com/pdf/daten/engl/AEROSIL_300.pdf. Acesso em: 20 dez. 2019.

AFFONSO NETTO, Rafael; MENEZES, Fabrícia Faria De; MACIEL FILHO, Rubens; BARTOLI, Julio Roberto. Poly(methyl methacrylate) and silica nanocomposites as new materials for polymeric optical devices. **Polímeros**, *[S. l.]*, v. 32, n. 3, 2022. DOI: 10.1590/0104-1428.20220009. Disponível em: http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0104-14282022000300407&tlng=en.

AHMED, H.; KENNEDY, M.; CONFREY, T.; DORAN, J.; MCCORMACK, S. J.; GALINDO, S.; SÁNCHEZ, C. Voz; GONZÁLEZ, J. Puigdollers. Lumogen Violet Dye as Luminescent Down-Shifting Layer for c-Silicon Solar Cells. *In*: 27TH EUROPEAN PHOTOVOLTAIC SOLAR ENERGY CONFERENCE AND EXHIBITION 2012, **Anais** [...]. [s.l: s.n.] p. 311–313. DOI: 10.4229/27thEUPVSEC2012-1BV.7.20. Disponível em: https://www.eupvsec-proceedings.com/proceedings?paper=15345.

ALBALADEJO-SIGUAN, Miguel; BAIRD, Elizabeth C.; BECKER-KOCH, David; LI, Yanxiu; ROGACH, Andrey L.; VAYNZOF, Yana. Stability of Quantum Dot Solar Cells: A Matter of (Life)Time. Advanced Energy Materials, [S. 1.], v. 11, n. 12, p. 2003457, 2021. DOI: 10.1002/aenm.202003457. Disponível em: https://onlinelibrary.wiley.com/doi/10.1002/aenm.202003457.

ALBERT, Jacques; SHAO, Li-Yang; CAUCHETEUR, Christophe. Tilted fiber Bragg grating sensors. Laser & Photonics Reviews, [S. l.], v. 7, n. 1, p. 83–108, 2013. DOI: 10.1002/lpor.201100039. Disponível em: https://onlinelibrary.wiley.com/doi/10.1002/lpor.201100039. ALEXANDRE, Michael; DUBOIS, Philippe. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. **Materials Science and Engineering: R: Reports**, [S. l.], v. 28, n. 1–2, p. 1–63, 2000. DOI: 10.1016/S0927-796X(00)00012-7. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0927796X00000127.

ALI, Umar; KARIM, Khairil Juhanni Bt. Abd; BUANG, Nor Aziah. A Review of the Properties and Applications of Poly (Methyl Methacrylate) (PMMA). **Polymer Reviews**, *[S. l.]*, v. 55, n. 4, p. 678–705, 2015. DOI: 10.1080/15583724.2015.1031377. Disponível em: http://www.tandfonline.com/doi/full/10.1080/15583724.2015.1031377.

AMATO, Francesco; CACIOPPO, Michele; ARCUDI, Francesca; PRATO, Maurizio; MITUO, Melina; FERNANDES, Elizabeth G.; CARREÑO, Marcelo N. P.; PEREYRA, Inés; BARTOLI, Julio R. Nitrogen-Doped Carbon Nanodots/PMMA Nanocomposites for Solar Cells Applications. **Chemical Engineering Transactions**, *[S. l.]*, v. 74, p. 1105–1110, 2019. DOI: 10.3303/CET1974185. Disponível em: https://www.aidic.it/cet/19/74/185.pdf.

AMATO, Francesco; SOARES, Marco César Prado; CABRAL, Thiago Destri; FUJIWARA, Eric; CORDEIRO, Cristiano Monteiro de Barros; CRIADO, Alejandro; PRATO, Maurizio; BARTOLI, Julio Roberto. Agarose-Based Fluorescent Waveguide with Embedded Silica Nanoparticle–Carbon Nanodot Hybrids for pH Sensing. **ACS Applied Nano Materials**, *[S. l.]*, v. 4, n. 9, p. 9738–9751, 2021. DOI: 10.1021/acsanm.1c02127. Disponível em: https://pubs.acs.org/doi/10.1021/acsanm.1c02127.

AMRANI, F.; HABOUCHA, A.; SALHI, M.; LEBLOND, H.; KOMAROV, A.; GRELU, Ph.; SANCHEZ, F. Passively mode-locked erbium-doped double-clad fiber laser operating at the 322nd harmonic. **Optics Letters**, *[S. l.]*, v. 34, n. 14, p. 2120, 2009. DOI: 10.1364/OL.34.002120. Disponível em: https://opg.optica.org/abstract.cfm?URI=ol-34-14-2120.

AN, Jia; CHEN, Rubing; CHEN, Meizhu; HU, Yongqin; LYU, Ying; LIU, Yufei. An Ultrasensitive Turn-On Ratiometric Fluorescent Probes for Detection of Ag+ Based On Carbon Dots/SiO2 and Gold Nanoclusters. **Sensors and Actuators B: Chemical**, *[S. l.]*, n. July, p. 129097, 2020. DOI: 10.1016/j.snb.2020.129097. Disponível em: https://doi.org/10.1016/j.snb.2020.129097.

AN, Yanqing; CHEN, Miao; XUE, Qunji; LIU, Weimin. Preparation and self-assembly of carboxylic acid-functionalized silica. **Journal of Colloid and Interface Science**, *[S. l.]*, v. 311, n. 2, p. 507–513, 2007. DOI: 10.1016/j.jcis.2007.02.084. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0021979707002639.

ANGELI, P.; HEWITT, G. .. Flow structure in horizontal oil-water flow. InternationalJournal of Multiphase Flow, [S. l.], v. 26, n. 7, p. 1117–1140, 2000. DOI: 10.1016/S0301-9322(99)00081-6.Disponívelhttps://linkinghub.elsevier.com/retrieve/pii/S0301932299000816.

ANNA, Shelley Lynn. Droplets and Bubbles in Microfluidic Devices. **Annual Review of Fluid Mechanics**, *[S. l.]*, v. 48, n. 1, p. 285–309, 2016. DOI: 10.1146/annurev-fluid-122414-034425. Disponível em: https://www.annualreviews.org/doi/10.1146/annurev-fluid-122414-034425.

ARCUDI, Francesca; ĎORĎEVIĆ, Luka; PRATO, Maurizio. Design, Synthesis, and Functionalization Strategies of Tailored Carbon Nanodots. Accounts of Chemical Research, *[S. l.]*, v. 52, n. 8, p. 2070–2079, 2019. DOI: 10.1021/acs.accounts.9b00249.

ARCUDI, Francesca; ĐORĐEVIĆ, Luka; PRATO, Maurizio. Synthesis, Separation, and Characterization of Small and Highly Fluorescent Nitrogen-Doped Carbon NanoDots. **Angewandte Chemie International Edition**, *[S. l.]*, v. 55, n. 6, p. 2107–2112, 2016. DOI: 10.1002/ange.201510158. Disponível em: http://doi.wiley.com/10.1002/anie.201510158.

ARCUDI, Francesca; ĐORĐEVIĆ, Luka; PRATO, Maurizio. Rationally Designed Carbon Nanodots towards Pure White-Light Emission. **Angewandte Chemie International Edition**, *[S. l.]*, v. 56, n. 15, p. 4170–4173, 2017. DOI: 10.1002/anie.201612160. Disponível em: http://doi.wiley.com/10.1002/anie.201612160.

ARCUDI, Francesca; ĐORĐEVIĆ, Luka; PRATO, Maurizio. Design, Synthesis, and Functionalization Strategies of Tailored Carbon Nanodots. Accounts of Chemical Research, *[S. l.]*, v. 52, n. 8, p. 2070–2079, 2019. DOI: 10.1021/acs.accounts.9b00249. Disponível em: https://pubs.acs.org/doi/10.1021/acs.accounts.9b00249.

ARISTILDE, Stenio; CORDEIRO, Cristiano M. B.; OSÓRIO, Jonas H. Gasoline Quality Sensor Based on Tilted Fiber Bragg Gratings. **Photonics**, *[S. l.]*, v. 6, n. 2, p. 51, 2019. DOI: 10.3390/photonics6020051. Disponível em: https://www.mdpi.com/2304-6732/6/2/51.

ARISTILDE, Stenio; RODRIGUES, Gildo; FRUETT, Fabiano; CORDEIRO, Cristiano M. B. B. Optofluidic Device based on a 3D Printed Chip and a Sensing Tilted Fiber Bragg Gratings. *In*: 2018 SBFOTON INTERNATIONAL OPTICS AND PHOTONICS CONFERENCE (SBFOTON IOPC) 2018, **Anais** [...]. : IEEE, 2018. p. 1–4. DOI: 10.1109/SBFoton-IOPC.2018.8610934. Disponível em: https://ieeexplore.ieee.org/document/8610934/.

ARISTILDE, Stenio; SOARES, Marco Cesar Prado; CABRAL, Thiago D.; RODRIGUES, Gildo; FUJIWARA, Eric; FRUETT, Fabiano; CORDEIRO, Cristiano M. B. Measurement of Multiphase Flow by Tilted Optical Fiber Bragg Grating Sensor. **IEEE Sensors Journal**, *[S. l.]*, v. 21, n. 2, p. 1534–1539, 2021. DOI: 10.1109/JSEN.2020.3016616. Disponível em: https://ieeexplore.ieee.org/document/9166562/.

ASTM E70-19. Standard Test Method for pH of Aqueous Solutions With the Glass Electrode. West Conshohocken, PA, USA: ASTM International, 2019. DOI: 10.1520/E0070-07.2.

ASTRUC, Didier; ORNELAS, Cátia; RUIZ, Jaime. Dendritic Molecular Electrochromic Batteries Based on Redox-Robust Metallocenes. **Chemistry - A European Journal**, *[S. l.]*, v. 15, n. 36, p. 8936–8944, 2009. DOI: 10.1002/chem.200901294. Disponível em: https://onlinelibrary.wiley.com/doi/10.1002/chem.200901294.

BAILEY, J.; OLLIS, D. **Biochemical Engineering Fundamentals**. New York City, NY, USA: McGraw-Hill, 1986.

BAKER, Sheila N.; BAKER, Gary A. Luminescent Carbon Nanodots: Emergent Nanolights. **Angewandte Chemie International Edition**, *[S. l.]*, v. 49, n. 38, p. 6726–6744, 2010. DOI: 10.1002/anie.200906623. Disponível em: https://onlinelibrary.wiley.com/doi/10.1002/anie.200906623.

BANO, Daraksha; KUMAR, Vijay; SINGH, Vikas Kumar; CHANDRA, Subhash; SINGH, Devendra Kumar; YADAV, Pradeep Kumar; TALAT, Mahe; HASAN, Syed Hadi. A Facile and Simple Strategy for the Synthesis of Label Free Carbon Quantum Dots from the latex of Euphorbia milii and Its Peroxidase-Mimic Activity for the Naked Eye Detection of Glutathione in a Human Blood Serum. **ACS Sustainable Chemistry & Engineering**, *[S. l.]*, v. 7, n. 2, p. 1923–1932, 2019. DOI: 10.1021/acssuschemeng.8b04067. Disponível em: https://pubs.acs.org/doi/10.1021/acssuschemeng.8b04067.

BARIK, Puspendu; PRADHAN, Manik. Plasmonic luminescent solar concentrator. **Solar Energy**, *[S. l.]*, v. 216, p. 61–74, 2021. DOI: 10.1016/j.solener.2021.01.018. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0038092X21000347.

BAROUD, Charles N.; GALLAIRE, Francois; DANGLA, Rémi. Dynamics of microfluidic droplets. Lab on a Chip, [S. l.], v. 10, n. 16, p. 2032, 2010. DOI: 10.1039/c001191f. Disponível em: http://xlink.rsc.org/?DOI=c001191f.

BARTOLOMEI, Beatrice; DOSSO, Jacopo; PRATO, Maurizio. New trends in nonconventional carbon dot synthesis. **Trends in Chemistry**, *[S. l.]*, v. 3, n. 11, p. 943–953, 2021. DOI: 10.1016/j.trechm.2021.09.003. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S2589597421001945.

BEADIE, G.; BRINDZA, Michael; FLYNN, Richard A.; ROSENBERG, A.; SHIRK, James S. Refractive index measurements of poly(methyl methacrylate) (PMMA) from 04–16 μm. **Applied Optics**, *[S. l.]*, v. 54, n. 31, p. F139, 2015. DOI: 10.1364/AO.54.00F139. Disponível em: https://opg.optica.org/abstract.cfm?URI=ao-54-31-F139.

BEGANSKIENĖ, A.; SIRUTKAITIS, V.; KURTINAITIENĖ, M.; JUŠKĖNAS, R.; KAREIVA, A. FTIR, TEM and NMR linvestigations of Stöber Silica Nanoparticles. **Materials** Science, *[S. l.]*, v. 10, n. 4, p. 287–290, 2004.

BELTRÁN-MEJÍA, Felipe; CORDEIRO, Cristiano M. B.; ANDRÉS, Pedro; SILVESTRE, Enrique. Broadband dispersion compensation using inner cladding modes in photonic crystal fibers. **Optics Express**, *[S. l.]*, v. 20, n. 4, p. 3467, 2012. DOI: 10.1364/OE.20.003467. Disponível em: https://opg.optica.org/oe/abstract.cfm?uri=oe-20-4-3467.

BERNE, B. J.; PECORA, R. Dynamic Light Scattering with Applications to Chemistry, Biology and Physics. Hoboken, NJ, USA: John Wiley and Sons, 1976.

BOAKYE-YIADOM, Kofi Oti et al. Carbon dots: Applications in bioimaging and theranostics.International Journal of Pharmaceutics, [S. l.], v. 564, p. 308–317, 2019. DOI:10.1016/j.ijpharm.2019.04.055.Disponívelhttps://linkinghub.elsevier.com/retrieve/pii/S037851731930314X.

BOHIDAR, Himadri B.; JENA, Sidhartha S. Kinetics of sol-gel transition in thermoreversible gelation of gelatin. **The Journal of Chemical Physics**, *[S. l.]*, v. 98, n. 11, p. 8970–8977, 1993.

DOI: 10.1063/1.464456. Disponível em: http://aip.scitation.org/doi/10.1063/1.464456.

BOOBALAN, T.; SETHUPATHI, M.; SENGOTTUVELAN, N.; KUMAR, Ponnuchamy; BALAJI, P.; GULYÁS, Balázs; PADMANABHAN, Parasuraman; SELVAN, Subramanian Tamil; ARUN, A. Mushroom-Derived Carbon Dots for Toxic Metal Ion Detection and as Antibacterial and Anticancer Agents. **ACS Applied Nano Materials**, *[S. l.]*, v. 3, n. 6, p. 5910– 5919, 2020. DOI: 10.1021/acsanm.0c01058.

BOTTRILL, Melanie; GREEN, Mark. Some aspects of quantum dot toxicity. **Chemical Communications**, *[S. l.]*, v. 47, n. 25, p. 7039, 2011. DOI: 10.1039/c1cc10692a. Disponível em: http://xlink.rsc.org/?DOI=c1cc10692a.

BOUKNAITIR, Ilham; PANNIELLO, Annamaria; TEIXEIRA, Silvia Soreto; KREIT, Lamyaa; CORRICELLI, Michela; STRICCOLI, Marinella; COSTA, Luis Cadillon; ACHOUR, Mohamed Essaid. Optical and dielectric properties of PMMA (poly(methyl methacrylate))/carbon dots composites. **Polymer Composites**, *[S. l.]*, v. 40, n. S2, p. E1312–E1319, 2019. DOI: 10.1002/pc.24977. Disponível em: https://onlinelibrary.wiley.com/doi/10.1002/pc.24977.

BRESSANIN, Jéssica M.; ASSIS JÚNIOR, Valdir A.; BARTOLI, Julio R. Electrically conductive nanocomposites of PMMA and carbon nanotubes prepared by in situ polymerization under probe sonication. **Chemical Papers**, *[S. l.]*, v. 72, n. 7, p. 1799–1810, 2018. DOI: 10.1007/s11696-018-0443-5. Disponível em: http://link.springer.com/10.1007/s11696-018-0443-5.

BROUWER, Albert M. Standards for photoluminescence quantum yield measurements in solution (IUPAC Technical Report). **Pure and Applied Chemistry**, *[S. l.]*, v. 83, n. 12, p. 2213–2228, 2011. DOI: 10.1351/PAC-REP-10-09-31. Disponível em: https://www.degruyter.com/document/doi/10.1351/PAC-REP-10-09-31/html.

