Nanocrystalline anatase TiO$_2$/reduced graphene oxide composite films as photoanodes for photoelectrochemical water splitting studies: the role of reduced graphene oxide†

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Nanocrystalline TiO$_2$ and reduced graphene oxide (TiO$_2$/RGO) composite films were prepared by combining a sol–gel method with hydrothermal treatment, employing titanium isopropoxide (Ti(O(i-Pr)$_4$) and graphene oxide (GO) as starting materials. Although several reports in the literature have explored the benefits of RGO addition in titania films for photocatalysis and water splitting reactions, the role of RGO in the composite is always described as that of a material that is able to act as an electron acceptor and transport electrons more efficiently. However, in most of these reports, no clear evidence for this “role” is presented, and the main focus is deviated to the improved efficiency and not to the reasons for said efficiency. In this study, we employed several techniques to definitively present our understanding of the role of RGO in titania composite films. The TiO$_2$/RGO composite films were characterized by X ray diffraction, Raman spectroscopy, microscopy and electrochemical techniques. In photoelectrochemical water splitting studies, the TiO$_2$/RGO$_{0.1\%}$ photoelectrodes showed the highest photocurrent density values (0.20 mA cm$^{-2}$ at 1.23 V RHE) compared to other electrodes, with an increase of 78% in relation to pristine TiO$_2$ film (0.11 mA cm$^{-2}$ at 1.23 V RHE). The transient absorption spectroscopy (TAS) results indicated increases in the lifetime and yield of both the photogenerated holes and electrons. Interestingly, the TiO$_2$/RGO$_{0.1\%}$ film exhibited the best charge generation upon excitation, corroborating the photoelectrochemical data. We proposed that in films with lower concentrations (<0.1 wt%), the RGO sheets are electron acceptors, and a decrease in the charge recombination processes is the immediate consequence. Thus, both holes and electrons live longer and contribute more effectively to the photocurrent density.

Introduction

Since Fujishima and Honda (1972) published the first report of the photoelectrochemical splitting of water into hydrogen (H$_2$) and oxygen (O$_2$) over titanium dioxide or titania (TiO$_2$) photoanodes, different types of semiconductors have been developed and evaluated as candidate photoelectrodes for solar-driven hydrogen production. Among these diverse semiconductors, TiO$_2$ is still one of the more studied as a photocatalyst, due to its excellent thermal, chemical and photochemical stability, its insolubility in water and its availability on a large scale. The photoactivity of this material is observed only when it is irradiated with ultraviolet light, which corresponds to only approximately 4% of incident solar energy. Many strategies to improve the absorption of TiO$_2$ in the visible part of the solar spectrum have been accomplished; these include the introduction of impurities (e.g. nitrogen atoms) to change the band gap of TiO$_2$, and sensitization with particles as CdS, CdSe or CdSTe. The development of new architectures, such as nanotubes, nanowires, nanorods and nanoparticles, is also an alternative to improve the performance of TiO$_2$ by increasing the semiconductor surface area and/or electronic transport.

Another challenge for the more efficient use of TiO$_2$ as a photocatalyst for water splitting or pollutant oxidation is to...
improve the electronic transport that occurs by diffusion in the oxide semiconductor film. 10 In this case, the diffusion of the photogenerated charge carriers is relatively “slow” on conventional TiO2 films; therefore, the charge recombination probability increases, resulting in a decrease in the photocurrent density and photocatalytic efficiency for several reactions. 11 An interesting alternative to reduce this effect is the incorporation of carbon-based materials into nanocrystalline TiO2 films such as carbon nanotubes, 12 carbon black 13 and carbon quantum dots. 14 Our group has successfully demonstrated the use of boron or nitrogen-doped hollow carbon in TiO2(P25) films for photoelectrochemical studies 15 and TiO2/MWCNT as photoanodes in dye sensitized solar cells. 16 Another carbonaceous material that has been widely used for this application is graphene, due to its high surface area (2630 m2 g-1), photodegradation resistance, optical transparency (∼97.7%) and high charge mobility values (200 000 cm2 V-1 s-1). 17

