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# Temporal drift in Raman signal intensity during SERS measurements performed on analytes in liquid solutions<sup>†</sup>

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In this communication, we report one factor that could limit the quantitative analysis by SERS, which has not yet been discussed in the literature. Our results show that SERS experiments performed with the substrate immersed in liquid solutions are subjected to a temporal drift in the Raman signal intensity. Measurements were performed using gold nanoparticle suspensions and gold-covered nanostructured ITO surfaces as SERS substrates, immersed in analyte solutions of crystal violet and 4-mercaptobenzoic acid. Depending on the substrate and the conditions used for measurements, the Raman signal can take between 30 min and several hours to stabilize. This effect, if not taken into account, could have a negative impact on the results of the quantitative chemical analysis by SERS performed *in situ* in liquid solutions.

The surface enhanced Raman scattering (SERS) effect has been widely studied, particularly because it allows the application of Raman spectroscopy to chemical analysis in very dilute solutions,<sup>1</sup> and in some cases even single molecule detection.<sup>2</sup> Accordingly, a large amount of research effort has been invested in the development of SERS substrates in order to reach higher signal enhancements and reproducibility.<sup>3,4</sup>

In spite of the large number of reports involving SERS, its quantitative application is known to be very difficult due to a number of factors. Difficulties in reproducibility during the fabrication of the SERS substrates are probably one of the most important problems, especially for nanostructured SERS-active surfaces.<sup>4</sup> For nanoparticles, small differences in dimension can give rise to big differences in the Raman signal intensity.<sup>5</sup> Even when a reliable process for substrate fabrication is used, the homogeneous distribution of the analyte over a nanostructured surface is not an easily achieved goal.<sup>6</sup> Researchers are not usually concerned about the kinetics of

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the interaction between the analyte and the substrate immersed in solution. The reason for this is that SERS substrates made of nanostructured surfaces are not generally applied in measurements performed in liquid media. Either a small drop of the analyte solution is added to the substrate surface and the spectrum is obtained after drying<sup>7</sup> or the substrate is immersed in the analyte solution for a pre-determined time, removed, washed and dried before the measurement.<sup>8,9</sup>

A number of strategies have been developed to overcome the problems of reproducibility in the fabrication and measurement procedures. Chemometrics is one of the most useful tools when quantification of SERS measurements is intended,<sup>10</sup> since it allows the discrimination of the components related to the analyte in complex spectra.<sup>7,11,12</sup> Another strategy is the use of internal standards, which make it relatively straightforward to monitor and automatically correct for changes in laser power.<sup>13,14</sup>

Microfluidic devices exhibit some advantages for SERSbased chemical analysis under the conditions of continuous flow, allowing more homogeneity in the mixing of analytes and metal nanoparticles.<sup>6</sup> However, these devices can present problems which have to be solved for quantitative analysis, for example, clogging of the channels and adsorption of metal nanoparticles at the microchannel walls.<sup>6,15,16</sup> Immunoassays have also been performed in microchannels using solid SERSactive nanostructured surfaces and marked analytes.<sup>17</sup>

In the course of a research project whose final aim was to perform *in situ* SERS measurements in aqueous solutions flowing inside microfluidic channels, our group was confronted with inconsistent results regarding the reproducibility of Raman peak intensities. In those experiments, measurements were carried out after SERS substrates made of nanostructured surfaces were immersed in analyte solutions, thus providing a configuration similar to the one expected to take place in the microfluidic devices. As the number of measurements performed grew, one could notice the emergence of a pattern indicating a temporal drift in the Raman signal intensity. This observation was the driving force for undertaking the studies reported in this communication. According to the

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results, the time elapsed from the moment the analyte and the substrate are brought into contact for the measurements should be controlled in order to decrease the spread in the peak intensities used for quantitative SERS-based measurements.

The nanostructured SERS substrates used in this work consisted of one-dimensional gold-covered tin-doped indium oxide (ITO) nanostructures (nanorods or nanowires) grown by radio frequency (RF) sputtering on oxidized silicon wafers and microscope glass slides.

A custom-built sputtering system configured with three RF sputtering guns and a rotating sample holder with halogen lamp heating was used for growing the gold-covered ITO nanostructures to be applied as SERS substrates. The fabrication procedure has previously been reported.<sup>18</sup> The sequence of fabrication is schematically illustrated in Fig. 1.