BUREY, P.; BHANDARI, B. R.; HOWES, T.; GIDLEY, M. J. Hydrocolloid gel particles: Formation, characterization, and application. **Critical Reviews in Food Science and Nutrition**, *[S. l.]*, v. 48, n. 5, p. 361–377, 2008. DOI: 10.1080/10408390701347801.

BUSINESS, Sustainable. How Much Land Does it Take to Produce Solar Energy for 1000 Homes? 2013. Disponível em: https://www.sustainablebusiness.com/2013/08/how-muchland-does-it-take-to-produce-solar-energy-for-1000-homes-51784/. Acesso em: 12 mar. 2023.

CABRAL, Thiago D.; DA SILVA, Luiz E.; FUJIWARA, Eric; NG, Alson K. L.; EBENDORFF-HEIDEPRIEM, Heike; CORDEIRO, Cristiano M. B. Reusable polymer optical fiber strain sensor with memory capability based on ABS crazing. **Applied Optics**, *[S. l.]*, v. 58, n. 36, p. 9870, 2019. DOI: 10.1364/AO.58.009870. Disponível em: https://opg.optica.org/abstract.cfm?URI=ao-58-36-9870.

CACIOPPO, Michele; SCHARL, Tobias; ĐORĐEVIĆ, Luka; CADRANEL, Alejandro; ARCUDI, Francesca; GULDI, Dirk M.; PRATO, Maurizio. Symmetry-Breaking Charge-Transfer Chromophore Interactions Supported by Carbon Nanodots. **Angewandte Chemie -International Edition**, *[S. l.]*, v. 59, n. 31, p. 12779–12784, 2020. DOI: 10.1002/anie.202004638.

CADRANEL, Alejandro et al. Screening Supramolecular Interactions between Carbon Nanodots and Porphyrins. **Journal of the American Chemical Society**, *[S. l.]*, v. 140, n. 3, p. 904–907, 2018. DOI: 10.1021/jacs.7b12434. Disponível em: https://pubs.acs.org/doi/10.1021/jacs.7b12434.

CADRANEL, Alejandro; MARGRAF, Johannes T.; STRAUSS, Volker; CLARK, Timothy; GULDI, Dirk M. Carbon Nanodots for Charge-Transfer Processes. Accounts of Chemical Research, *[S. l.]*, v. 52, n. 4, p. 955–963, 2019. DOI: 10.1021/acs.accounts.8b00673. Disponível em: https://pubs.acs.org/doi/10.1021/acs.accounts.8b00673.

CAMPIGLIO, Chiara Emma; CONTESSI NEGRINI, Nicola; FARÈ, Silvia; DRAGHI, Lorenza. Cross-Linking Strategies for Electrospun Gelatin Scaffolds. **Materials**, *[S. l.]*, v. 12, n. 15, p. 2476, 2019. DOI: 10.3390/ma12152476. Disponível em: https://www.mdpi.com/1996-1944/12/15/2476.

CANNAS, Marco; CAMARDA, Pietro; VACCARO, Lavinia; AMATO, Francesco; MESSINA, Fabrizio; FIORE, Tiziana; AGNELLO, Simonpietro; GELARDI, Franco Mario. Luminescence Efficiency of Si/SiO 2 Nanoparticles Produced by Laser Ablation. **physica status solidi (a)**, *[S. l.]*, v. 216, n. 3, p. 1800565, 2019. DOI: 10.1002/pssa.201800565. Disponível em: https://onlinelibrary.wiley.com/doi/abs/10.1002/pssa.201800565.

CAO, Li et al. Carbon dots for multiphoton bioimaging. Journal of the American Chemical

Society, /S. l.], v. 129, n. 37, p. 11318–11319, 2007. DOI: 10.1021/ja0735271.

CARDONA-MAYA, Yamile; SOCORRO, Abian B.; DEL VILLAR, Ignacio; CRUZ, José Luis; CORRES, Jesus M.; BOTERO-CADAVID, Juan F. Label-free wavelength and phase detection based SMS fiber immunosensors optimized with cladding etching. **Sensors and Actuators, B: Chemical**, *[S. l.]*, v. 265, p. 10–19, 2018. DOI: 10.1016/j.snb.2018.03.002. Disponível em: https://doi.org/10.1016/j.snb.2018.03.002.

CARLOS, Luiz; OLITTA, Thiago; NITSCHE, Saul. Ethanol Production in Brazil: The Industrial Process and Its Impact on Yeast Fermentation. *In*: **Biofuel Production-Recent Developments and Prospects**. [s.l.] : InTech, 2011. DOI: 10.5772/17047. Disponível em: http://www.intechopen.com/books/biofuel-production-recent-developments-and-prospects/ethanol-production-in-brazil-the-industrial-process-and-its-impact-on-yeast-fermentation.

CARR, R. J. G. Fibre optic sensors for the characterization of particle size and flow velocity. **Sensors and Actuators A: Physical**, *[S. l.]*, v. 23, n. 1–3, p. 1111–1117, 1990. DOI: 10.1016/0924-4247(90)87098-4. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/0924424790870984.

CASAMASSIMA, M.; DARQUE-CERETTI, E.; DELAMARE, F.; AUCOUTURIER, M. C. R. Characterization by XPS of electron donor/acceptor properties of aluminum and silicon oxyde surfaces. Acad. Sci. Ser. II, *[S. l.]*, v. 313, p. 25–30, 1991.

CENNAMO, Nunzio; CHIAVAIOLI, Francesco; TRONO, Cosimo; TOMBELLI, Sara; GIANNETTI, Ambra; BALDINI, Francesco; ZENI, Luigi. A complete optical sensor system based on a POF-SPR platform and a thermo-stabilized flow cell for biochemical applications. **Sensors (Switzerland)**, *[S. l.]*, v. 16, n. 2, 2016. DOI: 10.3390/s16020196.

CÉSAR PRADO SOARES, Marco; SANTOS RODRIGUES, Matheus; ALEXANDRE SCHENKEL, Egont; PERLI, Gabriel; HIDEAK ARITA SILVA, Willian; KAUÊ GOMES, Matheus; FUJIWARA, Eric; KENICHI SUZUKI, Carlos. Evaluation of Silica Nanofluids in Static and Dynamic Conditions by an Optical Fiber Sensor. **Sensors**, *[S. l.]*, v. 20, n. 3, p. 707, 2020. DOI: 10.3390/s20030707. Disponível em: https://www.mdpi.com/1424-8220/20/3/707.

CHANDRA, Subhash; SINGH, Vikas Kumar; YADAV, Pradeep Kumar; BANO, Daraksha;

KUMAR, Vijay; PANDEY, Vinay Kumar; TALAT, Mahe; HASAN, Syed Hadi. Mustard seeds derived fluorescent carbon quantum dots and their peroxidase-like activity for colorimetric detection of H 2 O 2 and ascorbic acid in a real sample. **Analytica Chimica Acta**, *[S. l.]*, v. 1054, n. January, p. 145–156, 2019. DOI: 10.1016/j.aca.2018.12.024.

CHEN, Bing; XIE, Hongzhen Houpeng; WANG, Sui; GUO, Zhiyong; HU, Yufang; XIE, Hongzhen Houpeng. UV light-tunable fluorescent inks and polymer hydrogel films based on carbon nanodots and lanthanide for enhancing anti-counterfeiting. **Luminescence**, *[S. l.]*, v. 34, n. 4, p. 437–443, 2019. DOI: 10.1002/bio.3636. Disponível em: https://onlinelibrary.wiley.com/doi/10.1002/bio.3636.

CHEN, Gang; YU, Wenhua; SINGH, Dileep; COOKSON, David; ROUTBORT, Jules. Application of SAXS to the study of particle-size-dependent thermal conductivity in silica nanofluids. **Journal of Nanoparticle Research**, *[S. l.]*, v. 10, n. 7, p. 1109–1114, 2008. DOI: 10.1007/s11051-007-9347-y. Disponível em: http://link.springer.com/10.1007/s11051-007-9347-y.

CHEN, Yinyin et al. Green and high-yield synthesis of carbon dots for ratiometric fluorescent determination of pH and enzyme reactions. **Materials Science and Engineering C**, *[S. l.]*, v. 117, n. April, p. 111264, 2020. DOI: 10.1016/j.msec.2020.111264. Disponível em: https://doi.org/10.1016/j.msec.2020.111264.

CHEN, Z. J.; GRUDININ, A. B.; PORTA, J.; MINELLY, J. D. Enhanced Q switching in double-clad fiber lasers. **Optics Letters**, *[S. l.]*, v. 23, n. 6, p. 454, 1998. DOI: 10.1364/OL.23.000454. Disponível em: https://opg.optica.org/abstract.cfm?URI=ol-23-6-454.

CHEN, Zhongping; MILNER, Thomas E.; DAVE, Digant; NELSON, J. Stuart. Optical Doppler tomographic imaging of fluid flow velocity in highly scattering media. **Optics Letters**, *[S. l.]*, v. 22, n. 1, p. 64, 1997. DOI: 10.1364/OL.22.000064. Disponível em: https://opg.optica.org/abstract.cfm?URI=ol-22-1-64.

CHIN, L. K.; LIU, A. Q.; ZHANG, J. B.; LIM, C. S.; SOH, Y. C. An on-chip liquid tunable grating using multiphase droplet microfluidics. **Applied Physics Letters**, *[S. l.]*, v. 93, n. 16, p. 164107, 2008. DOI: 10.1063/1.3009560. Disponível em: http://aip.scitation.org/doi/10.1063/1.3009560.

CHOI, Myunghwan; CHOI, Jin Woo; KIM, Seonghoon; NIZAMOGLU, Sedat; HAHN, Sei Kwang; YUN, Seok Hyun. Light-guiding hydrogels for cell-based sensing and optogenetic synthesis in vivo. **Nature Photonics**, *[S. l.]*, v. 7, n. 12, p. 987–994, 2013. DOI: 10.1038/nphoton.2013.278.

CHOI, Myunghwan; HUMAR, Matjaž; KIM, Seonghoon; YUN, Seok Hyun. Step-Index Optical Fiber Made of Biocompatible Hydrogels. Advanced Materials, [S. l.], v. 27, n. 27, p. 4081–4086, 2015. DOI: 10.1002/adma.201501603.

CHOI, Yujin; JO, Seongho; CHAE, Ari; KIM, Young Kwang; PARK, Jeong Eun; LIM, Donggun; PARK, Sung Young; IN, Insik. Simple Microwave-Assisted Synthesis of Amphiphilic Carbon Quantum Dots from A 3 /B 2 Polyamidation Monomer Set. **ACS Applied Materials & Interfaces**, *[S. l.]*, v. 9, n. 33, p. 27883–27893, 2017. DOI: 10.1021/acsami.7b06066. Disponível em: https://pubs.acs.org/doi/10.1021/acsami.7b06066.

CHOWDHURY, D. P.; SORENSEN, C. M.; TAYLOR, T. W.; MERKLIN, J. F.; LESTER, T. W. Application of photon correlation spectroscopy to flowing Brownian motion systems. **Applied Optics**, *[S. l.]*, v. 23, n. 22, p. 4149, 1984. DOI: 10.1364/AO.23.004149. Disponível em: https://opg.optica.org/abstract.cfm?URI=ao-23-22-4149.

CHUNG, In; LEE, Byunghong; HE, Jiaqing; CHANG, Robert P. H.; KANATZIDIS, Mercouri G. All-solid-state dye-sensitized solar cells with high efficiency. Nature, [S. l.], v. 485, n. 7399, p. 486–489, 2012. DOI: 10.1038/nature11067. Disponível em: http://www.nature.com/articles/nature11067.

CIPELLETTI, Luca; WEITZ, D. A. Ultralow-angle dynamic light scattering with a charge coupled device camera based multispeckle, multitau correlator. **Review of Scientific Instruments**, *[S. l.]*, v. 70, n. 8, p. 3214–3221, 1999. DOI: 10.1063/1.1149894. Disponível em: http://aip.scitation.org/doi/10.1063/1.1149894.

COLOMBO, Marco; FAIRWEATHER, Michael. Multiphase turbulence in bubbly flows: RANS simulations. **International Journal of Multiphase Flow**, [S. l.], v. 77, p. 222–243, 2015. DOI: 10.1016/j.ijmultiphaseflow.2015.09.003. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0301932215002013.

CORDEIRO, Cristiano M. B.; NG, Alson K. L.; EBENDORFF-HEIDEPRIEM, Heike. Ultra-

simplified Single-Step Fabrication of Microstructured Optical Fiber. **Scientific Reports**, *[S. l.]*, v. 10, n. 1, p. 9678, 2020. DOI: 10.1038/s41598-020-66632-3. Disponível em: https://www.nature.com/articles/s41598-020-66632-3.

CORDEIRO, Cristiano Monteiro de Barros; ARISTILDE, Stenio; SOARES, Marco César Prado; FUJIWARA, Eric; RODRIGUES, Gildo Santos; FRUETT, Fabiano. Sistema Óptico Para Caracterização de Escoamento Multifásico em Tubulações e Processo de Análise de Tubulações para a Caracterização de Escoamento Multifásico, BR1020190209666, 2019.

CORSARO, Carmelo; NERI, Giulia; SANTORO, Antonio; FAZIO, Enza. Acrylate and Methacrylate Polymers' Applications: Second Life with Inexpensive and Sustainable Recycling Approaches. **Materials**, *[S. l.]*, v. 15, n. 1, p. 282, 2021. DOI: 10.3390/ma15010282. Disponível em: https://www.mdpi.com/1996-1944/15/1/282.

DAS, Rashmita; BANDYOPADHYAY, Rajib; PRAMANIK, Panchanan. Carbon quantum dots from natural resource: A review. **Materials Today Chemistry**, *[S. l.]*, v. 8, p. 96–109, 2018. DOI: 10.1016/j.mtchem.2018.03.003. Disponível em: https://doi.org/10.1016/j.mtchem.2018.03.003.

DAVID, Nigel; DJILALI, Ned; WILD, Peter. Fiber Bragg grating sensor for two-phase flow in microchannels. **Microfluidics and Nanofluidics**, *[S. l.]*, v. 13, n. 1, p. 99–106, 2012. DOI: 10.1007/s10404-012-0945-3. Disponível em: http://link.springer.com/10.1007/s10404-012-0945-3.

DEVI, Ramamoorthy; DHAMODHARAN, Raghavachari. Sustainable Process for Separating Chitin and Simultaneous Synthesis of Carbon Nanodots from Shellfish Waste Using 2% Aqueous Urea Solution. **ACS Sustainable Chemistry & Engineering**, *[S. l.]*, v. 6, n. 9, p. 11313–11325, 2018. DOI: 10.1021/acssuschemeng.8b00877. Disponível em: https://pubs.acs.org/doi/10.1021/acssuschemeng.8b00877.

DJABOUROV, Madeleine. Gelation—A review. **Polymer International**, *[S. l.]*, v. 25, n. 3, p. 135–143, 1991. DOI: 10.1002/pi.4990250302. Disponível em: https://onlinelibrary.wiley.com/doi/10.1002/pi.4990250302.

DONG, Xiuli; LIANG, Weixiong; MEZIANI, Mohammed J.; SUN, Ya Ping; YANG, Liju. Carbon dots as potent antimicrobial agents. **Theranostics**, *[S. l.]*, v. 10, n. 2, p. 671–686, 2020.

DOI: 10.7150/thno.39863.

DORAN, Pauline.BioprocessEngineeringPrinciples.[s.l.]: Elsevier, 2013.DOI:10.1016/C2009-0-22348-8.Disponívelem:https://linkinghub.elsevier.com/retrieve/pii/C20090223488.

ĐORĐEVIĆ, Luka; ARCUDI, Francesca; CACIOPPO, Michele; PRATO, Maurizio. A multifunctional chemical toolbox to engineer carbon dots for biomedical and energy applications. **Nature Nanotechnology**, *[S. l.]*, v. 17, n. 2, p. 112–130, 2022. DOI: 10.1038/s41565-021-01051-7. Disponível em: https://www.nature.com/articles/s41565-021-01051-7.

ĐORĐEVIĆ, Luka; ARCUDI, Francesca; D'URSO, Alessandro; CACIOPPO, Michele; MICALI, Norberto; BÜRGI, Thomas; PURRELLO, Roberto; PRATO, Maurizio. Design principles of chiral carbon nanodots help convey chirality from molecular to nanoscale level. **Nature Communications**, *[S. l.]*, v. 9, n. 1, p. 3442, 2018. DOI: 10.1038/s41467-018-05561-2. Disponível em: http://www.nature.com/articles/s41467-018-05561-2.