Graphene oxide (GO), a graphene derivative, is an electrically insulating material and usually exhibits a rich assortment of oxygen-containing groups such as carboxylic, hydroxyl, carbonyl, and epoxide groups. The electrical conductivity of GO can be increased by reduction and partial restoration of the sp2-hybridized network; the resulting product, also known as reduced graphene oxide (RGO), has properties similar to graphene (although the reduction methods do not fully restore the ideal characteristics of graphene sheets). 17, 18

However, the combination of TiO2 nanoparticles and RGO sheets remains a good strategy to improve the photocatalytic performance of semiconductor oxides for several reactions. The electron-accepting ability presented by the RGO sheets can be used to enhance the electronic transport properties of the TiO2 films. 19-22 For instance, Ng et al. 23 reported that TiO2 (P25)-RGO nanocomposite electrodes showed significant activity for the photocatalytic decomposition of 2,4-dichlorophenoxacyclic acid, and Bell et al. 24 proposed the use of these nanocomposite films for photoelectrochemical water splitting. These researchers observed a significant increase in photocurrent density values compared to pure TiO2 film for all wavelengths in the ultraviolet region. Li and Cui 25 observed that TiO2/RGO (0.2 wt%) reached a hydrogen production rate of 43.8 μmol h-1, which was 1.6 times greater than that of a TiO2 sample. Recently, our research group demonstrated that the presence of RGO in TiO2/CdS films can increase methanol production from the photoreduction of carbon dioxide (CO2), 26 whereas TiO2/Cu2O films may favor the photocatalytic degradation of methylene blue dye. 27 In addition, films of TiO2/RGO applied as electron transport layers improved the efficiency of P3HT/PC61BM organic solar cells. 28 Although the advantages of the incorporation of RGO sheets in the TiO2 matrix are well known, unfortunately, a detailed understanding of the role of graphene and its derivatives is still very controversial and scarce in the literature. Some studies suggest that the RGO can facilitate electron injection and assist in electron transport, 29, 30 whereas other studies have reported that RGO can act as a sensitizer in semiconductor oxide films. 31-33 For this reason, there is a need for a more detailed and definitive investigation of the role of RGO sheets in the TiO2 matrix, and how this successful combination of materials has improved the photocatalytic performance of several oxides.

Herein, we report a facile route for the growth of nanocrystalline TiO2 particles on RGO sheets by combining a sol–gel method with hydrothermal treatment, employing titanium isopropoxide (Ti(OiPr)4) and graphene oxide (GO) as starting materials. In photoelectrochemical water splitting studies, the influence of the addition of different amounts of RGO to the TiO2 matrix was investigated by cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy (EIS) analysis. Charge generation/recombination dynamics (electrons and holes) using transient absorption spectroscopy (TAS) was also employed to correlate the excited state dynamics with the electrochemical reactions at the photoanode.

Experimental

Materials

All reagents were of analytical grade and used without further purification. The natural graphite powder was purchased from Nacional de Grafite LTDA (code: Micrograf 99507UJ). All other reagents were purchased from Sigma-Aldrich. The fluorine-doped tin oxide (FTO) conductive glasses (Hartford glass, R∞ ≤ 10 Ω sq-1) were cleaned ultrasonically with water–detergent solution, water, acetone, methanol and isopropanol successively in ultrasonic baths for 15 min. All substrates were dried with compressed nitrogen gas and treated with UV-ozone for 20 min.

