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One-pot *in situ* photochemical synthesis of graphene oxide/gold nanorods nanocomposite for surface-enhanced Raman spectroscopy

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Nanoscale engineered plasmonic materials that can sustain strong surface enhanced Raman scattering (SERS) have been strongly pursued for high sensitivity molecular detection. In this work, we report the production of gold nanorods / graphene oxide (GNR/GO) nanocomposites by a simple, one-pot process whereby GNR are formed directly onto the GO flakes in solution by UV light irradiation. The proposed method is easily scalable and results in GNRs with low dispersion in size and aspect ratio ~ 3. The GNR/GO hybrids were deposited in glass by filtration yielding homogenous films that were systematic tested as SERS active substrate. Raman spectroscopy mapping revealed that the tested substrates present spatially homogenous and reproducible SERS response. Analysis of Raman spectroscopy by using a model molecule (Cresyl violet perchlorate) indicates that the produced substrate can provide very large SERS enhancement factors (~10^6) and very low molecular detection limits (10^{-11} M).

1. Introduction

Plasmonic nanostructures have been a topic of intense research interest in recent years, mainly because of their excellent optical properties and many applications. This is due to the phenomenon of localized surface plasmon resonances (LSPRs) of noble metal nanoparticles which is associated with oscillations of electrons on the metal surfaces, inducing a resonant optical absorption. This SPR plasmon resonance phenomenon makes these metallic nanostructures behave as nanoantennas, amplifying the electromagnetic fields around its surface. This behavior leads to an important effect called surface-enhanced Raman spectroscopy (SERS) discovered by Richard Van Duyne in 1976[1]. This effect has been extensively studied since it is a highly sensitive technique that opens the possibility of studying molecules at very low concentrations, interesting for applications such as biosensing techniques[2]. This SERS effect originates by two principal mechanisms: the first one is due to charge exchange between the substrate and the molecule under study, and the other is due to the intense electromagnetic field originated by plasmon resonance around the metallic nanostructures[3,4]. The second one is the most relevant in the gaps between two nanoparticles, called hot-spots, the electric field is more intense and the highest enhancement is obtained[5]. Homogeneous and reproducible fabrication of SERS active substrates is being widely studied[6, 7]. Many substrates have been reported with different preparation methods[8-10] and metal nanostructures of several morphologies such as, gold nanospheres[11], gold nanorods[12], gold nanostars[13] and gold nanostarfruit[14] has been used.

Gold nanorods[15-16] are excellent substrates for SERS due to strong electric field enhancements at the ends caused by high curvature and its well-developed tunability of the surface plasmon resonance in the wide spectral range in order to match the excitation lasers. Many synthetic methods have been reported in recent years to obtain gold nanorods with high monodispersity, stability and homogeneity[17]. The seed-mediated method has been the most traditional since it was discovered by El-Sayed *et al*[18] and Murphy *et al*[19]. The synthesis of gold nanorods mediated by ultraviolet irradiation, described by Yang *et al*[20] has the advantage of being faster and more easily scalable to large scale production. Graphene oxide (GO)[21] and reduced graphene oxide (rGO)[22], are normally obtained by acid/base treatments. GO has abundant surface functional groups such as hydroxyl, carbonyl, and carboxyl, which are responsible for the high solubility in various solvents. This solubility makes this material a great candidate for the formation of hybrids with metallic nanostructures as recently reported by Dong *et al* (2013)[23] and Yin *et al* (2013)[24]. The formation of hybrids between graphene oxide and gold nanorods have been reported by several authors, and the methods employed usually make use of linkers to promote electrostatic interaction of GO with gold nanorods[25-28]. Chaofan Hu *et al*[25] have report the fabrication of a graphene oxide/gold nanorod hybrid material by electrostatic self-assembly and their application in SERS. In this method, the gold nanorods were synthesized separately and interacted with graphene oxide, through polymers. Recently Jayabal *et al*[27] reported a method for the preparation of reduced graphene oxide/gold nanorods embedded in an amine functionalized silicate sol–gel matrix. Dembereldorj *et al*[28] has formed hybrids between gold nanorods and PEGylated-GO to photothermal cancer therapy. Other authors have used similar methods to form hybrids between gold nanorods and graphene oxide[29-34].

In this article we report a simple one-pot *in situ* photochemical formation process of graphene oxide and gold nanorods hybrids by UV light irradiation. This method has the advantage of being fast, simple and performed in just one step. The GO/GNR hybrids were furthermore used to produce highly sensitive SERS substrate.