ĐORĐEVIĆ, Luka; ARCUDI, Francesca; PRATO, Maurizio. Preparation, functionalization and characterization of engineered carbon nanodots. **Nature Protocols**, *[S. l.]*, v. 14, n. 10, p. 2931–2953, 2019. DOI: 10.1038/s41596-019-0207-x. Disponível em: http://www.nature.com/articles/s41596-019-0207-x.

ĐORĐEVIĆ, Luka; HAINES, Philipp; CACIOPPO, Michele; ARCUDI, Francesca; SCHARL, Tobias; CADRANEL, Alejandro; GULDI, Dirk M.; PRATO, Maurizio. Synthesis and excited state processes of arrays containing amine-rich carbon dots and unsymmetrical rylene diimides. **Materials Chemistry Frontiers**, *[S. l.]*, v. 4, n. 12, p. 3640–3648, 2020. DOI: 10.1039/D0QM00407C. Disponível em: http://xlink.rsc.org/?DOI=D0QM00407C.

DOYA, Valérie; LEGRAND, Olivier; MORTESSAGNE, Fabrice. Optimized absorption in a chaotic double-clad fiber amplifier. **Optics Letters**, *[S. l.]*, v. 26, n. 12, p. 872, 2001. DOI: 10.1364/OL.26.000872. Disponível em: https://opg.optica.org/abstract.cfm?URI=ol-26-12-872.

DUARAH, Rituparna; KARAK, Niranjan. Facile and Ultrafast Green Approach to Synthesize Biobased Luminescent Reduced Carbon Nanodot: An Efficient Photocatalyst. ACS
 Sustainable Chemistry & Engineering, [S. l.], v. 5, n. 10, p. 9454–9466, 2017. DOI:

 10.1021/acssuschemeng.7b02590.
 Disponível
 em:

 https://pubs.acs.org/doi/10.1021/acssuschemeng.7b02590.
 Engineering
 Philosofte

DUTTA, Sibasish; SARMA, Dhrubajyoti; NATH, Pabitra. Ground and river water qualitymonitoring using a smartphone-based pH sensor. AIP Advances, [S. l.], v. 5, n. 5, p. 057151,2015.DOI:10.1063/1.4921835.Disponívelhttp://aip.scitation.org/doi/10.1063/1.4921835.

EDERER, Jakub; JANOŠ, Pavel; ECORCHARD, Petra; TOLASZ, Jakub; ŠTENGL, Václav; BENEŠ, Hynek; PERCHACZ, Magdalena; POP-GEORGIEVSKI, Ognen. Determination of amino groups on functionalized graphene oxide for polyurethane nanomaterials: XPS quantitation vs. functional speciation. **RSC Advances**, *[S. l.]*, v. 7, n. 21, p. 12464–12473, 2017. DOI: 10.1039/C6RA28745J. Disponível em: http://xlink.rsc.org/?DOI=C6RA28745J.

ELLIOTT, Stacey L.; BUTERA, Robert J.; HANUS, Leo H.; WAGNER, Norman J. Fundamentals of aggregation in concentrated dispersions: Fiber-optic quasielastic light scattering and linear viscoelastic measurements. **Faraday Discussions**, *[S. l.]*, v. 123, p. 369–383, 2003. DOI: 10.1039/b204416a. Disponível em: http://xlink.rsc.org/?DOI=b204416a.

ELSHERIF, Mohamed; MOREDDU, Rosalia; HASSAN, Muhammad Umair; YETISEN, Ali K.; BUTT, Haider. Real-time optical fiber sensors based on light diffusing microlens arrays. **Lab on a Chip**, *[S. l.]*, v. 19, n. 12, p. 2060–2070, 2019. DOI: 10.1039/c9lc00242a.

ENOKSSON, P.; STEMME, G.; STEMME, E. A silicon resonant sensor structure for Coriolis mass-flow measurements. **Journal of Microelectromechanical Systems**, *[S. l.]*, v. 6, n. 2, p. 119–125, 1997. DOI: 10.1109/84.585789. Disponível em: http://ieeexplore.ieee.org/document/585789/.

EUSER, T. G.; GARBOS, M. K.; CHEN, J. S. Y.; RUSSELL, P. St. J. Precise balancing of viscous and radiation forces on a particle in liquid-filled photonic bandgap fiber. **Optics Letters**, *[S. l.]*, v. 34, n. 23, p. 3674, 2009. DOI: 10.1364/OL.34.003674. Disponível em: https://opg.optica.org/abstract.cfm?URI=oI-34-23-3674.

FAN, Long; XU, Nong; WANG, Zhiqiang; SHI, Hanchang. PDA experiments and CFD simulation of a lab-scale oxidation ditch with surface aerators. Chemical Engineering

Research and Design, *[S. l.]*, v. 88, n. 1, p. 23–33, 2010. DOI: 10.1016/j.cherd.2009.07.013. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0263876209001853.

FENG, Fu; CHEN, Wang; CHEN, Dihan; LIN, Wei; CHEN, Shih Chi. In-situ ultrasensitive label-free DNA hybridization detection using optical fiber specklegram. **Sensors and Actuators, B: Chemical**, *[S. l.]*, v. 272, n. May, p. 160–165, 2018. DOI: 10.1016/j.snb.2018.05.099. Disponível em: https://doi.org/10.1016/j.snb.2018.05.099.

FILIPPINI, Giacomo; AMATO, Francesco; ROSSO, Cristian; RAGAZZON, Giulio; VEGA-PEÑALOZA, Alberto; COMPANYÓ, Xavier; DELL'AMICO, Luca; BONCHIO, Marcella; PRATO, Maurizio. Mapping the Surface Groups of Amine-Rich Carbon Dots Enables Covalent Catalysis in Aqueous Media. **Chem**, *[S. l.]*, p. 3022–3037, 2020. DOI: 10.1016/j.chempr.2020.08.009.

FILIPPOV, V.; CHAMOROVSKII, Yu.; KERTTULA, J.; GOLANT, K.; PESSA, M.; OKHOTNIKOV, O. G. Double clad tapered fiber for high power applications. **Optics Express**, *[S. l.]*, v. 16, n. 3, p. 1929, 2008. DOI: 10.1364/OE.16.001929. Disponível em: https://opg.optica.org/oe/abstract.cfm?uri=oe-16-3-1929.

FILIPPOV, Valery; KERTTULA, Juho; CHAMOROVSKII, Yuri; GOLANT, Konstantin; OKHOTNIKOV, Oleg G. Highly efficient 750 W tapered double-clad ytterbium fiber laser. **Optics Express**, *[S. l.]*, v. 18, n. 12, p. 12499, 2010. DOI: 10.1364/OE.18.012499. Disponível em: https://opg.optica.org/oe/abstract.cfm?uri=oe-18-12-12499.

FINER, E. G.; FRANKS, F.; PHILLIPS, M. C.; SUGGETT, A. Gel formation from solutionsof single-chain gelatin. Biopolymers, [S. l.], v. 14, n. 10, p. 1995–2005, 1975. DOI:10.1002/bip.1975.360141002.Disponívelem:https://onlinelibrary.wiley.com/doi/10.1002/bip.1975.360141002.

FINSY, Robert. Particle sizing by quasi-elastic light scattering. Advances in Colloid and Interface Science, [S. l.], v. 52, p. 79–143, 1994. DOI: 10.1016/0001-8686(94)80041-3. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/0001868694800413.

FISCHER, Hartmut. Polymer nanocomposites: from fundamental research to specificapplications. Materials Science and Engineering: C, [S. l.], v. 23, n. 6–8, p. 763–772, 2003.DOI:10.1016/j.msec.2003.09.148.Disponívelem:

https://linkinghub.elsevier.com/retrieve/pii/S0928493103002054.

FOUST, A. S.; WENZEL, L. A.; CLUMP, C. W.; MAUS, L.; ANDERSEN, L. B. Principles of Unit Operations. 2nd. ed. Hoboken, NJ, USA: John Wiley and Sons, 1980.

FUJIWARA, Eric; CABRAL, Thiago D.; SATO, Miko; OKU, Hiromasa; CORDEIRO, Cristiano M. B. Agarose-based structured optical fibre. Scientific Reports, [S. l.], v. 10, n. 1, p. 7035, 2020. DOI: 10.1038/s41598-020-64103-3. Disponível em: https://www.nature.com/articles/s41598-020-64103-3.

GAN, Zhixing; XU, Hao; HAO, Yanling. Mechanism for excitation-dependent photoluminescence from graphene quantum dots and other graphene oxide derivates: consensus, debates and challenges. **Nanoscale**, *[S. l.]*, v. 8, n. 15, p. 7794–7807, 2016. DOI: 10.1039/C6NR00605A. Disponível em: http://xlink.rsc.org/?DOI=C6NR00605A.

GAO, Xiaohui; DU, Cheng; ZHUANG, Zhihua; CHEN, Wei. Carbon quantum dot-based nanoprobes for metal ion detection. Journal of Materials Chemistry C, [S. l.], v. 4, n. 29, p. 6927–6945, 2016. DOI: 10.1039/C6TC02055K. Disponível em: http://xlink.rsc.org/?DOI=C6TC02055K.

THYAGARAJAN, K. Optical Waveguides Fibers. In: GHATAK, Ajoy; and ROYCHOUDHURI, Chandrasekhar (org.). Fundamentals of Photonics. [s.l.] : SPIE: The International Society for Optics and Photonics, 2000. Disponível em: https://spie.org/publications/fundamentals-of-photonics-modules?SSO=1.

GHOSH, Trisita; DAS, Tushar Kanti; DAS, Poushali; BANERJI, Pallab; DAS, Narayan Ch. Current scenario and recent advancement of doped carbon dots: a short review scientocracy update (2013–2022). **Carbon Letters**, *[S. l.]*, v. 32, n. 4, p. 953–977, 2022. DOI: 10.1007/s42823-022-00339-5. Disponível em: https://link.springer.com/10.1007/s42823-022-00339-5.

GONÇALVES, Helena M. R.; DUARTE, Abel J.; ESTEVES DA SILVA, Joaquim C. G. Optical fiber sensor for Hg(II) based on carbon dots. **Biosensors and Bioelectronics**, *[S. l.]*, v. 26, n. 4, p. 1302–1306, 2010. DOI: 10.1016/j.bios.2010.07.018. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0956566310003933.

GONG, Chaoyang; GONG, Yuan; CHEN, Qiushu; RAO, Yun Jiang; PENG, Gang Ding; FAN,

Xudong. Reproducible fiber optofluidic laser for disposable and array applications. Lab on a Chip, [S. l.], v. 17, n. 20, p. 3431–3436, 2017. DOI: 10.1039/c7lc00708f. Disponível em: http://dx.doi.org/10.1039/C7LC00708F.

GONG, Xiao; MA, Wenwen; LI, Yunxia; ZHONG, Lingqi; LI, Wenjing; ZHAO, Xiujian. Fabrication of high-performance luminescent solar concentrators using N-doped carbon dots/PMMA mixed matrix slab. **Organic Electronics**, *[S. l.]*, v. 63, p. 237–243, 2018. DOI: 10.1016/j.orgel.2018.09.028. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S1566119918304932.

GONG, Xiao; ZHENG, Shuyang; ZHAO, Xiujian; VOMIERO, Alberto. Engineering highemissive silicon-doped carbon nanodots towards efficient large-area luminescent solar concentrators. $\int S$. *l.*], 101, 107617, 2022. DOI: Nano Energy, v. p. 10.1016/j.nanoen.2022.107617. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S2211285522006954.

GÖTZE, J.; MÖCKEL, R. Quartz: Deposits, Mineralogy and Analytics. Berlin, Germany: Springer Berlin Heidelberg, 2012.

GUO, Jinhong. Uric Acid Monitoring with a Smartphone as the Electrochemical Analyzer. **Analytical Chemistry**, [S. l.], v. 88, n. 24, p. 11986–11989, 2016. DOI: 10.1021/acs.analchem.6b04345. Disponível em: https://pubs.acs.org/doi/10.1021/acs.analchem.6b04345.

GUO, Tuan; LIU, Fu; GUAN, Bai-Ou; ALBERT, Jacques. [INVITED] Tilted fiber grating mechanical and biochemical sensors. **Optics & Laser Technology**, *[S. l.]*, v. 78, p. 19–33, 2016. DOI: 10.1016/j.optlastec.2015.10.007. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0030399215303893.

GUPTA, Vinay; CHAUDHARY, Neeraj; SRIVASTAVA, Ritu; SHARMA, Gauri Datt; BHARDWAJ, Ramil; CHAND, Suresh. Luminscent Graphene Quantum Dots for Organic Photovoltaic Devices. Journal of the American Chemical Society, [S. l.], v. 133, n. 26, p. 9960–9963, 2011. DOI: 10.1021/ja2036749. Disponível em: https://pubs.acs.org/doi/10.1021/ja2036749.

HAN, Yueying; LV, Shanshan. Synthesis of chemically crosslinked pullulan/gelatin-based

extracellular matrix-mimetic gels. International Journal of Biological Macromolecules, [S. l.], v. 122, p. 1262–1270, 2019. DOI: 10.1016/j.ijbiomac.2018.09.080. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S014181301833633X.

HASENFRATZ, David; SAUKH, Olga; STURZENEGGER, Silvan; THIELE, Lothar. Participatory Air Pollution Monitoring Using Smartphones. *In*: PROCEEDINGS OF THE 2ND INTERNATIONAL WORKSHOP ON MOBILE SENSING. MOBILE SENSING: FROM SMARTPHONES AND WEARABLES TO BIG DATA. WORKSHOP CO-LOCATED WITH IPSN '12 AND CPSWEEK 2012, Beijing, China, April 16. **Anais** [...]. Beijing, China, April 16: Academic Press, 2012. Disponível em: https://www.researchcollection.ethz.ch:443/handle/20.500.11850/50921. Acesso em: 26 nov. 2020.

HAUPTMANN, Peter; LUCKLUM, Ralf; PÜTTMER, Alf; HENNING, Bernd. Ultrasonic sensors for process monitoring and chemical analysis: state-of-the-art and trends. **Sensors and** Actuators A: Physical, [S. l.], v. 67, n. 1–3, p. 32–48, 1998. DOI: 10.1016/S0924-4247(97)01725-1. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0924424797017251.

HIDEUR, Ammar; CHARTIER, Thierry; ÖZKUL, Cafer; SANCHEZ, François. Dynamicsand stabilization of a high power side-pumped Yb-doped double-clad fiber laser. OpticsCommunications, [S. l.], v. 186, n. 4–6, p. 311–317, 2000. DOI: 10.1016/S0030-4018(00)01066-X.Disponívelem:https://linkinghub.elsevier.com/retrieve/pii/S003040180001066X.

HONSBERG, C. B.; BOWDEN, S. G. Short-Circuit Current. 2019a. Disponível em: https://www.pveducation.org/pvcdrom/solar-cell-operation/short-circuit-current. Acesso em: 24 jan. 2023.

HONSBERG, C. B.; BOWDEN, S. G. **Open-Circuit Voltage**. 2019b. Disponível em: https://www.pveducation.org/pvcdrom/solar-cell-operation/open-circuit-voltage. Acesso em: 24 jan. 2023.

HONSBERG, C. B.; BOWDEN, S. G. Fill Factor. 2019c. Disponível em: https://www.pveducation.org/pvcdrom/solar-cell-operation/fill-factor. Acesso em: 24 jan. 2023. HSIEH, Yu-Wen; WANG, An-Bang; LU, Xuan-Yi; WANG, Lon A. High-throughput on-line multi-detection for refractive index, velocity, size, and concentration measurements of microtwo-phase flow using optical microfibers. **Sensors and Actuators B: Chemical**, *[S. l.]*, v. 237, p. 841–848, 2016. DOI: 10.1016/j.snb.2016.07.027. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0925400516310619.

HUANG, Ke; LIU, Junlong; YUAN, Jianjuan; ZHAO, Wenchao; ZHAO, Kui; ZHOU, Zhihua. Perovskite-quantum dot hybrid solar cells: a multi-win strategy for high performance and stability. **Journal of Materials Chemistry A**, *[S. l.]*, v. 11, n. 9, p. 4487–4509, 2023. DOI: 10.1039/D2TA09434G. Disponível em: http://xlink.rsc.org/?DOI=D2TA09434G.

HUANG, Xinglu et al. Effect of Injection Routes on the Biodistribution, Clearance, and Tumor Uptake of Carbon Dots. **ACS Nano**, *[S. l.]*, v. 7, n. 7, p. 5684–5693, 2013. DOI: 10.1021/nn401911k. Disponível em: https://pubs.acs.org/doi/10.1021/nn401911k.