Preparation of nanocrystalline TiO2/RGO pastes

The synthesis of reduced graphene oxide (RGO) from graphite and its characterization by XRD, Raman spectroscopy, TGA, FEG-SEM and HRTEM is described in the ESI† (Fig. S2–S6, Tables S1 and S2). In the ESI, † detailed characterizations of graphite and graphene oxide (precursors in the synthesis of the RGO sheets) are also available. Moreover, X-ray photoelectron analyses (XPS) were used to determine the chemical composition of the graphite, graphite oxide and RGO-hydrothermal samples. Pastes containing nanocrystalline TiO2 particles and RGO (TiO2/RGO) were prepared using titanium isopropoxide (Ti(OiPr)4) and GO as starting materials. First, the 1.8% w/w GO dispersion (5.8 g) was dispersed in 0.10 mol L-1 HNO3 solution (100 mL) using an ultrasonic bath for 30 min. Moreover, glacial acetic acid (3.5 mL) was added to Ti(OiPr)4 (16 mL) under stirring in a closed system that was previously purged with nitrogen. The TiO2 precursors were then injected into the acid GO dispersion and heated and maintained at 80 °C for 8 h in reflux; subsequently, the suspension was autoclaved at 220 °C for 12 h. Finally, using a rotary evaporator, the resulting homogeneous suspension was concentrated to a colloidal paste, composed of 11 wt% nanocrystalline TiO2 particles and 5.0 wt% RGO (designated as TiO2/RGO(5%)). Furthermore, polyethylene glycol (PEG, Mw = 2000) was added in a proportion of 40% of the total TiO2 weight.

A TiO2 paste was also prepared by the same procedure in the absence of RGO. Pastes containing different relative amounts...
of RGO, TiO$_2$/RGO(0.01%), TiO$_2$/RGO(0.05%), TiO$_2$/RGO(0.1%), TiO$_2$/RGO(0.5%), TiO$_2$/RGO(1%) and TiO$_2$/RGO(2%) were prepared using adequate amounts of TiO$_2$/RGO(5%) and the TiO$_2$ pastes (see Fig. S1 in the ESI†). The resulting pastes were stored in screw-threaded glass bottles.

**Preparation of TiO$_2$/RGO films**

For the preparation of the electrodes, an aliquot of TiO$_2$ or TiO$_2$/RGO paste was spread onto a fluorine-doped tin oxide conductive substrate (glass-FTO) by the doctor blading technique, using adhesive tape (Scotch Magic Tape, 3M, thickness <50 μm) to control the film thickness. After drying in air for 30 min, the films were heated at 350 °C for 2 h with a heating rate of 10 °C min$^{-1}$. The resulting films were uniform, without any noticeable cracks; the average thicknesses were measured with a Taylor-Hobson Form Talysurf 50 profilometer. These samples were cut into 1 x 1.5 cm$^2$ pieces, resulting in electrodes with geometrical active areas of 1.0 cm$^2$. These electrodes were stored in a dry atmosphere.

**Characterization of TiO$_2$/RGO films**

X ray diffraction (XRD) measurements were performed using a Shimadzu XRD7000 diffractometer (40 kV, 30 mA) with Cu (λ = 1.54178 Å) irradiation in the 2θ range of 3–80°. The Raman spectra were obtained using a confocal Raman spectrometer (model 764000 – Jobin Yvon – USA) equipped with a CCD (charge coupled device) detector and an Olympus BTH 2 microscope. The excitation laser was set at 514 nm with a 20-fold magnification objective lens. Optical microscopy images were taken with a Nikon Eclipse 5i (H5505, Nikon, Japan) microscope equipped with a Digital Sight Camera System (DS-Fi1 Nikon, Japan) and using an objective lens with a magnification of 20×. Field emission gun scanning electron microscopy (FEG-SEM) images were taken on a FEI Inspect F50 microscope at a voltage of 10 kV. High-resolution transmission electron microscopy (HRTEM) images were acquired using a JEM 3010 URN microscope at an accelerating voltage of 300 kV.