2. Experimental Section

2.1. Chemicals and reagents

Tetrachloroauric acid ($HAuCl_4$-$3H_2O$), silver nitrate ($AgNO_3$), ascorbic acid, cetyltrimethylammonium bromide (CTAB), acetone, cyclohexane, $NaNO_3$ (99% purity), H_2SO_4 (95 to 98%), $KMnO_4$ (9%), H_2O_2, manganese oxide (Mn_2O_7), were purchased from Sigma Aldrich. Graphite powder 99% purity was supplied by the National de Graphite Ltda, Brazil. All solvents were obtained from commercial suppliers and used without further purification. Milli-Q water with a resistivity of 18.2 MΩ.cm was used. GO was synthesized using the Hummers method[35].

2.2 Synthesis of graphene oxide /gold nanorods hybrid

First a 15 mL solution of CTAB (0.1 M) was prepared and 100 µL of $HAuCl_4$ (0.1 M) were added. The solution was stirred for 15 minutes. Next, in sequence, 1 mL (1mM) of silver nitrate, 400 µL cyclohexane, 330 µL of acetone and 100 µL (0.1 M) of ascorbic acid, were added. The solution changed from yellow to transparent, showing the reduction of Au^{+3} to Au^{+1}. The dispersion of GO (0,01 mg/ml) in water was assisted by sonication. Finally 5 ml of GO was added to the previous solution and the dispersion placed under UV-irradiation (256 nm, 30 W) for 25 minutes in a quartz tube. The final colloidal solution stayed stable for several months.

2.3 Characterization techniques

The optical characterization was carried out by UV-VIS-NIR using Shimadzu UV 3600 spectrophotometer with 10 mm path length quartz cuvettes. TEM measurements were performed on a TEM TECNAI G2-20, using an accelerating voltage of 200 kV. Samples were prepared by drop-casting from the dispersion onto a TEM grid (200 mesh, Hole carbon). Raman experiments were conducted using a Dilor XY triple spectrometer with an Ar laser with excitation wavelength of 647 nm with a 10X objective. The laser power on the sample was kept at 1 mW. The spectra were acquired for 10 seconds with one accumulation.

2.4 Substrate and SERS measurements

In order to prepare SERS substrates, excess CTAB was removed from the GNRs/GO solution through three rounds of centrifugation (5600g for 10 min) and re-dispersion in deionized water (18.2 MΩ). After which the solution of hybrid material was filtered and washed with isopropanol several times using a 0.22 mm Millipore cellulose filter. The material collected in the filter was transferred to a glass substrate. The cellulose membrane/glass substrate was vacuum dried and then immersed in an acetone bath to remove the cellulose membrane. A thin film was formed by the hybrid material GO/ GNR.

Cresyl violet perchlorate (CV) dye was used as model molecule for SERS measurements. CV was diluted in pure ethanol at different concentrations. The substrate was dipped into this solution for 20 seconds and dried at room temperature. The surface enhanced Raman spectra were recorded with the 647 nm wavelength excitation with one 10 seconds accumulation. SERS measurements were also performed with wavelength lasers 488 nm, 514 nm and 568 nm. The laser power on the sample was kept low at 1 mW, focused in by an objective 10X. The reference Raman spectrum measured in a standard glass substrate was performed with 647 nm excitation wavelength with 60 seconds accumulation and focused in by an objective 100X. A SERS Mapping was performed on Raman Microscope alpha 30R (Witec), with 633 nm excitation wavelengths with 0.3 seconds accumulation. The laser power on the sample was kept low at 1 mW focused in by an objective 10X.

3. Results and discussion

The synthesis process of GNRs/GO hybrids was carried out by photochemical reduction of Au ions in presence of GO, under irradiation of ultraviolet light. The photochemical reactions promote the growth of gold nanorods onto graphene oxide sheets *in situ*. However, a specific environment has to be setup by a solution containing cetyltrimethylammonium bromide (CTAB) as surfactant, chloroauric acid ($HAuCl_4$) as precursor of gold, silver nitrate which acts in the induction of anisotropic growth of gold nanorods similar to the one demonstrated by Placido *et al*[36]. Cyclohexane promotes the formation of micelle templates thus assisting the anisotropic growth, ascorbic acid promotes the reduction of Au^{+3} to Au^{+1} a first reduction of the gold precursor and acetone generates ketyl radicals that promote the reduction of gold Au^{+1} to Au^0 being considered as the radical initiator[37-38]. Silver nitrate and acetone are critical for the photochemical synthesis of GNR/GO hybrids. There is no growth of gold nanorods without their presence and without irradiation by ultraviolet light there is no formation of any type of nanoparticles. After this process, the solution of GNRs/GO hybrid material in CTAB is obtained. The Transmission Electron Microscopy

(TEM) images (Figure 1 and S1 in support information) show the GNRs/GO hybrid material obtained by photochemical synthesis. In Figure 1(a-c), the gold nanorods were supported in graphene oxide sheets, as schematically shown in Figure 1e. Figure 1(a-c) shows clearly a large number of gold nanorods efficiently dispersed on graphene oxide sheets. The dimensions and aspect ratios of gold nanorods were evaluated by statistical analysis, showing an average aspect ratio of 3 (30 nm/10 nm), as shown in Figure 1d.