HUNTER, R. J. Foundations of Colloid Science. 2nd. ed. Oxford, UK: Oxford University Press, 2004.

ILER, R. K. The chemistry of silica. Hoboken, NJ, USA: John Wiley and Sons, 1979.

JI, Tianjiao et al. Cathode and Anode Interlayers Based on Polymer Carbon Dots via Work Function Regulation for Efficient Polymer Solar Cells. **Advanced Materials Interfaces**, *[S. l.]*, v. 5, n. 6, p. 1701519, 2018. DOI: 10.1002/admi.201701519. Disponível em: https://onlinelibrary.wiley.com/doi/10.1002/admi.201701519.

JIANG, Bei; DAI, Hailang; ZOU, Yun; CHEN, Xianfeng. Continuous detection of microparticles by fiber Bragg grating Fabry-Pérot flow cytometer. **Optics Express**, *[S. l.]*, v. 26, n. 10, p. 12579, 2018. a. DOI: 10.1364/oe.26.012579.

JIANG, Kai; WANG, Yuhui; LI, Zhongjun; LIN, Hengwei. Afterglow of carbon dots: mechanism, strategy and applications. **Materials Chemistry Frontiers**, *[S. l.]*, v. 4, n. 2, p. 386–399, 2020. DOI: 10.1039/C9QM00578A. Disponível em: http://xlink.rsc.org/?DOI=C9QM00578A.

JIANG, Nan; AHMED, Rajib; RIFAT, Ahmmed A.; GUO, Jingjing; YIN, Yixia; MONTELONGO, Yunuen; BUTT, Haider; YETISEN, Ali K. Functionalized Flexible Soft Polymer Optical Fibers for Laser Photomedicine. Advanced Optical Materials, *[S. l.]*, v. 6, n.

3, p. 1701118, 2018. b. DOI: 10.1002/adom.201701118. Disponível em: http://doi.wiley.com/10.1002/adom.201701118.

JOANICOT, Mathieu; AJDARI, Armand. Droplet Control for Microfluidics. Science, [S. l.], v. 309, n. 5736, p. 887–888, 2005. DOI: 10.1126/science.1112615. Disponível em: https://www.science.org/doi/10.1126/science.1112615.

JU, Huangxian; KANDIMALLA, Vivek Babu. Biosensors for pesticides. In: ElectrochemicalSensors, Biosensors and their Biomedical Applications. [s.l.] : Elsevier, 2008. p. 31–56.DOI:10.1016/B978-012373738-0.50004-0.Disponívelem:https://linkinghub.elsevier.com/retrieve/pii/B9780123737380500040.Elsevier.com/retrieve/pii/B9780123737380500040.

KANG, Zhenhui; LEE, Shuit-Tong. Carbon dots: advances in nanocarbon applications. **Nanoscale**, *[S. l.]*, v. 11, n. 41, p. 19214–19224, 2019. DOI: 10.1039/C9NR05647E. Disponível em: http://xlink.rsc.org/?DOI=C9NR05647E.

KEISER, Gerd. Optical Fiber Communication. [s.l.] : McGraw Hill India, 2013.

KOBAYASHI, Yoshio; MATSUDO, Hiromu; NAKAGAWA, Tomohiko; KUBOTA, Yohsuke; GONDA, Kohsuke; OHUCHI, Noriaki. In-vivo fluorescence imaging technique using colloid solution of multiple quantum dots/silica/poly(ethylene glycol) nanoparticles. **Journal of Sol-Gel Science and Technology**, *[S. l.]*, v. 66, n. 1, p. 31–37, 2013. DOI: 10.1007/s10971-013-2962-4. Disponível em: http://link.springer.com/10.1007/s10971-013-2962-4.

KOHAVI, Ron; LI, Chia-Hsin. Oblivious decision trees graphs and top down pruning. **IJCAI'95: Proceedings of the 14th international joint conference on Artificial intelligence**, *[S. l.]*, v. 2, p. 1071–1077, 1995. Disponível em: https://dl.acm.org/doi/10.5555/1643031.1643039.

KOPPEL, Dennis E. Analysis of Macromolecular Polydispersity in Intensity Correlation Spectroscopy: The Method of Cumulants. **The Journal of Chemical Physics**, *[S. l.]*, v. 57, n. 11, p. 4814–4820, 1972. DOI: 10.1063/1.1678153. Disponível em: http://aip.scitation.org/doi/10.1063/1.1678153.

KRAUS, Tobias; GÜNTHER, Axel; DE MAS, Nuria; SCHMIDT, Martin A.; JENSEN, Klavs F. An integrated multiphase flow sensor for microchannels. **Experiments in Fluids**, *[S. l.]*, v.

36, n. 6, p. 819–832, 2004. DOI: 10.1007/s00348-003-0764-0. Disponível em: http://link.springer.com/10.1007/s00348-003-0764-0.

KUMAR GUNDA, Naga Siva; NAICKER, Selvaraj; SHINDE, Sujit; KIMBAHUNE, Sanjay; SHRIVASTAVA, Sandhya; MITRA, Sushanta. Mobile Water Kit (MWK): a smartphone compatible low-cost water monitoring system for rapid detection of total coliform and E. coli. **Analytical Methods**, *[S. l.]*, v. 6, n. 16, p. 6236, 2014. DOI: 10.1039/C4AY01245C. Disponível em: http://xlink.rsc.org/?DOI=C4AY01245C.

KWON, Woosung; DO, Sungan; LEE, Jinuk; HWANG, Sunyong; KIM, Jong Kyu; RHEE, Shi-Woo. Freestanding Luminescent Films of Nitrogen-Rich Carbon Nanodots toward Large-Scale Phosphor-Based White-Light-Emitting Devices. **Chemistry of Materials**, *[S. l.]*, v. 25, n. 9, p. 1893–1899, 2013. DOI: 10.1021/cm400517g. Disponível em: https://pubs.acs.org/doi/10.1021/cm400517g.

LAKOWICZ, Joseph R. **Principles of fluorescence spectroscopy**. Third ed. Boston, MA: Springer US, 2006. DOI: 10.1007/978-0-387-46312-4. Disponível em: https://www.springer.com/gp/book/9780387312781#aboutBook.

LAROCHE, M.; CHARDON, A. M.; NILSSON, J.; SHEPHERD, D. P.; CLARKSON, W. A.; GIRARD, S.; MONCORGÉ, R. Compact diode-pumped passively Q-switched tunable Er–Yb double-clad fiber laser. **Optics Letters**, *[S. l.]*, v. 27, n. 22, p. 1980, 2002. DOI: 10.1364/OL.27.001980. Disponível em: https://opg.optica.org/abstract.cfm?URI=ol-27-22-1980.

LEE, B.; JEONG, Y. Interrogation Techniques for Fiber Grating Sensors and the Theory of Fiber Gratings. *In*: YU, F. T. S.; YIN, S. (org.). **Fiber Optic Sensors**. [s.l.] : Marcel Dekker, 2002.

LEE, Byoungho. Review of the present status of optical fiber sensors. **Optical Fiber Technology**, *[S. l.]*, v. 9, n. 2, p. 57–79, 2003. DOI: 10.1016/S1068-5200(02)00527-8. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S1068520002005278.

LEMIRE-RENAUD, Simon; RIVARD, Maxime; STRUPLER, Mathias; MORNEAU, Dominic; VERPILLAT, Frédéric; DAXHELET, Xavier; GODBOUT, Nicolas; BOUDOUX, Caroline. Double-clad fiber coupler for endoscopy. **Optics Express**, *[S. l.]*, v. 18, n. 10, p.

9755, 2010. DOI: 10.1364/OE.18.009755. Disponível em: https://opg.optica.org/abstract.cfm?URI=oe-18-10-9755.

LEUNG, Alfred B.; SUH, Kwang I.; ANSARI, Rafat R. Particle-size and velocity measurements in flowing conditions using dynamic light scattering. **Applied Optics**, *[S. l.]*, v. 45, n. 10, p. 2186, 2006. DOI: 10.1364/AO.45.002186. Disponível em: https://opg.optica.org/abstract.cfm?URI=ao-45-10-2186.

LEUNG, Angela; SHANKAR, P. Mohana; MUTHARASAN, Raj. A review of fiber-optic biosensors. **Sensors and Actuators B: Chemical**, *[S. l.]*, v. 125, n. 2, p. 688–703, 2007. DOI: 10.1016/j.snb.2007.03.010. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0925400507001931.

LI, Haitao et al. Water-Soluble Fluorescent Carbon Quantum Dots and Photocatalyst Design. **Angewandte Chemie International Edition**, *[S. l.]*, v. 49, n. 26, p. 4430–4434, 2010. DOI: 10.1002/anie.200906154. Disponível em: https://onlinelibrary.wiley.com/doi/10.1002/anie.200906154.

LI, Hui-Jun et al. Redox Induced Fluorescence On–Off Switching Based on Nitrogen Enriched Graphene Quantum Dots for Formaldehyde Detection and Bioimaging. **ACS Sustainable Chemistry & Engineering**, *[S. l.]*, v. 6, n. 2, p. 1708–1716, 2018. a. DOI: 10.1021/acssuschemeng.7b02941. Disponível em: https://pubs.acs.org/doi/10.1021/acssuschemeng.7b02941.

LI, Jiurong; ZHAO, Haiguang; ZHAO, Xiujian; GONG, Xiao. Boosting efficiency of luminescent solar concentrators using ultra-bright carbon dots with large Stokes shift. **Nanoscale Horizons**, *[S. l.]*, v. 8, n. 1, p. 83–94, 2023. DOI: 10.1039/D2NH00360K. Disponível em: http://xlink.rsc.org/?DOI=D2NH00360K.

LI, Kaiwei; ZHANG, Nan; YING ZHANG, Nancy Meng; ZHOU, Wenchao; ZHANG, Ting; CHEN, Ming; WEI, Lei. Birefringence induced Vernier effect in optical fiber modal interferometers for enhanced sensing. **Sensors and Actuators, B: Chemical**, *[S. l.]*, v. 275, n. July, p. 16–24, 2018. b. DOI: 10.1016/j.snb.2018.08.027. Disponível em: https://doi.org/10.1016/j.snb.2018.08.027.

LI, Xuegang; NGUYEN, Linh V.; ZHAO, Yong; EBENDORFF-HEIDEPRIEM, Heike;

WARREN-SMITH, Stephen C. High-sensitivity Sagnac-interferometer biosensor based on exposed core microstructured optical fiber. **Sensors and Actuators, B: Chemical**, *[S. l.]*, v. 269, p. 103–109, 2018. c. DOI: 10.1016/j.snb.2018.04.165. Disponível em: https://doi.org/10.1016/j.snb.2018.04.165.

LI, Yanjiao; ZHOU, Jing'en; TUNG, Simon; SCHNEIDER, Eric; XI, Shengqi. A review on development of nanofluid preparation and characterization. **Powder Technology**, *[S. l.]*, v. 196, n. 2, p. 89–101, 2009. DOI: 10.1016/j.powtec.2009.07.025. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0032591009004483.

LI, Yunxia; MIAO, Peng; ZHOU, Wei; GONG, Xiao; ZHAO, Xiujian. N-doped carbon-dots for luminescent solar concentrators. **J. Mater. Chem. A**, *[S. l.]*, v. 5, n. 40, p. 21452–21459, 2017. DOI: 10.1039/C7TA05220K. Disponível em: http://xlink.rsc.org/?DOI=C7TA05220K.

LIANG, Shanshan; SAIDI, Arya; JING, Joe; LIU, Gangjun; LI, Jiawen; ZHANG, Jun; SUN, Changsen; NARULA, Jagat; CHEN, Zhongping. Intravascular atherosclerotic imaging with combined fluorescence and optical coherence tomography probe based on a double-clad fiber combiner. Journal of Biomedical Optics, [S. l.], v. 17, n. 7, p. 0705011, 2012. DOI: 10.1117/1.JBO.17.7.070501. Disponível em:

http://biomedicaloptics.spiedigitallibrary.org/article.aspx?doi=10.1117/1.JBO.17.7.070501.

LIM, Ho-Joon; CHANG, Kuang-An; SU, Chin B.; CHEN, Chi-Yueh. Bubble velocity, diameter, and void fraction measurements in a multiphase flow using fiber optic reflectometer. **Review of Scientific Instruments**, *[S. l.]*, v. 79, n. 12, p. 125105, 2008. DOI: 10.1063/1.3053271. Disponível em: http://aip.scitation.org/doi/10.1063/1.3053271.

LIMPERT, J. et al. High-power rod-type photonic crystal fiber laser. **Optics Express**, [S. l.], v. 13, n. 4, p. 1055, 2005. DOI: 10.1364/OPEX.13.001055. Disponível em: https://opg.optica.org/oe/abstract.cfm?uri=oe-13-4-1055.

LIMPERT, Jens et al. High-power air-clad large-mode-area photonic crystal fiber laser. **Optics Express**, *[S. l.]*, v. 11, n. 7, p. 818, 2003. DOI: 10.1364/OE.11.000818. Disponível em: https://opg.optica.org/oe/abstract.cfm?uri=oe-11-7-818.

LIN, Haitao; HUANG, Jun; DING, Liyun. A Recyclable Optical Fiber Sensor Based on Fluorescent Carbon Dots for the Determination of Ferric Ion Concentrations. Journal of Lightwave Technology, [S. l.], v. 37, n. 18, p. 4815–4822, 2019. DOI: 10.1109/JLT.2019.2922375. Disponível em: https://ieeexplore.ieee.org/document/8735777/.

LIN, Xiaofeng et al. Interfacial modification layers based on carbon dots for efficient inverted polymer solar cells exceeding 10% power conversion efficiency. **Nano Energy**, *[S. l.]*, v. 26, p. 216–223, 2016. DOI: 10.1016/j.nanoen.2016.05.011. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S221128551630132X.

LIU, Chun; YE, Chenchun; LUO, Zhengqian; CHENG, Huihui; WU, Duanduan; ZHENG, Yonglong; LIU, Zhen; QU, Biao. High-energy passively Q-switched 2 μm Tm³⁺-doped double-clad fiber laser using graphene-oxide-deposited fiber taper. **Optics Express**, *[S. l.]*, v. 21, n. 1, p. 204, 2013. DOI: 10.1364/OE.21.000204. Disponível em: https://opg.optica.org/oe/abstract.cfm?uri=oe-21-1-204.

LIU, Guiju; MAZZARO, Raffaello; SUN, Changchun; ZHANG, Yuanming; WANG, Yiqian; ZHAO, Haiguang; HAN, Guangting; VOMIERO, Alberto. Role of refractive index in highly efficient laminated luminescent solar concentrators. **Nano Energy**, *[S. l.]*, v. 70, p. 104470, 2020. DOI: 10.1016/j.nanoen.2020.104470. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S2211285520300264.

LIU, Zexu et al. Liquid surface tension and refractive index sensor based on a tilted fiber Bragg grating. **Journal of the Optical Society of America B**, *[S. l.]*, v. 35, n. 6, p. 1282, 2018. DOI: 10.1364/JOSAB.35.001282. Disponível em: https://opg.optica.org/abstract.cfm?URI=josab-35-6-1282.

LUDOVICO, Paula; SOUSA, Maria João; SILVA, Manuel T.; LEÃO, Cecília; CÔRTE-REAL, Manuela. Saccharomyces cerevisiae commits to a programmed cell death process in response to acetic acid. **Microbiology**, *[S. l.]*, v. 147, n. 9, p. 2409–2415, 2001. DOI: 10.1099/00221287-147-9-2409. Disponível em:

https://www.microbiologyresearch.org/content/journal/micro/10.1099/00221287-147-9-2409.

LUO, Zhengtang; LU, Ye; SOMERS, Luke A.; JOHNSON, A. T. Charlie. High Yield Preparation of Macroscopic Graphene Oxide Membranes. Journal of the American Chemical Society, [S. l.], v. 131, n. 3, p. 898–899, 2009. DOI: 10.1021/ja807934n. Disponível em: https://pubs.acs.org/doi/10.1021/ja807934n.

MA, Wenwen; LI, Wenjing; LIU, Ruiyuan; CAO, Mengyan; ZHAO, Xiujian; GONG, Xiao. Carbon dots and AIE molecules for highly efficient tandem luminescent solar concentrators. **Chemical Communications**, *[S. l.]*, v. 55, n. 52, p. 7486–7489, 2019. DOI: 10.1039/C9CC02676B. Disponível em: http://xlink.rsc.org/?DOI=C9CC02676B.