**Photoelectrochemical studies of TiO$_2$/RGO films**

Electrochemical measurements were carried out in an Autolab® model PGSTAT 10N potentiostat/galvanostat (Ecosp Chemie). The electrochemical impedance spectroscopy (EIS) measurements were carried out in an Autolab® model PGSTAT-302-N potentiostat/galvanostat with a frequency response analyzer (EIS) module (Eco Chemie). The EIS measurements were performed at the open circuit potential with a sinusoidal voltage perturbation of 10 mV, in the frequency range from 50 kHz to 5 mHz. A conventional three-electrode photoelectrochemical cell, consisting of glass-FTO|TiO$_2$ or glass-FTO|TiO$_2$/RGO as the working electrode (active area of 1 cm$^2$), a platinum wire as the counter electrode and Ag/AgCl in a KCl solution (3.0 mol L$^{-1}$) as the reference electrode, was used in the experiments. An aqueous H$_2$SO$_4$ solution (0.5 mol L$^{-1}$) was used as the electrolyte. The measured $E_{Ag/AgCl}$ potential values were converted to the reversible hydrogen electrode potentials ($E_{RHE}$) using the Nernst equation and considering the standard potential of the reference electrode, $E_{Ag/AgCl}^0$, which corresponds to 0.21 V RHE at 25 °C:

$$E_{RHE} = E_{Ag/AgCl}^0 + E_{Ag/AgCl} + 0.059 \text{pH}$$

The photoelectrochemical cell was placed in an optical bench consisting of an Oriel Xe (Hg) 250 W lamp coupled to an AM 1.5G filter (Oriel) and collimating lenses. The light intensity was calibrated with an optical power meter, model 1830-C ( Newport), to 100 mW cm$^{-2}$; however, no correction was made to discount reflection and transmission losses.

**Transient absorption spectroscopy**

The investigation of the recombination dynamics of the photogenerated electrons and holes in the TiO$_2$ and TiO$_2$/RGO films was performed using transient absorption spectroscopy (TAS). All transient absorption measurements on the μs-s time scale were performed using a Nd:YAG laser (Continuum Surelite I-10) as the UV excitation source (355 nm, ~200 μJ cm$^{-2}$ per pulse, typically 1 Hz repetition rate and 6 ns pulse width). The 75 W xenon lamp (Hamamatsu) was used as the continuous light source (probe beam). The lamp wavelengths were selected, using a monochromator, at 460 nm and 900 nm for lifetime monitoring of the photogenerated holes and electrons, respectively. The second monochromator after the sample was used to reduce the emission intensity and scattering from the laser before reaching the Si PIN photodiode. The detection system was comprised of a silicon photodiode (Hamamatsu Photonics) coupled to a digital oscilloscope (Tektronix TDS220) triggered by the laser excitation pulse. The transient decay data is the result of averaging between 300 laser shots. The TiO$_2$ and TiO$_2$/RGO films were placed in a sealed quartz cuvette and were thoroughly degassed with nitrogen prior to use. In this study, AOD means the transient absorption change.

**Results and discussion**

**Structural and morphological properties of TiO$_2$ and TiO$_2$/RGO nanoparticles and films**

The morphological characterization of the TiO$_2$ and TiO$_2$/RGO materials was investigated through FEG-SEM and HRTEM. Fig. 1(a) shows that TiO$_2$ particles have varied sizes and shapes, with an average diameter of ~15 nm. These features were also observed in the composite samples with different RGO concentrations. For the TiO$_2$/RGO composite, HKTEM and FEG-SEM images indicate that the RGO sheets are completely covered and decorated with TiO$_2$ nanoparticles (Fig. 1(b-d)). This strong interaction between the RGO sheets and the TiO$_2$ nanoparticles is important to achieve a good electronic coupling between these two materials.