Microscope slides or oxidized silicon wafers were laser-cut into 3 mm squares and sequentially washed with acetone, isopropyl alcohol, and deionized water, and dried using vigorous nitrogen flow. The sputtering procedure, using 2 inch diameter indium, ITO, and gold targets (Kurt J. Lesker, 99.9% minimum purity) can be described as follows: 15-20 substrates were placed inside the chamber and after evacuation until a base pressure below  $5 \times 10^{-6}$  mbar, argon was added at a constant flow of 10 sccm and the deposition pressure  $(1 \times 10^{-2} \text{ mbar})$ was adjusted by partially closing a gate valve separating the pumping system from the chamber. The substrates were heated to a temperature of 210 °C and a 20 nm layer of indium was then deposited by applying an RF power of 20 W to the indium target. After that, ITO was deposited by applying 160 W to the ITO target for 10 minutes. Since the temperature of the substrate was higher than the indium melting point and liquid indium does not wet the substrate surfaces used, droplets of this metal were formed and acted as seeds for unidimensional ITO growth through the vapor-liquid-solid (VLS) mechanism. These 10 min oxide depositions were repeated



Fig. 1 Diagram of the sequence of steps in the fabrication of goldcovered ITO nanostructures by RF sputtering.

another two times and between each of these ITO deposition steps, additional indium was deposited for 2 minutes, in order to maintain a metal-rich environment and to ensure an adequate amount of liquid for unidirectional VLS growth. After cooling the samples, the pressure was adjusted to  $5 \times 10^{-3}$  mbar and a 20 nm thick gold layer was deposited over the ITO nanostructures by applying an RF power of 30 W to the corresponding target.

The dimensions and morphology of the nanostructures grown by the sputtering method were assessed using a field emission scanning electron microscope (FE-SEM, FEI Inspect F50). The nanostructures are needle-shaped, having square cross-sections, lengths around 800 nm and thicknesses of approximately 80 nm at the base and 10 to 20 nm at the tip. Typical results are shown in Fig. 2, where one can observe, in the SEM photographs, that the substrates are uniformly covered by the nanostructures with an areal density of approximately  $3 \times 10^7$  mm<sup>-2</sup>.

SERS measurements with the substrate immersed in aqueous Crystal Violet (CV) solutions with concentrations of



**Fig. 2** SEM images of nanowires on the SERS substrate. (a) Low magnification view of the nanowires showing the homogeneous covering of the surface. (b) High magnification view showing the morphology of the nanowires.

#### Analyst

1, 10, and 100  $\mu$ mol L<sup>-1</sup> were performed with the configuration schematically shown in Fig. 3 using a Raman spectrometer (Perkin Elmer RamanStation 400F) with a 785 nm laser having a power of 250 mW and a spot size of 100  $\mu$ m diameter. The level of liquid over the substrates was kept constant at 3 mm for all measurements.

The SERS substrates were fixed at the bottom of a container measuring  $2.7 \times 2.7 \times 0.4$  cm. The laser was focused at the surface of the SERS substrate and 2.5 mL of solution was added to the container. The Raman spectra were acquired by exposing the substrate to the laser for 3 times of 12 seconds each. A "blank" spectrum of the substrates, previously obtained using deionized water, was subtracted from all Raman measurements in order to minimize the interference of fluorescence or Raman peaks from the underlying glass. Immediately after the addition of CV solutions to the vessel, sequential spectra were acquired at regular intervals for a period of one hour. The measurements were conducted at the same spot during the entire period of the experiment. Fig. 4a shows a SERS spectrum of CV obtained with a 10  $\mu$ mol L<sup>-1</sup> solution. The results of the measurements as a function of time for two solutions with different CV concentrations are shown in Fig. 4b (raw spectra obtained during these measurements are available in the ESI<sup>†</sup>). The height of the peak with a Raman shift of 1173 cm<sup>-1</sup> (generated by in-plane vibrations of ring C-H bonds)<sup>19</sup> was used for following the drift in signal intensity with time of contact between the CV solutions and the nanostructured surfaces.