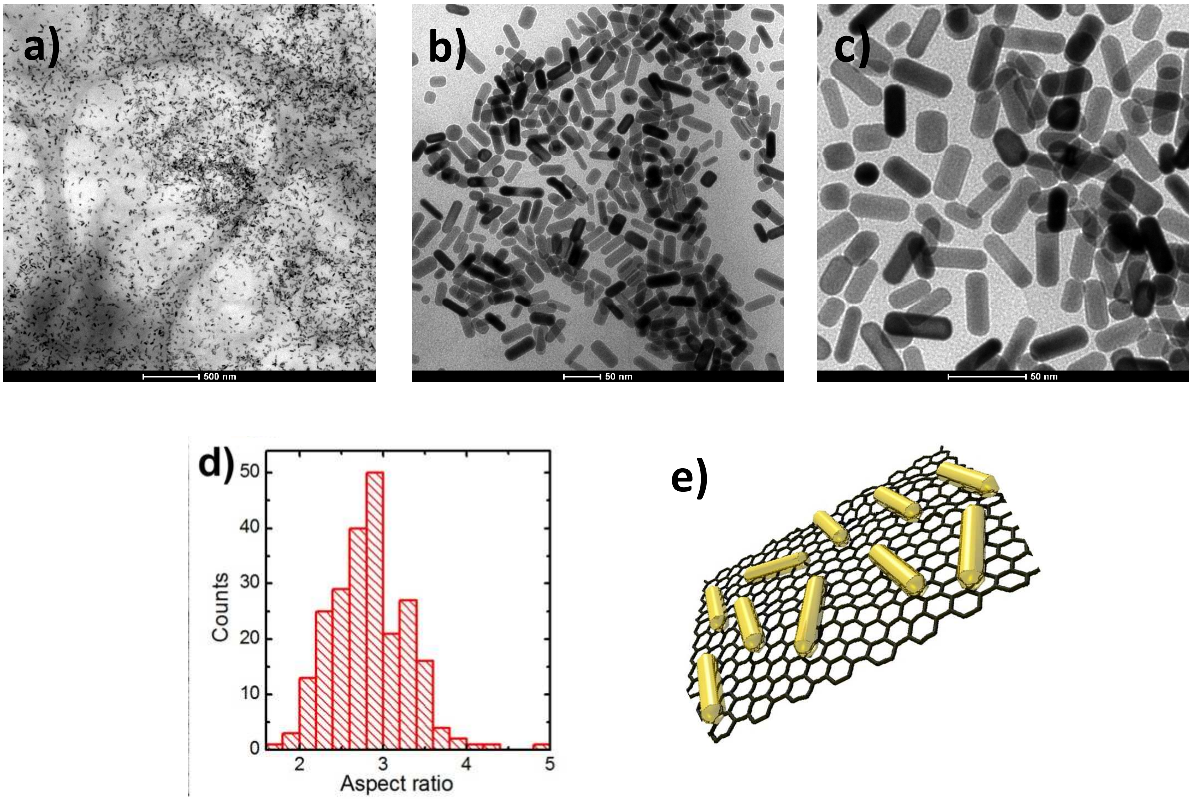

Figure 1 – (a, c) TEM image of hybrid GNR/GO at different magnifications. (d) Aspect ratios statistical distribution (e) Schematic representation hybrid GNR/GO. (Note hole carbon microscopy grid).

The plasmon resonance of the GNRs/GO was measured by optical absorption in aqueous solution. Figure 2 shows the optical absorption spectra of GO (red line), GNRs (blue line) and GNRs/GO (black line). The GNRs were synthesized by the same process described previously but without the presence of GO. The spectrum presents two absorption bands centered at 514 and 750 nm corresponding to the transversal and longitudinal plasmon modes respectively. When the synthesis was carried out in the presence of GO an increase of the transverse was observed. The longitudinal resonance peak is shifted to 740 nm when the nanorods were allocated onto GO. The longitudinal plasmon damping and transverse peak increase is related to the strong interaction of the lateral surface of the gold nanorods with graphene oxide, the change of the local dielectric environment surrounding the surface of the nanorods and mainly to an increase in polydispersity when the synthesis is performed in the presence of GO.