The XRD patterns obtained for the TiO$_2$ and TiO$_2$/RGO(5%) films and powder TiO$_2$/RGO(5%) nanocomposite are presented in Fig. 2(a). The diffractograms also include the Joint Committee on Powder Diffraction Standards (JCPDS) information for the anatase and rutile phases, 21-1272 and 21-1276, respectively. The Raman spectra obtained for the TiO$_2$ and TiO$_2$/RGO(5%) films are presented in Fig. 2(b).
The XRD pattern of the TiO$_2$/RGO(5%) nanocomposite (powder) showed the presence of TiO$_2$ crystalline structure, predominantly the anatase allotropic form. This information can also be observed in the TiO$_2$ and TiO$_2$/RGO(5%) films; however, the signals are less intense. The diffraction peaks marked with an asterisk (*) correspond to the crystalline phases of the FTO substrate. Comparison of the XRD diffraction peaks for the TiO$_2$/RGO(5%) composite and the pure TiO$_2$ films demonstrates that the presence of RGO did not change the TiO$_2$ preferential crystal orientations. The typical diffraction peaks of carbon species, observed at 20 = 25° in Fig. S5(a) (ESI†), are not observed in the composite, probably due to the relatively low RGO low amount.

The Raman results showed specific vibration modes located around 150 cm$^{-1}$ (Eg), 200 cm$^{-1}$ (Eg), 400 cm$^{-1}$ (B1g), 510 cm$^{-1}$ (B1g + A1g) and 630 cm$^{-1}$ (Eg), indicating the presence of anatase phase. No peak assigned to the rutile or brookite phase was observed, which is consistent with the XRD results. For the TiO$_2$/RGO(5%) film, two additional prominent peaks centered at 1324 cm$^{-1}$ (D band) and 1600 cm$^{-1}$ (G band) are also observed in the Raman spectrum, suggesting that the structure of RGO was maintained in the composite. Furthermore, an I_D/I_G ratio of 1.09, higher than that of the RGO-hydrothermal sample (I_D/I_G = 1.02) (see Fig. S5(b) in the ESI†) was observed, suggesting structural disorder related to the strong interaction between the TiO$_2$ nanoparticles and the RGO sheets after the reduction process by the hydrothermal method.

Fig. 3 shows images of the surfaces of the electrodes obtained by optical microscopy and FEG-SEM. While a transparent film was obtained from the deposition of the pristine TiO$_2$ suspension on glass-FTO, a dark film resulted from the TiO$_2$/RGO(5%) suspension (Fig. 3(a)). Films with different TiO$_2$/RGO relative amounts were obtained from suspensions prepared by the mixture of pristine TiO$_2$ and TiO$_2$/RGO(5%) suspensions; the images clearly show that the composite films become darker as the relative RGO concentration increases. Furthermore, different morphologies can be observed for the films of TiO$_2$ and TiO$_2$/RGO composites. Images of all the nanocomposite films are available in Fig. S7 in the ESI. The surface and cross-section images (Fig. 3(f and g)) show that the TiO$_2$/RGO(5%) film has a high porosity, interconnected pores and a thickness of around 5.3 μm.

Fig. 4 shows the UV-visible absorption spectra of the TiO$_2$, TiO$_2$/RGO(0.1%), TiO$_2$/RGO(2%) and TiO$_2$/RGO(5%) films. A significant increase in the absorption at wavelengths shorter than 400 nm is assigned to TiO$_2$ (~3.2 eV). For the composites,
the light absorption remains unchanged for relative RGO concentrations of < 1.0 wt%. On the other hand, there is a marked increase in the light absorption intensity in the entire investigated region when the RGO concentration is greater than 1.0 wt%. In this case, light scattering must also be considered, mainly in the visible and near-infrared regions. The films become darker, and this behavior will have important implications in the photoelectrochemical response of these films, as will be discussed in the last section. Tauc plots were used to determine the optical band gap in the films. The results showed that the addition of RGO decreases the band gap energy ($E_g$) from 3.6 eV (pristine TiO$_2$) to 3.4 eV (sample with 5.0 wt% of RGO). This small variation, although positive, is not expected to play a major role in the photocurrent values.

Transient absorption spectroscopy studies of the TiO$_2$/RGO films

TAS measurements were performed to study the charge carrier dynamics (holes and electrons) after Nd:YAG laser excitation (350 µJ cm$^{-2}$) in the ultraviolet region (355 nm) for the TiO$_2$ and TiO$_2$/RGO composites with RGO relative concentrations of 0.1, 2 and 5 wt%. Fig. 5(a) and (b) show the spectra obtained using the probe wavelengths at 460 nm (mainly photohole absorption) and 900 nm (mainly photoelectron absorption).