MANSHIAN, Bella B.; JIMÉNEZ, Julio; HIMMELREICH, Uwe; SOENEN, Stefaan J. Personalized medicine and follow-up of therapeutic delivery through exploitation of quantum dot toxicity. **Biomaterials.** S. *l.*], v. 127, p. 1 - 12. 2017. DOI: 10.1016/j.biomaterials.2017.02.039. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0142961217301278.

MARTINDALE, Benjamin C. M.; HUTTON, Georgina A. M.; CAPUTO, Christine A.; REISNER, Erwin. Solar Hydrogen Production Using Carbon Quantum Dots and a Molecular Nickel Catalyst. Journal of the American Chemical Society, [S. l.], v. 137, n. 18, p. 6018–6025, 2015. DOI: 10.1021/jacs.5b01650.

MAXIM, Askar A.; SADYK, Shynggys N.; AIDARKHANOV, Damir; SURYA, Charles; NG, Annie; HWANG, Yoon-Hwae; ATABAEV, Timur Sh.; JUMABEKOV, Askhat N. PMMA Thin Film with Embedded Carbon Quantum Dots for Post-Fabrication Improvement of Light Harvesting in Perovskite Solar Cells. **Nanomaterials**, *[S. l.]*, v. 10, n. 2, p. 291, 2020. DOI: 10.3390/nano10020291. Disponível em: https://www.mdpi.com/2079-4991/10/2/291.

MAZZUCCO, Mateus LC; MARCHESIN, Marcel S.; FERNANDES, Elizabeth G.; DA COSTA, Ricardo A.; MARINI, Juliano; BRETAS, Rosario ES; BARTOLI, Julio R. Nanocomposites of acrylonitrile-butadiene-styrene/montmorillonite/styrene block copolymers: Structural, rheological, mechanical and flammability studies on the effect of organoclays and compatibilizers using statistically designed experiments. **Journal of Composite Materials**, *[S. l.]*, v. 50, n. 6, p. 771–782, 2016. DOI: 10.1177/0021998315581509. Disponível em: http://journals.sagepub.com/doi/10.1177/0021998315581509.

MCCABE, W. L.; SMITH, J. C.; HARRIOTT, P. Unit Operations of Chemical Engineering. 5th. ed. New York, NY, USA: McGraw-Hill, 1993.

MENG, Weixue; BAI, Xue; WANG, Boyang; LIU, Zhongyi; LU, Siyu; YANG, Bai. Biomass-Derived Carbon Dots and Their Applications. **ENERGY & ENVIRONMENTAL MATERIALS**, *[S. l.]*, v. 2, n. 3, p. 172–192, 2019. DOI: 10.1002/eem2.12038. Disponível em: https://onlinelibrary.wiley.com/doi/10.1002/eem2.12038.

METHROHM. **780 pH-Meter + 781 pH/Ion Meter**. [s.d.]. Disponível em: https://partners.metrohm.com/GetDocumentPublic?action=get_dms_document&docid=69247 0. Acesso em: 13 set. 2020.

MICHELINI, Elisa; CALABRETTA, Maria Maddalena; CEVENINI, Luca; LOPRESIDE, Antonia; SOUTHWORTH, Tara; FONTAINE, Danielle M.; SIMONI, Patrizia; BRANCHINI, Bruce R.; RODA, Aldo. Smartphone-based multicolor bioluminescent 3D spheroid biosensors for monitoring inflammatory activity. **Biosensors and Bioelectronics**, *[S. l.]*, v. 123, p. 269– 277, 2019. DOI: 10.1016/j.bios.2018.09.012. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0956566318306936.

MOHAN, Kiranjyoti; BORA, Anindita; DOLUI, Swapan Kumar. Efficient Way of Enhancing the Efficiency of a Quasi-Solid-State Dye-Sensitized Solar Cell by Harvesting the Unused Higher Energy Visible Light Using Carbon Dots. **ACS Sustainable Chemistry & Engineering**, *[S. l.]*, v. 6, n. 8, p. 10914–10922, 2018. DOI: 10.1021/acssuschemeng.8b02244. Disponível em: https://pubs.acs.org/doi/10.1021/acssuschemeng.8b02244.

MOON, Hyungsuk; LEE, Changmin; LEE, Woosuk; KIM, Jungwoo; CHAE, Heeyeop. Stability of Quantum Dots, Quantum Dot Films, and Quantum Dot Light-Emitting Diodes for Display Applications. Advanced Materials, [S. l.], v. 31, n. 34, p. 1804294, 2019. DOI: 10.1002/adma.201804294. Disponível em: https://onlinelibrary.wiley.com/doi/10.1002/adma.201804294.

MURATA, H. Recent developments in vapor phase axial deposition. Journal of Lightwave Technology, [S. l.], v. 4, n. 8, p. 1026–1033, 1986. DOI: 10.1109/JLT.1986.1074835. Disponível em: http://ieeexplore.ieee.org/document/1074835/.

NIELSEN, Kristian; NOORDEGRAAF, Danny; SØRENSEN, Thorkild; BJARKLEV, Anders; HANSEN, Theis P. Selective filling of photonic crystal fibres. **Journal of Optics A: Pure and Applied Optics**, *[S. l.]*, v. 7, n. 8, p. L13–L20, 2005. DOI: 10.1088/1464-4258/7/8/L02. Disponível em: https://iopscience.iop.org/article/10.1088/1464-4258/7/8/L02.

NILSSON, Gert E.; TENLAND, Torsten; OBERG, P. Ake. Evaluation of a Laser Doppler Flowmeter for Measurement of Tissue Blood Flow. **IEEE Transactions on Biomedical** Engineering, [S. l.], v. BME-27, n. 10, p. 597–604, 1980. DOI: 10.1109/TBME.1980.326582. Disponível em: http://ieeexplore.ieee.org/document/4123142/.

OLIVEIRA, Ricardo; BILRO, Lucia; MARQUES, Thiago H. R.; NAPIERALA, Marek; TENDERENDA, Tadeusz; MERGO, Pawel; NASILOWSKI, Tomasz; CORDEIRO, Cristiano M. B.; NOGUEIRA, Rogerio. Bragg Gratings Inscription in Highly Birefringent Microstructured POFs. **IEEE Photonics Technology Letters**, *[S. l.]*, v. 28, n. 6, p. 621–624, 2016. DOI: 10.1109/LPT.2015.2503241. Disponível em: http://ieeexplore.ieee.org/document/7335574/.

OLIVERIO, Manuela; PEROTTO, Sara; MESSINA, Gabriele C.; LOVATO, Laura; DE ANGELIS, Francesco. Chemical Functionalization of Plasmonic Surface Biosensors: A Tutorial Review on Issues, Strategies, and Costs. **ACS Applied Materials and Interfaces**, *[S. l.]*, v. 9, n. 35, p. 29394–29411, 2017. DOI: 10.1021/acsami.7b01583.

OMENETTO, Fiorenzo G.; KAPLAN, David L. A new route for silk. **Nature Photonics**, *[S. l.]*, v. 2, n. 11, p. 641–643, 2008. DOI: 10.1038/nphoton.2008.207. Disponível em: http://www.nature.com/articles/nphoton.2008.207.

ONG, Sean; CAMPBELL, Clinton; DENHOLM, Paul; MARGOLIS, Robert; HEATH, Garvin. Land-Use Requirements for Solar Power Plants in the United States. [s.l: s.n.]. Disponível em: https://www.nrel.gov/docs/fy13osti/56290.pdf.

ORNELAS, Catia; RUIZ, Jaime; BELIN, Colette; ASTRUC, Didier. Giant Dendritic Molecular Electrochrome Batteries with Ferrocenyl and Pentamethylferrocenyl Termini. **Journal of the American Chemical Society**, *[S. l.]*, v. 131, n. 2, p. 590–601, 2009. DOI: 10.1021/ja8062343. Disponível em: https://pubs.acs.org/doi/10.1021/ja8062343.

PAN, Dengyu et al. Cutting sp2 clusters in graphene sheets into colloidal graphene quantum dots with strong green fluorescence. **Journal of Materials Chemistry**, *[S. l.]*, v. 22, n. 8, p. 3314, 2012. DOI: 10.1039/c2jm16005f. Disponível em: http://xlink.rsc.org/?DOI=c2jm16005f.

PAN, Ming; SIKORSKI, Janusz; KASTNER, Catharine A.; AKROYD, Jethro; MOSBACH, Sebastian; LAU, Raymond; KRAFT, Markus. Applying Industry 4.0 to the Jurong Island Ecoindustrial Park. **Energy Procedia**, *[S. l.]*, v. 75, p. 1536–1541, 2015. DOI:
10.1016/j.egypro.2015.07.313.Disponívelem:https://linkinghub.elsevier.com/retrieve/pii/S1876610215010814.

PANWAR, Nishtha; SOEHARTONO, Alana Mauluidy; CHAN, Kok Ken; ZENG, Shuwen; XU, Gaixia; QU, Junle; COQUET, Philippe; YONG, Ken-Tye; CHEN, Xiaoyuan. Nanocarbons for Biology and Medicine: Sensing, Imaging, and Drug Delivery. **Chemical Reviews**, *[S. 1.]*, v. 119, n. 16, p. 9559–9656, 2019. DOI: 10.1021/acs.chemrev.9b00099. Disponível em: https://pubs.acs.org/doi/10.1021/acs.chemrev.9b00099.

PARK, Y.; YOO, J.; LIM, B.; KWON, W.; RHEE, S. W. Improving the functionality of carbon nanodots: doping and surface functionalization. Journal of Materials Chemistry A, [S. l.], v. 4, n. 30, p. 11582–11603, 2016. DOI: 10.1039/C6TA04813G. Disponível em: http://xlink.rsc.org/?DOI=C6TA04813G.

PERLI, Gabriel et al. Synthesis of Carbon Nanodots from Sugarcane Syrup, and Their Incorporation into a Hydrogel-Based Composite to Fabricate Innovative Fluorescent Microstructured Polymer Optical Fibers. **Gels**, *[S. l.]*, v. 8, n. 9, p. 553, 2022. DOI: 10.3390/gels8090553. Disponível em: https://www.mdpi.com/2310-2861/8/9/553.

PETERS, Kara. Polymer optical fiber sensors - A review. Smart Materials and Structures, *[S. l.]*, v. 20, n. 1, 2011. DOI: 10.1088/0964-1726/20/1/013002.

PRADO, Bruna Rosa; BARTOLI, Julio Roberto. Synthesis and characterization of PMMA and organic modified montmorilonites nanocomposites via in situ polymerization assisted by sonication. **Applied Clay Science**, [S. l.], v. 160, p. 132–143, 2018. DOI: 10.1016/j.clay.2018.02.035. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0169131718300930.

QUINTANILLA-CARVAJAL, María Ximena; CAMACHO-DÍAZ, Brenda Hildeliza; MERAZ-TORRES, Lesvia Sofia; CHANONA-PÉREZ, José Jorge; ALAMILLA-BELTRÁN, Liliana; JIMENÉZ-APARICIO, Antonio; GUTIÉRREZ-LÓPEZ, Gustavo F. Nanoencapsulation: A New Trend in Food Engineering Processing. Food Engineering Reviews, [S. l.], v. 2, n. 1, p. 39–50, 2010. DOI: 10.1007/s12393-009-9012-6. Disponível em: http://link.springer.com/10.1007/s12393-009-9012-6.

RAHIMI, Mehdi; MAHANI, Mohamad; HASSANI, Zahra. Carbon quantum dots fluorescence

quenching for potassium optode construction. Luminescence, [S. l.], v. 34, n. 4, p. 402–406,2019.DOI:10.1002/bio.3634.Disponívelem:https://onlinelibrary.wiley.com/doi/10.1002/bio.3634.

RAN, Xin; QU, Qing; LI, Lei; ZUO, Limei; ZHANG, Shihong; GUI, Jingwei; KANG, Yaxin; YANG, Long. One-Step Synthesis of Novel Photoluminescent Nitrogen-Rich Carbon Nanodots from Allylamine for Highly Sensitive and Selective Fluorescence Detection of Trinitrophenol and Fluorescent Ink. **ACS Sustainable Chemistry & Engineering**, *[S. l.]*, v. 6, n. 9, p. 11716–11723, 2018. DOI: 10.1021/acssuschemeng.8b01977. Disponível em: https://pubs.acs.org/doi/10.1021/acssuschemeng.8b01977.

RAVISHANKAR, Kartik; SHELLY, K. M.; NARAYANAN, Abathodharanan; DHAMODHARAN, Raghavachari. Rapid, Solvent-Free Synthesis of Amorphous, Photoluminescent, Carbon Nanodots from Imidazole and Maleic Anhydride Solids. ACS Sustainable Chemistry & Engineering, [S. l.], v. 7, n. 15, p. 13206–13216, 2019. DOI: 10.1021/acssuschemeng.9b02446. Disponível em: https://pubs.acs.org/doi/10.1021/acssuschemeng.9b02446.

REICHARDT, Christian. Solvatochromic dyes as solvent polarity indicators. Chemical Reviews, [S. 1.], v. 94, n. 8, p. 2319–2358, 1994. DOI: 10.1021/cr00032a005.

REICHARDT, Christian. Polarity of ionic liquids determined empirically by means of solvatochromic pyridinium N-phenolate betaine dyes. **Green Chemistry**, *[S. l.]*, v. 7, n. 5, p. 339–351, 2005. DOI: 10.1039/b500106b.

REIS, Marco S.; KENETT, Ron. Assessing the value of information of data-centric activitiesin the chemical processing industry 4.0. AIChE Journal, [S. l.], v. 64, n. 11, p. 3868–3881,2018.DOI:10.1002/aic.16203.Disponívelhttps://onlinelibrary.wiley.com/doi/10.1002/aic.16203.

REISFELD, Renata; EYAL, Marek; CHERNYAK, Valeri; ZUSMAN, Rivka. Luminescent thin solar concentrators based on films of polymethylmethacrylate on а polymethylmethacrylate support. Solar Energy Materials, *[S. l.]*, v. 17, n. 6, p. 439–455, 1988. DOI: 10.1016/0165-1633(88)90004-4. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/0165163388900044.

REMANAN, Sanjay; GHOSH, Sabyasachi; DAS, Tushar Kanti; SHARMA, Maya; BOSE, Madhuparna; BOSE, Suryasarathi; DAS, Amit Kumar; DAS, Narayan Chandra. Gradient crystallinity and its influence on the poly(vinylidene fluoride)/poly(methyl methacrylate) membrane-derived by immersion precipitation method. Journal of Applied Polymer Science, 137, 27, 2020. DOI: 10.1002/app.48677. Disponível S. *l.*], v. n. em: https://onlinelibrary.wiley.com/doi/10.1002/app.48677.

RUMBLE, J. (ORG.). Concentrative Properties of Aqueous Solutions: Density, Refractive Index, Freezing Point Depression, and Viscosity. *In*: CRC Handbook of Chemistry and Physics. 100th. ed. Boca Raton, FL, USA: CRC Press (Taylor and Francis Group), 2019.

SADASIVAN, Sridhar; RASMUSSEN, Don H. Compact Fiber Optic Dynamic LightScattering System. Journal of Colloid and Interface Science, [S. l.], v. 193, n. 2, p. 145–151,1997.DOI:10.1006/jcis.1997.4916.Disponívelhttps://linkinghub.elsevier.com/retrieve/pii/S002197979794916X.

SAHU, Swagatika; BEHERA, Birendra; MAITI, Tapas K.; MOHAPATRA, Sasmita. Simple one-step synthesis of highly luminescent carbon dots from orange juice: Application as excellent bio-imaging agents. **Chemical Communications**, *[S. l.]*, v. 48, n. 70, p. 8835–8837, 2012. DOI: 10.1039/c2cc33796g.

SALEH, Bahaa E. A.; TEICH, Malvin Carl. Fundamentals of Photonics. New York, USA: John Wiley & Sons, Inc., 1991. DOI: 10.1002/0471213748. Disponível em: http://doi.wiley.com/10.1002/0471213748.

SANTOS, J. S.; ONO, E.; FUJIWARA, E.; MANFRIM, T. P.; SUZUKI, C. K. Control of optical properties of silica glass synthesized by VAD method for photonic components. **Optical Materials**, *[S. l.]*, v. 33, n. 12, p. 1879–1883, 2011. DOI: 10.1016/j.optmat.2011.03.007. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0925346711001285.

SCHYRR, Bastien; BODER-PASCHE, Stéphanie; ISCHER, Réal; SMAJDA, Rita; VOIRIN, Guy. Fiber-optic protease sensor based on the degradation of thin gelatin films. **Sensing and Bio-Sensing Research**, *[S. l.]*, v. 3, p. 65–73, 2015. DOI: 10.1016/j.sbsr.2014.12.004. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S2214180414000452.