One can notice in the results that the signal intensity for both CV solutions did not become stable within the period of time covered by the study. A fast signal increase in the initial stage of the experiment, more pronounced in the solution with higher CV concentration, was followed by a steady linear drift in the peak intensity as a function of time. The slope of the linear regions in the graph increases with CV concentration. No hint of any tendency for signal saturation could be discerned in the curves for both concentrations, indicating that signal stabilization was not expected to occur in a short time span. These results are highly relevant in the context of chemical analysis by Raman spectroscopy through the SERS effect. For both CV concentrations, the peak heights for the 1173 cm<sup>-1</sup> Raman shift more than doubled in the time elapsed during the measurements shown in Fig. 4b. Very



Fig. 3 Schematic illustration of the setup for *in situ* SERS measurements.

### View Article Online Communication



**Fig. 4** (a) Typical SERS spectrum of crystal violet obtained in this work. Inset: chemical structure of the dye. (b) Behavior of the Raman intensity as a function of time for measurements performed *in situ* in crystal violet solutions using the nanostructured solid surfaces fabricated by sputtering.

similar increases in intensity were also observed for other peaks in the CV spectra. If this temporal drift is not taken into account when performing quantitative analytical procedures in solutions, the effect would strongly increase the degree of uncertainty in the measurements.

With the aim of verifying whether a longer time of substrate immersion would lead to signal stabilization, the measurement was repeated for the solution with a CV concentration of 10  $\mu$ mol L<sup>-1</sup>. Once again, no tendency to stabilization was observed even after 6.5 h of measurements. ESI† is available, showing experimental data for these longer term SERS measurements.

Electric field enhancement simulations applied to a model resembling the dimensions and morphology of the goldcovered ITO nanostructures were carried out. These simulations, performed by the Discrete Dipole Approximation (DDA) method with a resolution of 2 nm, included the situation of two nanowires perpendicularly anchored to the substrate. The dielectric properties from the materials involved were introduced in the simulations using experimental data reported for Au and ITO.<sup>20,21</sup> A graph showing the position of plasmonic bands as a function of laser wavelength is available in the ESI.† A color-coded field enhancement map in the region close to the nanostructures is shown in Fig. 5, where the gold layer covering the nanostructures is represented in black.

The areas with the stronger field intensification according to the results from the DDA method, the so-called "hot spots" shown in dark red in the enhancement map in Fig. 5, are located near the underlying substrate, in the region of the base between two wires. This can help to explain the long time needed for signal stabilization if one takes into account the fact that analyte diffusion from the solution until the base of the nanostructures, at room temperature and in the absence of convection, can be a slow process. Furthermore, the SERS substrates with one-dimensional nanostructures grown by the sputtering method are highly hydrophobic. This could also be an important factor hindering analyte access to the regions of high field enhancement.

Gold coating through the sputtering method is almost a "line-of-sight" process, especially when performed at low pressures. Since the nanowires are randomly oriented, it is inevitable that during deposition gold is unable to reach some shadowed spots, leaving the ITO exposed in these regions. In order to change the surface of the SERS substrates from hydrophobic to hydrophilic, they were exposed to the UV radiation of a laser. Exposure of materials to UV radiation is a common strategy for changing oxide surfaces from hydrophobic to hydrophilic.<sup>22</sup> More details of the mechanisms involved can be found in the literature.<sup>23</sup> The ultraviolet radiation might also cause desorption of possible surface contaminants present in the gold surface, rendering the substrates highly hydrophilic. The UV treatment was performed using a frequency-tripled Nd:YVO<sub>4</sub> UV laser working at a wavelength of 355 nm (Spectra Physics, Pulseo 355-20). The SERS substrates were exposed to a

UV laser beam with a power of 0.5 W for a period of 2 minutes. The substrates were then immersed in a 1  $\mu$ mol L<sup>-1</sup> CV solution and SERS spectra were again obtained for a period of 1 h. Fig. 6 shows the intensity of the Raman signal as a function of time for a substrate treated with UV radiation and for a substrate not subjected to the UV treatment.

For this CV solution having a smaller concentration, the intensity of the Raman signal for the peak at 1173 cm<sup>-1</sup> could not be distinguished from the noise in the measurements when the SERS substrate was not subjected to the UV treatment. On the other hand, the UV-treated substrate gave rise to a measurable signal, even starting from the first measurement in the temporal series. Contrary to the initial expectations, the easier access of the solution to the interior of the nano-structured environment did not solve the problem of the temporal drift in the analyte signal. The UV treatment merely increased the threshold for CV detection without significantly affecting the kinetics of the process leading to signal stabilization. The peak heights once again exhibited a linear increase with time, as previously observed in the other solutions with higher CV concentrations.