The observed transient absorption decays in the TiO$_2$ and TiO$_2$/RGO films are attributed to electron–hole recombination when the experiments are carried out under nitrogen in the absence of any chemical scavengers. This behavior was also observed by Tang et al.$^{39}$ when studying the dynamics of the charge carriers in the nitrogen-doped-TiO$_2$ (nc-N-TiO$_2$) films. In all the nanocomposite films containing RGO sheets, we observed an increase in the amplitude of the long lived 460 nm (photohole) signals and also an increase in the amplitude of the long lived 900 nm (photoelectron) signals in comparison with the pristine TiO$_2$ film. The optical density variation ($OD$) observed is proportional to the number of charge carriers photogenerated, and it is significantly larger for the nanocomposites than for the pristine TiO$_2$ films. This is a strong indication of a decrease in the charge recombination.

The increase in the yield of the holes is clear: considering the RGO sheets as electron acceptors, the charge recombination reaction between the electrons and holes is minimized. In addition, the origin of the increase in the 900 nm signal is less clear and may be derived from the absorption of RGO electrons. According to Meng et al.$^{40}$ who used TAS as an additional tool to understand the photocatalytic improvement of TiO$_2$/α-Fe$_2$O$_3$ composite for water oxidation, the mechanism is associated with mobile electrons, which are initially created in semiconductors and quickly transfer to the RGO sheet, wherein they diffuse into trap states in the RGO on a time scale of picoseconds. These trapped electrons reach the photoelectrode, leading to an increase in the photocurrent.

Photoelectrochemical studies of the TiO$_2$/RGO films

Pristine TiO$_2$ and TiO$_2$/RGO films were employed as photoanodes in photoelectrochemical water splitting studies in 0.5 mol L$^{-1}$ H$_2$SO$_4$ medium. The cyclic voltammograms, obtained in the dark and under illumination (100 mW cm$^{-2}$, AM 1.5G) through the electrolyte–electrode interface (EE), are shown in Fig. 6.

In a wide potential range ($-0.4$ to $2.4 \text{ V}_{\text{RHE}}$), only a well-defined peak at $ca.$ $-0.29 \text{ V}_{\text{RHE}}$ is observed during the anodic sweep; this can be attributed to the oxidation of Ti(III) (hydr)oxide species ($\approx$Ti(OH)) on the TiO$_2$ surface. During the cathodic sweep, a reduction peak of the Ti(IV) (hydr)oxide species ($\approx$Ti(OH)$_4$) was also observed at potentials lower than $0.06 \text{ V}_{\text{RHE}}$ (see Fig. S9 in the ESI$^+$$^{41}$). In the dark, the electrodes exhibited a very small capacitive current; for potentials greater than 2.0 $\text{ V}_{\text{RHE}}$, the current is related to the oxygen evolution.
reaction (OER). Furthermore, a well-defined peak was observed at around 0.09 V_RHE during the cathodic sweep. The presence of this peak is widely discussed in the literature, and it has been associated with the reduction of species at surface states located below the semiconductor conduction band, mainly due to the presence of electronic traps in the films. At potentials below 0 V_RHE, the hydrogen evolution reaction (HER) also occurs.\footnote{42}

In illumination conditions, as expected for n-type semiconductor electrodes, all the films showed an anodic photocurrent. According to Fig. 5(b), the photocurrent is directly dependent on the RGO concentration in the TiO_2 composite electrode. At 1.23 V_RHE (standard potential for OER) for the pristine TiO_2 electrode, the photocurrent corresponds to 0.11 mA cm\(^{-2}\); for the composite electrodes, it increased with RGO relative concentration, and the maximum value of 0.20 mA cm\(^{-2}\) was observed for the composite containing 0.1 wt% RGO. The photocurrent decreased sharply to 0.02 mA cm\(^{-2}\) for the TiO_2/RGO_5\% film. The variation of the photocurrent density values (at 1.23 V_RHE) with the relative concentration of RGO in the TiO_2/RGO films electrodes is shown in Fig. S11 in the ESI. The TiO_2/RGO_0.1\% electrode has a maximum IPCE\(^{(350\text{nm})}\) of around 18\% (see Fig. S12 in the ESI), which is higher in comparison to other electrodes.