SCIENTIFIC, Thermo Fisher; THERMO SCIENTIFIC. pH Measurement Handbook. 1991.

DOI: 10.1016/S1074-7613(03)00204-8. Disponível em: https://assets.thermofisher.com/TFS-Assets/LSG/brochures/pH-Measurement-Handbook-S-PHREFBK-E.pdf. Acesso em: 13 set. 2020.

SCIORTINO, Alice; MARINO, Emanuele; DAM, Bart Van; SCHALL, Peter; CANNAS, Marco; MESSINA, Fabrizio. Solvatochromism Unravels the Emission Mechanism of Carbon Nanodots. Journal of Physical Chemistry Letters, *[S. l.]*, v. 7, n. 17, p. 3419–3423, 2016. DOI: 10.1021/acs.jpclett.6b01590.

SETIONO, Rudy. Feedforward Neural Network Construction Using Cross Validation. Neural Computation, [S. l.], v. 13, n. 12, p. 2865–2877, 2001. DOI: 10.1162/089976601317098565. Disponível em: https://direct.mit.edu/neco/article/13/12/2865-2877/6549.

SHARMA, Vinay; TIWARI, Pranav; MOBIN, Shaikh M. Sustainable carbon-dots: recent advances in green carbon dots for sensing and bioimaging. **Journal of Materials Chemistry B**, *[S. l.]*, v. 5, n. 45, p. 8904–8924, 2017. DOI: 10.1039/C7TB02484C. Disponível em: http://xlink.rsc.org/?DOI=C7TB02484C.

SHEN, Changyu; LIAN, Xiaokang; KAVUNGAL, Vishnu; ZHONG, Chuan; LIU, Dejun; SEMENOVA, Yuliya; FARRELL, Gerald; ALBERT, Jacques; DONEGAN, John F. Optical spectral sweep comb liquid flow rate sensor. **Optics Letters**, *[S. l.]*, v. 43, n. 4, p. 751, 2018. DOI: 10.1364/OL.43.000751. Disponível em: https://opg.optica.org/abstract.cfm?URI=ol-43-4-751.

SHEN, Changyu; LIU, Dejun; LIAN, Xiaokang; LANG, Tingting; ZHAO, Chunliu; SEMENOVA, Yuliya; ALBERT, Jacques. Microfluidic flow direction and rate vector sensor based on a partially gold-coated TFBG. **Optics Letters**, *[S. l.]*, v. 45, n. 10, p. 2776, 2020. DOI: 10.1364/OL.392511. Disponível em: https://opg.optica.org/abstract.cfm?URI=ol-45-10-2776.

SHEPPARD, Norman F.; TUCKER, Robert C.; SALEHI-HAD, Samira. Design of aconductimetric pH microsensor based on reversibly swelling hydrogels. Sensors andActuators B: Chemical, [S. l.], v. 10, n. 2, p. 73–77, 1993. DOI: 10.1016/0925-4005(93)80028-A.Disponívelem:https://linkinghub.elsevier.com/retrieve/pii/092540059380028A.

SILVERSTEIN, R. M.; WEBSTER, F. X.; KIEMLE, D. J. Spectrometric Identification of

Organic Compounds. 7th. ed. Hoboken, NJ, USA: John Wiley and Sons, 2005.

SKIBICKI, Jacek; GOLIJANEK-JĘDRZEJCZYK, Anna; DZWONKOWSKI, Ariel. The Influence of Camera and Optical System Parameters on the Uncertainty of Object Location Measurement in Vision Systems. **Sensors**, *[S. l.]*, v. 20, n. 18, p. 5433, 2020. DOI: 10.3390/s20185433. Disponível em: https://www.mdpi.com/1424-8220/20/18/5433.

SKOOG, D.; WEST, D.; HOLLER, F. J.; CROUCH, S. Fundamentals of Analytical Chemistry. Ninth ed. [s.l.] : Cengage Learning, 2014.

SNOEK, C. W. A selection of new developments in multiphase flow measurement techniques.Experimental Thermal and Fluid Science, [S. l.], v. 3, n. 1, p. 60–73, 1990. DOI:10.1016/0894-1777(90)90101-C.Disponívelhttps://linkinghub.elsevier.com/retrieve/pii/089417779090101C.

SOARES, M. C. P.; LUZ, G. F.; COSTA, A. C.; GOMES, M. K.; MENDES, B. F.; TORRE, L. G.; FUJIWARA, E. SACCHAROMYCES CEREVISIAE FED-BATCH FERMENTATION AND ARTIFICIAL INTELLIGENCE METHOD FOR ADJUSTING MODEL PARAMETERS TO EXPERIMENTAL DATA. *In*: (Congresso Brasileiro de Engenharia Química, Org.)BLUCHER CHEMICAL ENGINEERING PROCEEDINGS 2018a, São Paulo, SP, Brazil. **Anais** [...]. São Paulo, SP, Brazil: Editora Blucher, 2018. p. 2010–2014. DOI: 10.5151/cobeq2018-PT.0532. Disponível em: http://www.proceedings.blucher.com.br/articledetails/28903.

SOARES, M. C. P. Marco C. P.; MENDES, Beatriz F. B. F.; GOMES, M. K. Matheus K.; BATAGLIOLI, R. A. Rogerio A.; SCHENKEL, E. A. Egont A.; VIT, F. F. Franciele F.; DE LA TORRE, Lucimara G. L. G.; FUJIWARA, Eric; SUZUKI, C. K. Carlos K. Optical Fiber Sensor as an Alternative for Colorimetric Image Processing for the Assessment of Dye Concentration. *In*: 2018 SBFOTON INTERNATIONAL OPTICS AND PHOTONICS CONFERENCE (SBFOTON IOPC) 2018b, Campinas, SP, Brazil. **Anais** [...]. Campinas, SP, Brazil: IEEE, 2018. p. 1–5. DOI: 10.1109/SBFoton-IOPC.2018.8610912. Disponível em: https://ieeexplore.ieee.org/document/8610912/.

SOARES, M. C. P. Marco C. P.; PERLI, Gabriel; BARTOLI, J. R. Julio R.; BERTUZZI, D. L. Diego L.; TAKETA, Thiago B. T. B.; BATAGLIOLI, R. A. Rogerio A.; SUZUKI, C. K. Carlos K.; ORNELAS, Catia; FUJIWARA, Eric. Fast Microwave-Assisted Synthesis of Green-

Fluorescent Carbon Nanodots from Sugarcane Syrup. *In*: 2019 SBFOTON INTERNATIONAL OPTICS AND PHOTONICS CONFERENCE (SBFOTON IOPC) 2019a, São Paulo, SP, Brazil. **Anais** [...]. São Paulo, SP, Brazil: IEEE, 2019. p. 1–5. DOI: 10.1109/SBFoton-IOPC.2019.8910216. Disponível em: https://ieeexplore.ieee.org/document/8910216/.

SOARES, M. C. P. Marco César Prado; MENDES, Beatriz Ferreira B. F.; SCHENKEL, E. A. Egont Alexandre; SANTOS, Murilo Ferreira M. F.; FUJIWARA, Eric; SUZUKI, Carlos Kenichi C. K. Kinetic and Thermodynamic Study in Pozzolanic Chemical Systems as an Alternative for Chapelle Test. **Materials Research**, *[S. l.]*, v. 21, n. 4, p. e20180131, 2018. c. DOI: 10.1590/1980-5373-mr-2018-0131. Disponível em: http://www.scielo.br/scielo.php?script=sci_arttext&pid=S1516-14392018000400238&lng=en&tlng=en.

SOARES, Marco et al. Improving Solar Cells Efficiency with PMMA-Carbon Dots Nanocomposites. *In*: 2023 INTERNATIONAL CONFERENCE ON OPTICAL MEMS AND NANOPHOTONICS (OMN) AND SBFOTON INTERNATIONAL OPTICS AND PHOTONICS CONFERENCE (SBFOTON IOPC) 2023a, **Anais** [...]. : IEEE, 2023. p. 1–2. DOI: 10.1109/OMN/SBFotonIOPC58971.2023.10230988. Disponível em: https://ieeexplore.ieee.org/document/10230988/.

SOARES, Marco C. P. et al. Fabrication of fluorescent PMMA-carbon nanodots optical films and their feasibility in improving solar cells efficiency using low-cost sustainable materials. **Brazilian Journal of Chemical Engineering**, *[S. l.]*, n. 0123456789, 2023. b. DOI: 10.1007/s43153-023-00408-w. Disponível em: https://doi.org/10.1007/s43153-023-00408-w.

SOARES, Marco C. P.; PERLI, Gabriel; BERTUZZI, Diego L.; CABRAL, Thiago D.; CORDEIRO, Cristiano M. B.; ORNELAS, Cátia C. C.; BARTOLI, Julio R.; FUJIWARA, Eric. One-Step Synthesis of Fluorescent Carbon Nanodots from Two Widely Available Natural Sources. *In*: (L. Caspani, A. Tauke-Pedretti, F. Leo, B. Yang, Org.)OSA ADVANCED PHOTONICS CONGRESS (AP) 2020 (IPR, NP, NOMA, NETWORKS, PVLED, PSC, SPPCOM, SOF) 2020a, Washington, D.C. **Anais** [...]. Washington, D.C.: Optica Publishing Group, 2020. p. JTh3G.4. DOI: 10.1364/NOMA.2020.JTh3G.4. Disponível em: https://opg.optica.org/abstract.cfm?URI=NOMA-2020-JTh3G.4.

SOARES, Marco C. P.; VIT, Franciele F.; DE LA TORRE, Lucimara G.; FUJIWARA, Eric.

Online Monitoring of Cell Growth on PDMS-PDMS Reversible Microfluidic Bioreactor Integrated to Optical Fiber Sensor. *In*: 2019 SBFOTON INTERNATIONAL OPTICS AND PHOTONICS CONFERENCE (SBFOTON IOPC) 2019b, São Paulo, SP, Brazil. **Anais** [...]. São Paulo, SP, Brazil: IEEE, 2019. p. 1–5. DOI: 10.1109/SBFoton-IOPC.2019.8910241. Disponível em: https://ieeexplore.ieee.org/document/8910241/.

SOARES, Marco César Prado; CABRAL, Thiago Destri; LAZARI, Pedro Machado; RODRIGUES, Matheus dos Santos; RODRIGUES, Gildo Santos; FUJIWARA, Eric. Smartphone-Based Optical Fiber Sensor for the Assessment of a Fed-Batch Bioreactor. **Engineering Proceedings**, https://youtu.be/yv1KQfVwpA0, v. 2, n. 1, p. 26, 2020. b. DOI: 10.3390/ecsa-7-08157. Disponível em: https://www.mdpi.com/2673-4591/2/1/26.

SOARES, Marco César Prado; GOMES, Matheus Kauê; SCHENKEL, Egont Alexandre; RODRIGUES, Matheus dos Santos; SUZUKI, Carlos Kenichi; TORRE, Lucimara Gaziola de La; FUJIWARA, Eric. EVALUATION OF SILICA NANOPARTICLE COLLOIDAL STABILITY WITH A FIBER OPTIC QUASI-ELASTIC LIGHT SCATTERING SENSOR. **Brazilian Journal of Chemical Engineering**, *[S. l.]*, v. 36, n. 4, p. 1519–1534, 2019. c. DOI: 10.1590/0104-6632.20190364s20190042. Disponível em: http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0104-66322019000401519&tlng=en.

SOARES, Marco César Prado; PERLI, Gabriel; FUJIWARA, Eric; BARTOLI, Julio Roberto; ORNELAS MEGIATTO, Cátia Cristina Capêlo; BERTUZZI, Diego Luan; SUZUKI, Carlos Kenichi. Processo de Produção de Nanopartículas Fluorescentes de Carbono a Partir de Derivados da Cana-De-Açúcar e Uso Dessas Nanopartículas., BR1020190148810, 2019. d.

SOARES, Marco César Prado; VIT, Franciele Flores; SUZUKI, Carlos Kenichi; DE LA TORRE, Lucimara Gaziola; FUJIWARA, Eric. Perfusion microfermentor integrated into a fiber optic quasi-elastic light scattering sensor for fast screening of microbial growth parameters. **Sensors (Switzerland)**, *[S. l.]*, v. 19, n. 11, p. 2493, 2019. e. DOI: 10.3390/s19112493. Disponível em: https://www.mdpi.com/1424-8220/19/11/2493.

SOBON, Grzegorz; KRZEMPEK, Karol; KACZMAREK, Pawel; ABRAMSKI, Krzysztof M.; NIKODEM, Michal. 10GHz passive harmonic mode-locking in Er–Yb double-clad fiber laser.

STEM, Nair. Células solares de silício de alto rendimento: otimizações teóricas e implementações experimentais utilizando processos de baixo custo. 2007. Universidade de São Paulo, São Paulo, 2007. DOI: 10.11606/T.3.2007.tde-02042008-113959. Disponível em: http://www.teses.usp.br/teses/disponiveis/3/3140/tde-02042008-113959/.

STEPANIDENKO, Evgeniia A.; USHAKOVA, Elena V.; FEDOROV, Anatoly V.; ROGACH, Andrey L. Applications of Carbon Dots in Optoelectronics. **Nanomaterials**, *[S. l.]*, v. 11, n. 2, p. 364, 2021. DOI: 10.3390/nano11020364. Disponível em: https://www.mdpi.com/2079-4991/11/2/364.

STEPHANOPOULOS, G. Chemical Process Control: An Introduction to Theory and Practice. 1st. ed. Englewood Cliffs, NJ, USA: Prentice Hall, 1983.

SUN, Ya-ping et al. Quantum-Sized Carbon Dots for Bright and Colorful Photoluminescence. Journal of the American Chemical Society, [S. l.], v. 128, n. 24, p. 7756–7757, 2006. DOI: 10.1021/ja062677d. Disponível em: https://pubs.acs.org/doi/10.1021/ja062677d.

SUPPAN, Paul. Invited review solvatochromic shifts: The influence of the medium on the energy of electronic states. **Journal of Photochemistry and Photobiology, A: Chemistry**, *[S. l.]*, v. 50, n. 3, p. 293–330, 1990. DOI: 10.1016/1010-6030(90)87021-3.

SURENDRAN, Pandiyan; LAKSHMANAN, Arumugam; VINITHA, Gandhirajan; RAMALINGAM, Gopal; RAMESHKUMAR, Pitchan. Facile preparation of high fluorescent carbon quantum dots from orange waste peels for nonlinear optical applications. **Luminescence**, *[S. l.]*, v. 35, n. 2, p. 196–202, 2020. DOI: 10.1002/bio.3713. Disponível em: https://onlinelibrary.wiley.com/doi/10.1002/bio.3713.

TALATAISONG, Wanvisa et al. Mid-IR Hollow-core microstructured fiber drawn from a 3D printed PETG preform. **Scientific Reports**, *[S. l.]*, v. 8, n. 1, p. 8113, 2018. DOI: 10.1038/s41598-018-26561-8. Disponível em: https://www.nature.com/articles/s41598-018-26561-8.

TAYLOR, H. F. Fiber Optic Sensors Based upon the Fabry-Perot Interferometer. In: YU, F. T.

S.; YIN, S. (org.). Fiber Optic Sensors. [s.l.] : Marcel Dekker, 2002.

TAYLOR, Robert A.; OTANICAR, Todd P.; HERUKERRUPU, Yasitha; BREMOND, Fabienne; ROSENGARTEN, Gary; HAWKES, Evatt R.; JIANG, Xuchuan; COULOMBE, Sylvain. Feasibility of nanofluid-based optical filters. **Applied Optics**, *[S. l.]*, v. 52, n. 7, p. 1413, 2013. DOI: 10.1364/AO.52.001413. Disponível em: https://opg.optica.org/abstract.cfm?URI=ao-52-7-1413.

THORSEN, Todd; ROBERTS, Richard W.; ARNOLD, Frances H.; QUAKE, Stephen R. Dynamic Pattern Formation in a Vesicle-Generating Microfluidic Device. **Physical Review** Letters, *[S. l.]*, v. 86, n. 18, p. 4163–4166, 2001. DOI: 10.1103/PhysRevLett.86.4163. Disponível em: https://link.aps.org/doi/10.1103/PhysRevLett.86.4163.

TIAN, Xue-Tao; YIN, Xue-Bo. Carbon Dots, Unconventional Preparation Strategies, andApplications Beyond Photoluminescence. Small, [S. l.], v. 15, n. 48, p. 1901803, 2019. DOI:10.1002/smll.201901803.Disponívelhttps://onlinelibrary.wiley.com/doi/10.1002/smll.201901803.