Colloidal suspensions of gold nanoparticles are the most widely used SERS substrates for chemical analysis and contaminant detection. Free from the constraints of hydrophobic behavior, having free access to the analytes and aided by natural convection currents in the fluid, these nanometer-scale particles, either added to the analyte solution as-prepared or pre-agglomerated, should provide a very fast Raman signal stabilization. In order to test the validity of this assumption, measurements of Raman peak intensity as a function of time were performed using a gold suspension and a 0.1  $\mu$ mol L<sup>-1</sup> CV solution. The results from these measurements are shown in Fig. 7. Details of the experimental procedures for gold nanoparticle synthesis and SERS measurements can be found in the ESI.†



**Fig. 5** Color-coded map showing the results of simulation of the electric field intensification in the region close to two adjacent nanowires.



Fig. 6 Comparison of the results of measurements performed *in situ* in 1  $\mu$ mol L<sup>-1</sup> CV solution obtained with nanostructured surfaces with and without treatment with UV radiation.



Fig. 7 Behavior of the Raman intensity as a function of time for measurements performed *in situ* in crystal violet solutions using gold nanoparticles.

Perhaps surprisingly, even in this favourable situation, the Raman signal from CV only reached a steady state after approximately 30 minutes. In this particular case, since the absence of convection currents and impaired analyte access to the metal surface could be discarded, the likely motive for this temporal drift in the SERS signal could be attributed to the dynamics of particle aggregation in the gold suspension, which can be triggered by the analyte. According to Etchegoin and co-workers,<sup>24</sup> this is a process that takes roughly the same time as the SERS signal increase shown in Fig. 7. Another possible factor, dependent on the exact conditions of colloid preparation, may be the presence of citrate radicals from the chemical synthesis of the nanoparticles remaining attached to their surface. These groups would need time for their desorption from the gold surface before CV could be adsorbed, increasing the time for CV signal stabilization. In the initial time span of 30 minutes, the intensity of the CV peak at 1173 cm<sup>-1</sup> underwent a threefold increase, indicating that SERS analysis performed in liquids should always take into account the effect of measurement time, even when colloidal suspensions are employed.

In order to observe the behavior of a different analyte, regarding temporal signal stability, and considering that maybe a weak affinity existed between CV and our substrates, the measurements were repeated once again with the nano-structured SERS substrates obtained by sputtering, but this time 4-mercaptobenzoic acid (4-MBA) solutions with the concentrations of 10  $\mu$ mol L<sup>-1</sup> and 100  $\mu$ mol L<sup>-1</sup> were used. This simple thiol has a strong affinity to gold and was therefore expected to bind quickly and irreversibly to the nanostructured surface immersed in the solutions.

Fig. 8a shows a typical 4-MBA SERS spectrum obtained in this work, where one can notice two prominent peaks at  $1076 \text{ cm}^{-1}$  and  $1585 \text{ cm}^{-1}$  corresponding to benzene stretch modes. A weaker band can be observed around  $1180 \text{ cm}^{-1}$ 



**Fig. 8** (a) Typical SERS spectrum of 4-MBA obtained in this work. Inset: chemical structure of the thiol. (b) Behavior of the Raman intensity as a function of time for measurements performed *in situ* in 4-MBA solutions using the nanostructured solid surfaces fabricated by sputtering.

(C-H strain modes).<sup>8</sup> Fig. 8b shows the behavior of the peak at  $1076 \text{ cm}^{-1}$  as a function of time for the two concentrations of 4-MBA tested. As observed previously in the results of CV measurements, the Raman signal did not stabilize in the time covered by the experiments. These results indicate that the formation of chemical bonds between analyte and substrate surfaces was not capable of yielding a faster stabilization of the Raman signal intensity.

Results of adsorption studies of thiol molecules on SERSactive gold surfaces have been published.<sup>25</sup> The authors used commercially available Klarite® substrates and took the SERS signal as a probe for following the progress towards the adsorption equilibrium in thiophenol solutions. They performed the experiments by dipping the Klarite® substrates in solutions kept under vigorous mechanical agitation. Even under these conditions, the time needed for SERS signal stabilization was 5.5 hours. This is consistent with the results of our work, especially if one considers that Klarite® has a very open surface morphology when compared to our SERS

#### Communication

substrates grown by sputtering. Even taking aside the mechanical agitation, the diffusion of analytes among the hydrophobic "forest of nanowires" present in our substrates should clearly be more difficult than in the open Klarite® structure.