It is noteworthy that none of the onset potentials (\(\sim 0 \text{ V}_\text{RHE}\)) of the voltammograms changed, and thus it is possible to discount any catalytic effect of the RGO sheets. It is very important to emphasize that these measurements were also repeated using the same photoelectrodes and experimental conditions, but with the use of a UV blocking filter (<400 nm). The voltammogram profiles for all the photoelectrodes were similar to the results obtained in the dark (compare Fig. S10(a) and S13 in the ESI). Thus, we can discard the idea that the RGO sheets, at least in our study, are acting as sensitizers in the TiO_2 film. Kumar \textit{et al.}\footnote{43} have calculated the work function of rGO sheets as a function of the oxygen concentration. Thus, we expect that the work function for our sample is about 5.4 eV. The energy level of the conduction band of TiO_2 is about 4.4 eV.\footnote{44} This provides additional information that the energy levels do not allow electron transfer from the RGO to the conduction band of the titania film. However, in a recent report, Bharad \textit{et al.}\footnote{45} reported a mechanism for water splitting reactions based on TiO_2 sensitization by RGO and N-doped RGO. It is clear that this subject needs a deeper investigation to check the feasibility of electron transfer from the graphene-based materials to the titania films. The photoresponse ability and long-term stability of the same photoelectrodes were determined using chronoamperometric measurements under potentiostatic control at 1.23 V_RHE, as shown in Fig. 7. In general, the photoelectrodes exhibited a prompt photo-response under intermittent irradiation with high reproducibility during numerous ON/OFF cycles, as well as good electrochemical stability during continuous irradiation for 1 h. It is noteworthy that the photocurrent density values obtained by chronoamperometry were very similar to the cyclic voltammetry results.

The electrochemical and photoelectrochemical properties of these electrodes were also investigated by electrochemical impedance spectroscopy (EIS) measurements, carried out in H_2SO_4 aqueous solution at open circuit potential (V_{OC}) in the dark and under illumination. Fig. 8 presents the Nyquist and the Bode diagrams of the EIS data obtained for the TiO_2 and TiO_2/RGO photoelectrodes (represented by symbols), with their mathematical adjustments (represented by solid lines) obtained using Boukamp software with the suggested equivalent circuit (inset in Fig. 8(a)). At V_{OC} in the dark, all these electrodes exhibited similar electrochemical impedance spectra, with high impedance values and undefined time constants (Fig. 8(a) and (b)). Under illumination conditions, the general impedance value decreases considerably, and a well-defined capacitive arc and two time
constants can be displayed for all the photoelectrodes (Fig. 8(c) and (d)). An equivalent circuit $R_s(Q_1(R_1C_2))$ has been proposed for fitting the EIS data.\textsuperscript{15,46,47} All the adjustments have been made in the frequency range from 10 kHz to 0.1 Hz, due to the high dispersion of the data.

The proposed equivalent circuit (inset in Fig. 8(a)) considers a series resistance element ($R_s$), which includes the FTO resistance, the resistance related to the ionic conductivity of the electrolyte and the external contact resistance. The semiconductor|electrolyte interface can be represented by the capacitance at the Helmholtz layer ($Q_1$) on the electrolyte side and the charge transfer resistance ($R_1$). The electron transport in the semiconductor bulk can be represented by the resistance ($R_2$) and the capacitance ($C_2$) at the TiO\textsubscript{2} surface states. The contribution of the RGO sheets on the TiO\textsubscript{2} surface can also be visualized by these two parameters. Moreover, in photoelectrodes formed by nanostructured semiconductors, the capacitance is commonly well represented by a CPE, in which admittance depends on the parameters $Y_0$ and $n$ ($n$ is a constant ranging from 0 $\leq n \leq 1$). In this case, the semiconductor electrode|electrolyte interface cannot be represented by simple circuits such as RC or $R(RC)$; thus, the resultant capacitance should not vary with applied potential, as assumed by the Mott–Schottky relationship.\textsuperscript{15,46,47}