TIAN, Zhen; ZHANG, Xutao; LI, Di; ZHOU, Ding; JING, Pengtao; SHEN, Dezhen; QU, Songnan; ZBORIL, Radek; ROGACH, Andrey L. Full-Color Inorganic Carbon Dot Phosphors for White-Light-Emitting Diodes. Advanced Optical Materials, [S. l.], v. 5, n. 19, p. 1700416, 2017. DOI: 10.1002/adom.201700416. Disponível em: https://onlinelibrary.wiley.com/doi/10.1002/adom.201700416.

TOUGAARD, Sven. Improved XPS analysis by visual inspection of the survey spectrum. **Surface and Interface Analysis**, *[S. l.]*, v. 50, n. 6, p. 657–666, 2018. DOI: 10.1002/sia.6456. Disponível em: http://doi.wiley.com/10.1002/sia.6456.

TSAI, Meng-Lin; TU, Wei-Chen; TANG, Libin; WEI, Tzu-Chiao; WEI, Wan-Rou; LAU, Shu Ping; CHEN, Lih-Juann; HE, Jr-Hau. Efficiency Enhancement of Silicon Heterojunction Solar Cells via Photon Management Using Graphene Quantum Dot as Downconverters. **Nano Letters**, *[S. l.]*, v. 16, n. 1, p. 309–313, 2016. DOI: 10.1021/acs.nanolett.5b03814. Disponível em: https://pubs.acs.org/doi/10.1021/acs.nanolett.5b03814.

TUERHONG, Mhetaer; XU, Yang; YIN, Xue-Bo. Review on Carbon Dots and Their Applications. Chinese Journal of Analytical Chemistry, [S. l.], v. 45, n. 1, p. 139–150, 2017.

 DOI:
 10.1016/S1872-2040(16)60990-8.
 Disponível
 em:

 https://linkinghub.elsevier.com/retrieve/pii/S1872204016609908.

 </td

UCHINO, T.; ABOSHI, A.; KOHARA, S.; OHISHI, Y.; SAKASHITA, M.; AOKI, K. Microscopic structure of nanometer-sized silica particles. **Physical Review B - Condensed Matter and Materials Physics**, *[S. l.]*, v. 69, n. 15, p. 1–8, 2004. DOI: 10.1103/PhysRevB.69.155409.

UDD, E. Overview of Fiber Optic Sensors. *In*: YU, F. T. S.; YIN, S. (org.). Fiber Optic Sensors. [s.l.] : Marcel Dekker, 2002.

VAN EIJKELENBORG, Martijn et al. Microstructured polymer optical fibre. **Optics Express**, *[S. l.]*, v. 9, n. 7, p. 319, 2001. DOI: 10.1364/OE.9.000319. Disponível em: https://opg.optica.org/oe/abstract.cfm?uri=oe-9-7-319.

VEJRAŽKA, Jiří; VEČEŘ, Marek; ORVALHO, Sandra; SECHET, Philippe; RUZICKA, Marek C.; CARTELLIER, Alain. Measurement accuracy of a mono-fiber optical probe in a bubbly flow. **International Journal of Multiphase Flow**, *[S. l.]*, v. 36, n. 7, p. 533–548, 2010. DOI: 10.1016/j.ijmultiphaseflow.2010.03.007. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0301932210000625.

VOURVOULIAS, Aris. **Solar Panels**. 2023. Disponível em: https://www.greenmatch.co.uk/blog/2014/11/how-efficient-are-solar-panels. Acesso em: 12 mar. 2023.

WALDRON, Dennis L.; PRESKE, Amanda; ZAWODNY, Joseph M.; KRAUSS, Todd D.; GUPTA, Mool C. PbSe quantum dot based luminescent solar concentrators. **Nanotechnology**, *[S. l.]*, v. 28, n. 9, p. 095205, 2017. DOI: 10.1088/1361-6528/aa577f. Disponível em: https://iopscience.iop.org/article/10.1088/1361-6528/aa577f.

WANG, Boyang; LU, Siyu. The light of carbon dots: From mechanism to applications. **Matter**, *[S. l.]*, v. 5, n. 1, p. 110–149, 2022. DOI: 10.1016/j.matt.2021.10.016. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S2590238521005154.

WANG, Li; ZHOU, H. Susan. Green Synthesis of Luminescent Nitrogen-Doped Carbon Dots from Milk and Its Imaging Application. Analytical Chemistry, [S. l.], v. 86, n. 18, p. 8902–8905, 2014. DOI: 10.1021/ac502646x. Disponível em:

https://pubs.acs.org/doi/10.1021/ac502646x.

WANG, Liang; LI, Ming; LI, Weitao; HAN, Yu; LIU, Yijian; LI, Zhen; ZHANG, Baohua; PAN, Dengyu. Rationally Designed Efficient Dual-Mode Colorimetric/Fluorescence Sensor Based on Carbon Dots for Detection of pH and Cu2+ Ions. **ACS Sustainable Chemistry and Engineering**, *[S. l.]*, v. 6, n. 10, p. 12668–12674, 2018. DOI: 10.1021/acssuschemeng.8b01625.

WANG, Ling; CHOI, Hae Young; JUNG, Yongmin; LEE, Byeong Ha; KIM, Kwang-Taek. Optical probe based on double-clad optical fiber for fluorescence spectroscopy. **Optics Express**, *[S. l.]*, v. 15, n. 26, p. 17681, 2007. DOI: 10.1364/OE.15.017681. Disponível em: https://opg.optica.org/oe/abstract.cfm?uri=oe-15-26-17681.

WANG, Xiaohui; QU, Konggang; XU, Bailu; REN, Jinsong; QU, Xiaogang. Microwave assisted one-step green synthesis of cell-permeable multicolor photoluminescent carbon dots without surface passivation reagents. **Journal of Materials Chemistry**, *[S. l.]*, v. 21, n. 8, p. 2445, 2011. DOI: 10.1039/c0jm02963g. Disponível em: http://xlink.rsc.org/?DOI=c0jm02963g.

WANG, Xu-Dong; WOLFBEIS, Otto S. Fiber-Optic Chemical Sensors and Biosensors (2008–2012). Analytical Chemistry, [S. l.], v. 85, n. 2, p. 487–508, 2013. DOI: 10.1021/ac303159b. Disponível em: https://pubs.acs.org/doi/10.1021/ac303159b.

WANG, Xu Dong; WOLFBEIS, Otto S. Fiber-optic chemical sensors and biosensors (2015-2019). Analytical Chemistry, [S. l.], v. 92, n. 1, p. 397–430, 2020. DOI: 10.1021/acs.analchem.9b04708.

WANG, Youfu; HU, Aiguo. Carbon quantum dots: synthesis, properties and applications. **Journal of Materials Chemistry C**, *[S. l.]*, v. 2, n. 34, p. 6921, 2014. DOI: 10.1039/C4TC00988F. Disponível em: http://xlink.rsc.org/?DOI=C4TC00988F.

WARD, O. P. Fermentation Biotechnology: Principles, Processes and Products. Second ed. Hoboken, NJ, USA: John Wiley and Sons, 1991.

WEISS, Nicolás; VAN LEEUWEN, Ton G.; KALKMAN, Jeroen. Localized measurement of longitudinal and transverse flow velocities in colloidal suspensions using optical coherence tomography. **Physical Review E**, *[S. l.]*, v. 88, n. 4, p. 042312, 2013. DOI:

10.1103/PhysRevE.88.042312.Disponívelem:https://link.aps.org/doi/10.1103/PhysRevE.88.042312.

WELTY, J.; WICKS, C.; WILSON, R.; RORRER, G. Fundamentals of Momentum, Heat, and Mass Transfer. 5th. ed. Hoboken, NJ, USA: John Wiley and Sons, 2008.

WENCEL, Dorota; ABEL, Tobias; MCDONAGH, Colette. Optical Chemical pH Sensors. **Analytical Chemistry**, *[S. l.]*, v. 86, n. 1, p. 15–29, 2014. DOI: 10.1021/ac4035168. Disponível em: https://pubs.acs.org/doi/10.1021/ac4035168.

WIEDERHECKER, G. S.; CORDEIRO, C. M. B.; COUNY, F.; BENABID, F.; MAIER, S. A.; KNIGHT, J. C.; CRUZ, C. H. B.; FRAGNITO, H. L. Field enhancement within an optical fibre with a subwavelength air core. **Nature Photonics**, *[S. l.]*, v. 1, n. 2, p. 115–118, 2007. DOI: 10.1038/nphoton.2006.81. Disponível em: http://www.nature.com/articles/nphoton.2006.81.

WIESE, H.; HORN, D. Single-mode fibers in fiber-optic quasielastic light scattering: A study of the dynamics of concentrated latex dispersions. The Journal of Chemical Physics, [S. l.],
v. 94, n. 10, p. 6429–6443, 1991. DOI: 10.1063/1.460272. Disponível em: http://aip.scitation.org/doi/10.1063/1.460272.

WILLIAMS, Alun T. Rhys; WINFIELD, Stephen A.; MILLER, James N. Relative fluorescence quantum yields using a computer-controlled luminescence spectrometer. **The Analyst**, *[S. l.]*, v. 108, n. 1290, p. 1067, 1983. DOI: 10.1039/an9830801067. Disponível em: http://xlink.rsc.org/?DOI=an9830801067.

WOLFBEIS, Otto S. Fiber-optic chemical sensors and biosensors. Analytical Chemistry, [S. l.], v. 80, n. 12, p. 4269–4283, 2008. DOI: 10.1021/ac800473b.

WU, Jing; GU, Min. Microfluidic sensing: state of the art fabrication and detection techniques. Journal of Biomedical Optics, [S. l.], v. 16, n. 8, p. 080901, 2011. DOI: 10.1117/1.3607430. Disponível em:

http://biomedicaloptics.spiedigitallibrary.org/article.aspx?doi=10.1117/1.3607430.

WU, Siwu; WENG, Peijin; TANG, Zhenghai; GUO, Baochun. Sustainable Carbon Nanodots with Tunable Radical Scavenging Activity for Elastomers. **ACS Sustainable Chemistry & Engineering**, *[S. l.]*, v. 4, n. 1, p. 247–254, 2016. DOI: 10.1021/acssuschemeng.5b01069. Disponível em: https://pubs.acs.org/doi/10.1021/acssuschemeng.5b01069.

WU, Tianshu; TANG, Meng. Toxicity of quantum dots on respiratory system. **Inhalation Toxicology**, *[S. l.]*, v. 26, n. 2, p. 128–139, 2014. DOI: 10.3109/08958378.2013.871762. Disponível em: http://www.tandfonline.com/doi/full/10.3109/08958378.2013.871762.

XIA, Chunlei; ZHU, Shoujun; FENG, Tanglue; YANG, Mingxi; YANG, Bai. Evolution and Synthesis of Carbon Dots: From Carbon Dots to Carbonized Polymer Dots. **Advanced Science**, *[S. l.]*, v. 6, n. 23, p. 1901316, 2019. DOI: 10.1002/advs.201901316. Disponível em: https://onlinelibrary.wiley.com/doi/10.1002/advs.201901316.

XU, Huan; XIE, Lan; HAKKARAINEN, Minna. Coffee-Ground-Derived Quantum Dots for Aqueous Processable Nanoporous Graphene Membranes. **ACS Sustainable Chemistry & Engineering**, *[S. l.]*, v. 5, n. 6, p. 5360–5367, 2017. DOI: 10.1021/acssuschemeng.7b00663. Disponível em: https://pubs.acs.org/doi/10.1021/acssuschemeng.7b00663.

XU, Quan et al. Metal Charge Transfer Doped Carbon Dots with Reversibly Switchable, Ultra-High Quantum Yield Photoluminescence. **ACS Applied Nano Materials**, *[S. l.]*, v. 1, n. 4, p. 1886–1893, 2018. DOI: 10.1021/acsanm.8b00277. Disponível em: https://pubs.acs.org/doi/10.1021/acsanm.8b00277.

XU, Quan; LI, Weijun; DING, Lan; YANG, Wenjing; XIAO, Haihua; ONG, Wee Jun. Function-driven engineering of 1D carbon nanotubes and 0D carbon dots: Mechanism, properties and applications. **Nanoscale**, *[S. l.]*, v. 11, n. 4, p. 1475–1504, 2019. DOI: 10.1039/c8nr08738e.

XU, Xiaoyou; RAY, Robert; GU, Yunlong; PLOEHN, Harry J.; GEARHEART, Latha; RAKER, Kyle; SCRIVENS, Walter A. Electrophoretic Analysis and Purification of Fluorescent Single-Walled Carbon Nanotube Fragments. Journal of the American Chemical Society, *[S. l.]*, v. 126, n. 40, p. 12736–12737, 2004. DOI: 10.1021/ja040082h. Disponível em: https://pubs.acs.org/doi/10.1021/ja040082h.

YAGER, Paul; EDWARDS, Thayne; FU, Elain; HELTON, Kristen; NELSON, Kjell; TAM, Milton R.; WEIGL, Bernhard H. Microfluidic diagnostic technologies for global public health. **Nature**, *[S. l.]*, v. 442, n. 7101, p. 412–418, 2006. DOI: 10.1038/nature05064. Disponível em: http://www.nature.com/articles/nature05064.

YAN, Fang; LI, Jiurong; ZHAO, Xiujian; GONG, Xiao. Unveiling Unconventional

Luminescence Behavior of Multicolor Carbon Dots Derived from Phenylenediamine. TheJournal of Physical Chemistry Letters, [S. l.], v. 14, n. 26, p. 5975–5984, 2023. DOI:10.1021/acs.jpclett.3c01497.Disponívelhttps://pubs.acs.org/doi/10.1021/acs.jpclett.3c01497.

YAN, Fanyong; SUN, Zhonghui; ZHANG, Hao; SUN, Xiaodong; JIANG, Yingxia; BAI, Zhangjun. The fluorescence mechanism of carbon dots, and methods for tuning their emission color: a review. **Microchimica Acta**, *[S. l.]*, v. 186, n. 8, p. 583, 2019. DOI: 10.1007/s00604-019-3688-y. Disponível em: http://link.springer.com/10.1007/s00604-019-3688-y.

YAN, Yong; WANG, Lijuan; WANG, Tao; WANG, Xue; HU, Yonghui; DUAN, Quansheng.
Application of soft computing techniques to multiphase flow measurement: A review. Flow
Measurement and Instrumentation, [S. l.], v. 60, p. 30–43, 2018. DOI: 10.1016/j.flowmeasinst.2018.02.017. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S095559861730465X.

YANG, Xinghua et al. Optofluidic twin-core hollow fiber interferometer for label-free sensing of the streptavidin-biotin binding. **Sensors and Actuators B: Chemical**, *[S. l.]*, v. 277, n. September, p. 353–359, 2018. DOI: 10.1016/j.snb.2018.09.032. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0925400518316459.

YAO, Jiafeng; TAKEI, Masahiro. Application of Process Tomography to Multiphase Flow Measurement in Industrial and Biomedical Fields: A Review. IEEE Sensors Journal, [S. l.],
v. 17, n. 24, p. 8196–8205, 2017. DOI: 10.1109/JSEN.2017.2682929. Disponível em: http://ieeexplore.ieee.org/document/7879196/.

YE, C.; YAN, P.; HUANG, L.; LIU, Q.; GONG, M. Stimulated Brillouin scattering phenomena in a nanosecond linearly polarized Yb-doped double-clad fiber amplifier. **Laser Physics Letters**, *[S. l.]*, v. 4, n. 5, p. 376–381, 2007. DOI: 10.1002/lapl.200610123. Disponível em: https://iopscience.iop.org/article/10.1002/lapl.200610123.

YELIN, D.; BOUMA, B. E.; YUN, S. H.; TEARNEY, G. J. Double-clad fiber for endoscopy. **Optics Letters**, *[S. l.]*, v. 29, n. 20, p. 2408, 2004. DOI: 10.1364/OL.29.002408. Disponível em: https://opg.optica.org/abstract.cfm?URI=ol-29-20-2408.

YONG WANG; HONG PO. Dynamic characteristics of double-clad fiber amplifiers for high-

power pulse amplification. Journal of Lightwave Technology, [S. l.], v. 21, n. 10, p. 2262–2270, 2003. DOI: 10.1109/JLT.2003.818166. Disponível em: http://ieeexplore.ieee.org/document/1236497/.