The effect of fluid flow on the response time of nanostructured SERS surfaces inside liquid solutions could be studied in experiments conducted inside the channel of a microfluidic device. The microfluidic device used in this work consists of a piece of polydimethylsiloxane (PDMS) containing the microchannels sealed to a microscope glass slide in such a way that the nanostructures are positioned inside the microchannels after the PDMS/glass sealing operation.

The gold-covered ITO nanostructures were fabricated over the glass slide using the procedure already described. A shadow mask was placed over the glass before nanostructural growth in order to limit the deposition region. The shadow mask consists of a thin glass microscope slide with 100  $\mu$ m thickness containing four parallel slots measuring 7 mm length and 250  $\mu$ m width each. The slots were cut by using the same laser that was previously used for UV treatment. The master mold for PDMS replication containing four parallel microchannels was obtained by laser swelling of polymethylmethacrylate (PMMA).<sup>26</sup> The dimensions of each microchannel were 40  $\mu$ m height, 400  $\mu$ m width, and 5 cm length. Fig. 9 shows the sequence of steps involved in the fabrication of the microfluidic device. Details of mold and PDMS replica processing are provided in the ESI.<sup>†</sup>

The microfluidic device was placed in the Raman spectrometer and the laser was focused on the surface containing the SERS substrates, inside the microchannel. A syringe pump (New Era, NE-4000) was connected to the microchannels by using a silicone tube. Each microchannel was used for only one solution measurement. Before all measurements, water was injected into the microchannel and a spectrum was acquired (3 exposures of 12 s each). This "blank" spectrum was subtracted from each analyte spectrum for all experiments. The water was removed and crystal violet solution was injected into the microchannel. As soon as the solution reached the area containing the nanostructures, the acquisition of spectra was started with a 3 min interval between measurements. Crystal violet solutions with concentrations of 1 and 10  $\mu$ mol L<sup>-1</sup> and a volumetric flow rate of 5  $\mu$ L min<sup>-1</sup> were used in these experiments. In order to avoid bubble formation in the liquid inside the channels, only 50% (125 mW) of the maximum laser power was applied during these measurements. The results of peak intensities as a function of time for both CV concentrations are shown in Fig. 10.

The intensity of the Raman signal became stable after about 30 minutes for both solution concentrations. The reason for the faster signal stabilization could be the decrease in the path for analyte diffusion caused by the liquid flow, which is related to the renewal of solution near the nanostructures. Taking into account the volume of the channel region where the nanostructured SERS substrate is present, and if we consider the volumetric flow of solution, we can calculate that the solution is renewed 42 times per minute of the experiment. Another possible factor contributing to this acceleration of the adsorption process is the pressure inside the microchannels, which is higher than the pressure inside a liquid in an open container of similar dimensions. This increased pressure could force the liquid to enter into the space between the nanostructures, making it easier for the analyte to reach the region with the higher number of SERS hot spots.

In conclusion, SERS experiments performed with the substrate immersed in liquid solutions are subjected to a temporal drift in the Raman signal intensity. The work reported in this communication can be considered as preliminary, since we have not yet unambiguously determined the reason for this behavior. The answer probably involves a combination of factors whose degree of contribution depends on the exact details of the experiment. Our results indicate that analyte diffusion from the bulk of the solution to the SERS hot spots should probably be involved and might be the dominant feature in the majority of cases when solid SERS substrates are employed.



**Fig. 9** Schematic illustration of the steps for fabrication of microfluidic devices for SERS measurements in flowing solutions.



Fig. 10 Behavior of the SERS signal as a function of time for measurements performed on CV solution in continuous flow (5  $\mu$ L min<sup>-1</sup>) inside the microfluidic device.

Regardless of the mechanism responsible for this variation of the SERS signal with measurement time, we believe that the effect is pronounced and should be taken into account by every researcher involved in SERS measurements performed *in situ* in liquid solutions. Quantitative measurements, in particular, should either be performed at fixed times or the signal should be monitored until an equilibrium is reached.

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