The parameters obtained by fitting the EIS spectra with the equivalent circuit depicted in Fig. 7(a) are presented in Table 1. The circuit element values obtained in the dark are similar among the photoelectrodes, with $R_s$ values of ca. 14 $\Omega$, capacitances ($Q_1$ and $C_2$) of ca. 15 $\mu$F and resistances ($R_1$ and $R_2$) of 10 $\Omega$ and 312 $k\Omega$ on average, respectively. Under illumination, the TiO\textsubscript{2}/RGO(0.01 to 0.1\%) electrodes showed $R_1$ (5.3 to 4.8 $\Omega$) and $R_2$ (3.0 to 2.4 $k\Omega$) values lower than the pure TiO\textsubscript{2} electrode ($R_1 = 5.8 \Omega$ and $R_2 = 689 \Omega$). The capacitance values ($Q_1 \sim 316 \mu$F and $C_2 \sim 1010 \mu$F) were higher compared to the pristine TiO\textsubscript{2} electrode ($Q_1 = 166 \mu$F and $C_2 = 689 \mu$F). This behavior indicates a higher charge accumulation at the interface and faster electron transport, associated with the presence of RGO.

Note that a low concentration of RGO in the TiO\textsubscript{2} film (<0.1 wt%) does not significantly change the light absorption (see Fig. S8 in the ESI†). On the other hand, for RGO concentrations above 0.5 wt% in the TiO\textsubscript{2} films, the photocurrent density values decrease; many factors may be related to this process. Under illumination, the TiO\textsubscript{2}/RGO(0.5 to 5\%) electrodes showed increasing values of $R_1$ and $R_2$: 6.2 to 63 $\Omega$ and 2.2 to 6.2 $k\Omega$, respectively. In addition, there was a marked decrease in the values in one of the capacitances ($C_2$), from 835 to 367 $\mu$F. This can be directly related to the presence of agglomerations...
of RGO sheets that block light absorption in the TiO$_2$ nanoparticles. The light-block effect contributes to the decay of the photocurrent density values, corroborating the EIS data.

As the amount of RGO increases, charge recombination becomes more important, and this can explain our best result obtained by the films containing 0.1 wt% of RGO. Moreover, as the concentration of RGO increases, the films become darker; this seems to negatively affect the charge generation. As shown previously in Fig. 4, as the RGO content increases, the light absorption by the titania nanoparticles is compromised, decreasing the photoactivity towards water oxidation and also the charge generation. It is important to point out that the correspondence between the TAS and the photoelectrochemical studies. The sample that gave rise to the best performance in the water oxidation process [TiO$_2$/RGO(0.1%)] also originated the highest yield for both charge carriers.

Conclusions

Although several reports of the photocatalytic effect and water splitting reactions at the surface of TiO$_2$/RGO nanocomposite have been published in the last few years, a clear understanding of the RGO role is lacking. For instance, the sensitization effect of RGO in the titania film was not observed in our study. Moreover, the energy levels of both materials do not allow charge transfer from the RGO to the titania conduction band. Interestingly, the TiO$_2$/RGO(0.1%) film exhibited the best charge generation upon excitation, corroborating the photoelectrochemical studies. We propose that in films with lower concentrations (<0.1 wt%), the positive effect of the RGO sheets is due to their ability to accept and transfer electrons from TiO$_2$. The immediate consequence is a decrease in charge recombination, observed by the increase in the photogeneration of holes and electrons in TAS decays and a significant improvement in the photocurrent density in photoelectrochemical water splitting.

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Notes and references