YUAN, Fanglong; LI, Shuhua; FAN, Zetan; MENG, Xiangyue; FAN, Louzhen; YANG, Shihe. Shining carbon dots: Synthesis and biomedical and optoelectronic applications. **Nano Today**, *[S. l.]*, v. 11, n. 5, p. 565–586, 2016. DOI: 10.1016/j.nantod.2016.08.006. Disponível em: http://dx.doi.org/10.1016/j.nantod.2016.08.006.

ZAMARRENO, Carlos R.; MARTELLI, Cicero; BARONCINI, Virginia H. V.; DOS SANTOS, Eduardo N.; DA SILVA, Marco J.; MORALES, Rigoberto E. M.; ZUBIATE, Pablo; ARREGUI, Francisco J.; MATIAS, Ignacio R. Single and Multiphase Flow Characterization by Means of an Optical Fiber Bragg Grating Grid. Journal of Lightwave Technology, [S. l.], v. 33, n. 9, p. 1857–1862, 2015. DOI: 10.1109/JLT.2015.2394788. Disponível em: http://ieeexplore.ieee.org/document/7017483/.

ZENTENO, L. High-power double-clad fiber lasers. Journal of Lightwave Technology, [S. l.], v. 11, n. 9, p. 1435–1446, 1993. DOI: 10.1109/50.241933. Disponível em: http://ieeexplore.ieee.org/document/241933/.

ZHANG, Hu; ZHANG, Xiaoguang; LI, Hui; DENG, Yifan; XI, Lixia; TANG, Xianfeng; ZHANG, Wenbo. The Orbital Angular Momentum Modes Supporting Fibers Based on the Photonic Crystal Fiber Structure. **Crystals**, *[S. l.]*, v. 7, n. 10, p. 286, 2017. DOI: 10.3390/cryst7100286. Disponível em: http://www.mdpi.com/2073-4352/7/10/286.

ZHANG, L.; ZHANG, W.; BENNION, I. In-Fiber Grating Optic Sensors. *In*: YU, F. T. S.; YIN, S. (org.). Fiber Optic Sensors. [s.l.] : Marcel Dekker, 2002.

ZHANG, Tianyi; DONG, Si; ZHAO, Feifei; DENG, Mingxiao; FU, Yuqin; LÜ, Changli. Tricolor emissive carbon dots for ultra-wide range pH test papers and bioimaging. **Sensors and Actuators B: Chemical**, *[S. l.]*, v. 298, n. June, p. 126869, 2019. DOI: 10.1016/j.snb.2019.126869. Disponível em: https://doi.org/10.1016/j.snb.2019.126869.

ZHANG, Xinyue; JIANG, Mingyue; NIU, Na; CHEN, Zhijun; LI, Shujun; LIU, Shouxin; LI, Jian. Natural-Product-Derived Carbon Dots: From Natural Products to Functional Materials. **ChemSusChem**, *[S. l.]*, v. 11, n. 1, p. 11–24, 2018. DOI: 10.1002/cssc.201701847.

ZHANG, Zehui; SUN, Wenhui; WU, Peiyi. Highly Photoluminescent Carbon Dots Derived from Egg White: Facile and Green Synthesis, Photoluminescence Properties, and Multiple Applications. ACS Sustainable Chemistry & Engineering, [S. l.], v. 3, n. 7, p. 1412–1418, 2015. DOI: 10.1021/acssuschemeng.5b00156. Disponível em: https://pubs.acs.org/doi/10.1021/acssuschemeng.5b00156.

ZHAO, Haiguang. Refractive index dependent optical property of carbon dots integratedluminescent solar concentrators. Journal of Luminescence, [S. l.], v. 211, p. 150–156, 2019.DOI:10.1016/j.jlumin.2019.03.039.Disponívelem:https://linkinghub.elsevier.com/retrieve/pii/S0022231318323780.

ZHAO, Wen-Sheng et al. Controllable Photoelectric Properties of Carbon Dots and Their Application in Organic Solar Cells. **Chinese Journal of Polymer Science**, *[S. l.]*, v. 40, n. 1, p. 7–20, 2022. DOI: 10.1007/s10118-021-2637-5. Disponível em: https://link.springer.com/10.1007/s10118-021-2637-5.

ZHENGQIAN LUO et al. Topological-Insulator Passively Q-Switched Double-Clad Fiber Laser at 2 <formula formulatype="inline"> <tex Notation="TeX">\$\mu\$</tex></formula>m Wavelength. **IEEE Journal of Selected Topics in Quantum Electronics**, *[S. l.]*, v. 20, n. 5, p. 1–8, 2014. DOI: 10.1109/JSTQE.2014.2305834. Disponível em: http://ieeexplore.ieee.org/document/6739071/.

ZHOU, Minjuan; GUO, Jingjing; YANG, Changxi. Ratiometric fluorescence sensor for Fe3+ ions detection based on quantum dot-doped hydrogel optical fiber. **Sensors and Actuators B: Chemical**, *[S. l.]*, v. 264, p. 52–58, 2018. DOI: 10.1016/j.snb.2018.02.119. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0925400518303988.

ZHOU, Wei; WANG, Moo-Chin; ZHAO, Xiujian. Poly(methyl methacrylate) (PMMA) doped with DCJTB for luminescent solar concentrator applications. **Solar Energy**, *[S. l.]*, v. 115, p. 569–576, 2015. DOI: 10.1016/j.solener.2015.03.012. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0038092X15001309.

ZHU, Shoujun et al. Strongly green-photoluminescent graphene quantum dots for bioimaging applications. **Chemical Communications**, *[S. l.]*, v. 47, n. 24, p. 6858, 2011. DOI: 10.1039/c1cc11122a. Disponível em: http://xlink.rsc.org/?DOI=c1cc11122a.

ZHU, Shoujun; SONG, Yubin; ZHAO, Xiaohuan; SHAO, Jieren; ZHANG, Junhu; YANG, Bai. The photoluminescence mechanism in carbon dots (graphene quantum dots, carbon nanodots, and polymer dots): current state and future perspective. **Nano Research**, *[S. l.]*, v. 8, n. 2, p. 355–381, 2015. DOI: 10.1007/s12274-014-0644-3. Disponível em: http://link.springer.com/10.1007/s12274-014-0644-3.

ZHU, Ying; FANG, Qun. Analytical detection techniques for droplet microfluidics—A review. **Analytica Chimica Acta**, *[S. l.]*, v. 787, p. 24–35, 2013. DOI: 10.1016/j.aca.2013.04.064. Disponível em: https://linkinghub.elsevier.com/retrieve/pii/S0003267013006454.

ZUO, Pengli; LU, Xiuhua; SUN, Zhigang; GUO, Yuhan; HE, Hua. A review on syntheses, properties, characterization and bioanalytical applications of fluorescent carbon dots. **Microchimica Acta**, *[S. l.]*, v. 183, n. 2, p. 519–542, 2016. DOI: 10.1007/s00604-015-1705-3. Disponível em: http://link.springer.com/10.1007/s00604-015-1705-3.

Appendix 1: 3D-printed case for smartphone-based fermentation sensor - Project's blueprint (Fig. 57)



Figure A1. Case's blueprint. Quotes in millimeters (mm).

Appendix 2: Silica nanoparticles (Fig. 61) statistics

The DLS analysis resulted in the distribution shown in Fig. 61b, which clearly presents high skewness and kurtosis. So, since the curve is asymmetric, its behavior deviates from the Gaussian's. On the other hand, data has a format that resembles the normal curve. Thus, an alternative is the data characterization through probability density functions (PDFs) that are derived from the normal. When compared to the normal, these PDFs may present modifications or additional parameters for accounting for shape deviations. Examples of such functions include the lognormal and the Poisson, a particular case of the Gamma distribution.

The lognormal is defined as a random variable whose natural logarithm is described by a normal probability function. So, it has a high degree of correlation with the Gaussian fitting, what could explain the apparent resemblance of Fig. 61b with this bell-shaped distribution. Mathematically, the probability density function F(X) that represents the lognormal random variable X is defined by Equation (A1), where μ and σ are the fitting parameters of the curve and ln is the natural logarithm (e ≈ 2.718 is the base of natural logarithm).

$$F(X) = \frac{1}{X\sigma\sqrt{2\pi}}e^{-\frac{1}{2}\left(\frac{\ln X - \mu}{\sigma}\right)^2} (A1)$$

Naturally, Equation (A1) is an ideal situation where no translations are present. So, considering the presence of a vertical translation F_0 ; a multiplicative factor A; and $\mu = \ln(X_C)$, this equation may be modified to obtain a more general and powerful model, Equation (A2).

$$F(X) = F_0 + \frac{A}{X\sigma\sqrt{2\pi}}e^{-\frac{1}{2\sigma^2}\left(\ln\left(\frac{X}{X_C}\right)\right)^2} (A2)$$

The fitting of data to the lognormal PDF allows the evaluation of several statistics using the obtained parameters:

- Mean (expectation or expected value): $e^{(\mu + \sigma^2/2)}$;
- Variance: $(e^{\sigma^2} 1).e^{(2\mu + \sigma^2)};$
- Mode (PDF's point of maximum probability): $e^{(\mu \sigma^2)}$;
- Skewness (parameter representing PDF's asymmetry or distortion): $(e^{\sigma^2} + 2) \cdot (e^{\sigma^2} 1)^{0.5}$;
- Kurtosis (shape parameter that represents PDF's "*tailedness*" or "*long-tail effects*"): $(e^{4\sigma^2} + 2e^{3\sigma^2} + 3e^{2\sigma^2} 6)$.

Fig. 61b represents the counting of particles present on each diameter bin, where the discretization of bins is performed by the LDV equipment itself. Thus, the total number of assessed SiO_2 nanoparticles is obtained by simply summing all values used to plot this curve. Finally, the counting obtained for each bin is divided by the total number of particles to convert the LDV readings into the probabilities associated to each diameter interval. The histogram of

the probabilities is represented by the bars in Fig. A2a. Here, a sanity check is recommended: the sum of all calculated probabilities should be 1, representing 100% of the sample space.

The lognormal distribution is obtained by fitting the probability data from Fig. A2a to Equation (A2). It results in the parameters $F_0 = -1.83477 \times 10^{-4}$; A = 29.53614; X_C = 203.49999; and $\sigma = 0.19876$; with adjusted R² of 0.9938. Since $\mu = \ln(X_C)$, $\mu = 2.30856$. Consequently, the other shape and statistical parameters calculated for this curve are mode = 9.67030; mean = 10.26066; variance = 4.24244; skewness = 0.61031; and kurtosis = 0.66949.



Figure A2. Statistical characterization of SiO₂ nanoparticles: (a) lognormal (blue continuous line) fitted to the diameters' distribution. The bar chart represents the actual histogram (counting data was converted to probabilities); (b) cumulative probabilities fitted through a sigmoid curve (red continuous curve). The blue dashed lines for the 257 nm diameter represent the 95% accumulated probability, whereas the green lines for 288 nm represent an accumulated percent of 98% for the particles' diameters.

The fitting resulted in a mode that is lower than the mean; and in values of skewness and kurtosis that are significantly different from zero. The difference between the mean and the mode and the presence of non-zero skewness and kurtosis quantitatively explain why the data could not be fitted to the normal curve. The low variance, in turns, reflects the high degree of morphological control provided by the VAD process.

The values of mode and mean calculated through the fitting of data to Equation (A2) seem to differ from what is visually observed in the plot (Fig. A2a). It is a consequence from the scaling of the PDF with the parameters F_0 and A, but it is easy to convert the parameters to the real values.

The point of maximum of the lognormal fitted curve represents the most probable diameter to be obtained from the process, i.e., the PDF's mode. This point can be visually obtained on the plot; or may be calculated as the root from the 1st-order derivative: it is the 195 nm, which has an associated probability of 0.2969 = 29.69%. As this is the most probable diameter value that one would obtain, it was took as the center of the confidence interval used to represent the particles.

Again, the bars from Fig. A2a represent probabilities and their total sum must be 1. Then, it is possible to sort data in ascending order of diameters and calculate the cumulative

sum of probabilities. This procedure is equivalent to a numerical integration, resulting in the accumulated probabilities shown in Fig. A2b.

Since the cumulative probabilities in Fig. A2b present a sigmoid profile, they may be fitted by the logistic curve represented by Equation (A3). The fitting parameters obtained now are: $A_1 = -0.00107$; $A_2 = 0.99925$; $X_0 = 183.85621$; and p = 8.87896; with adjusted R² of 0.9996. Here, S(X) represents the sigmoid fitting obtained for a variable X. In this case, the sigmoid represents the cumulative probability, and X is the random variable (the diameter of silica nanoparticles) itself.

$$S(X) = A_2 + \frac{(A_1 - A_2)}{\left[1 + \left(\frac{X}{X_0}\right)^p\right]}$$
(A3)

For obtaining a symmetrical confidence interval, the uncertainty may be defined as the lowest interval around the most probable value (the mode) which comprehends at least 95% of the results. In other words, the confidence interval is set as the minimum range for which a cumulative probability \geq 95% is obtained, leading to the diameter a = (195 ± 93) nm.

The cumulative probability of 95% is verified for the range from diameter 102 nm (first value with accumulated percent higher than 0%) to 257 nm (value highlighted by the blue dashed lines in Fig. A2b). Due to the distortion of the curve, this range is not symmetric around the highest probability, though: (195 - 102) = 93 nm, whereas (257 - 195) = 62 nm. So, by picking the largest difference between the interval boundaries and the mode (93 nm), one guarantees that at least 95% of particles will be included. Actually, the cumulative percent for (195 + 93) = 288 nm is 98%, as highlighted by the green dashed lines in Fig. A2b.

The larger interval width obtained for the values lower than 195 nm (width of 93 nm, which is 50% higher than the 62 nm-width obtained for the values higher than 195 nm); and the achievement of a plateau in Fig. A2b (resulting in the need of large increments of diameter for obtaining low increases of accumulated probability) are direct consequences of the PDF distortion.

Once the skewed curve is more populated at the left-hand side of the mode (the region with lower diameters), most particles are in the first half of the range (195 ± 93) nm. On the other hand, the curve from Fig. A2a also shows a small number of particles for very high diameters, a consequence of its long tail (there is a high kurtosis, so the curve's tail on the right-hand side of the mode is longer than that observed on the left-hand side).

Appendix 3: Supervised students

[1] Co-supervision: scientific initiation/undergraduate research (PIBIC/CNPq): Beatriz Ferreira Mendes. Estudo das Propriedades Cinéticas da Reação Pozolânica Visando ao Maior Entendimento Sobre o Processo. Supervision: Prof. Dr. Carlos Kenichi Suzuki. University of Campinas, Mechanical Engineering, School of Mechanical Engineering (FEM/UNICAMP), SP, Brazil, 2016/2017.

[2] Co-supervision: scientific initiation/undergraduate research (FAPESP Grant 2017/06190-7): Matheus Kauê Gomes. Caracterização de nanofluidos de dióxido de silício utilizando sensor de fibra óptica. Supervision: Prof. Dr. Eric Fujiwara. University of Campinas, Control and Automation Engineering, School of Mechanical Engineering (FEM/UNICAMP), SP, Brazil, 2017/2018.

[3] Co-supervision: scientific initiation/undergraduate research (PIBIC/CNPq): Beatriz Ferreira Mendes. Estudo dos Parâmetros de Uso da Sílica para Adsorção de Corantes Visando à Otimização de Membranas Cerâmicas Filtrantes. Supervision: Prof. Dr. Carlos Kenichi Suzuki. University of Campinas, Mechanical Engineering, School of Mechanical Engineering (FEM/UNICAMP), SP, Brazil, 2017/2018.

[4] **Co-supervision: Undergraduate Conclusion Paper ("***Trabalho de Graduação*", **TG):** Guilherme Antonio Dutra Morais. **Análise da proliferação celular por processamento de imagem**. Supervision: Prof. Dr. Eric Fujiwara. University of Campinas, Control and Automation Engineering, School of Mechanical Engineering (FEM/UNICAMP), SP, Brazil, 2018.

[5] Co-supervision: scientific initiation/undergraduate research (PIBIC/CNPq): Matheus dos Santos Rodrigues. Caracterização de suspensões coloidais de sílica em regime dinâmico de escoamento utilizando sensor de fibra óptica. Supervision: Prof. Dr. Eric Fujiwara. University of Campinas, Control and Automation Engineering, School of Mechanical Engineering (FEM/UNICAMP), SP, Brazil, 2018/2019.

– This research was granted with "*Honorable Mention*" ("*Menção Honrosa*") among the best papers presented in **XXVII UNICAMP Scientific Initiation Conference** ("*XXVII Congresso de Iniciação Científica da UNICAMP*", 16-18 oct. 2019).