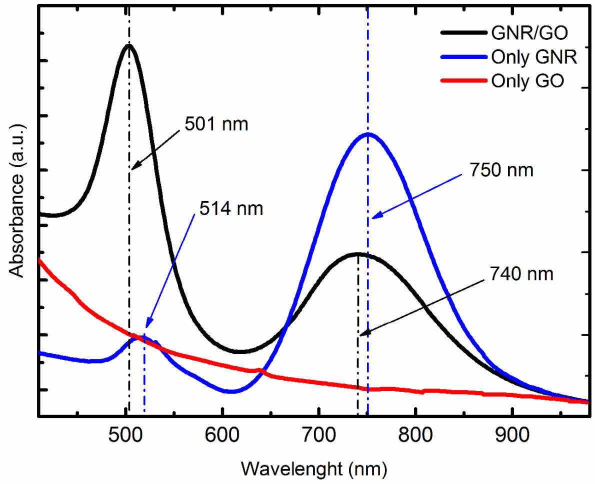

Figure 2 - Optical absorption spectra of GO (red line), pure gold nanorods (blue line) and hybrid of gold nanorods/graphene oxide (black line).

Considering using the GNR/GO hybrids as SERS substrate, the hybrid material was deposited onto a glass substrate as a thin film from solution. Figure S2 presents optical and scanning electron microcopy images demonstrating that the obtained films are homogeneous in both macroscopic and microscopic scales. The advantage of this substrate is that it is simple to manufacture and can be applied to large surface areas. The optical absorption spectrum of the GNR/GO film is shown in Figure 3 (black line), the spectrum of pure GO film is also shown for comparison (red line). The characteristic transverse and longitudinal peak can be observed in the GNR/GO film spectrum, however the longitudinal peak is strongly broadened and shifted in comparison with the peak in the GNR/GO in solution (Fig.2). Such effect is expected and has been observed in spectra of pure GNR films[39]. It is attributed to the stronger coupling between plasmons in neighbor nanorods as the density of GNR is much larger in the films than in solution. It can also be due to the interaction of the GNR and the glass substrate.

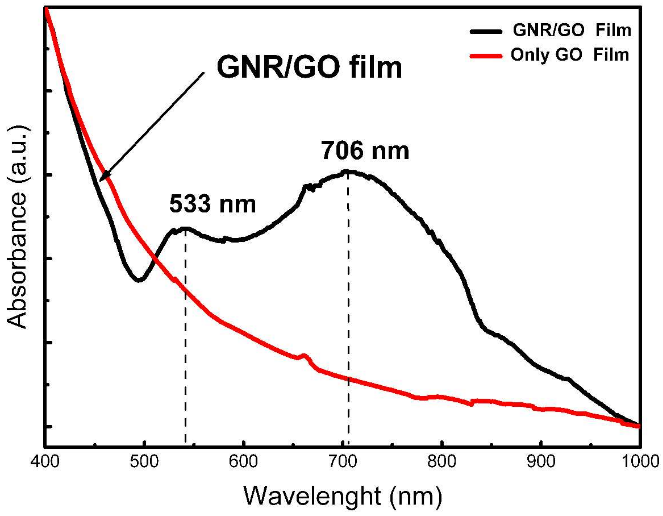

Figure 3 – Absorption spectrum of the GNR/GO film (black line) and pure GO film (red line).

SERS measurements

The dye cresyl violet perchlorate (CV)[40] was used for evaluation of the film as an active SERS substrate. The CV was deposited by drop casting on two substrates, standard glass and onto GNR/GO thin film. SERS measurements were carried out at various wavelengths to evaluate the best laser excitation resonance conditions of the GNR/GO film. Figure S3 shows SERS measurements with a laser wavelength at 488 nm, 514 nm, 568 nm and 647 nm. The 488 nm the laser was out of resonance of the gold nanorods and a very weak Raman signal of CV was observed, clearly displaying the D (1330 cm^{-1}) and G (1600 cm^{-1}) Raman bands of the GO. The 514 nm laser was close to the resonance the transverse plasmon mode of the gold nanorods and was observed a significant increase in signal was observed. The 568 nm and 647 nm lasers have the largest increases in the Raman signal since they approach the plasmon resonance due to the longitudinal plasmon of gold nanorods in the GNR/GO film. The 647 nm laser was chosen for SERS studies in this work because it is closest to the resonant plasmon for thin films of GNR/GO as shown in Figure 3.

The CV was deposited by drop casting on two substrates; on the standard glass and onto GNR/GO film. In both substrates three concentrations were used (10^{-5}, 10^{-8} and 10^{-11} M). In the glass substrate, a very weak Raman signal was detected and only at higher concentrations with long acquisition times (60 seconds - box in Figure 4). On the other hand, the SERS effect appears clearly on the GNR/GO substrate showing an excellent signal at all concentrations and a monotonically drop with the decreased concentration (Fig 4). The black line in the Figure 4 shows the Raman spectrum of CV on glass without any SERS effect.

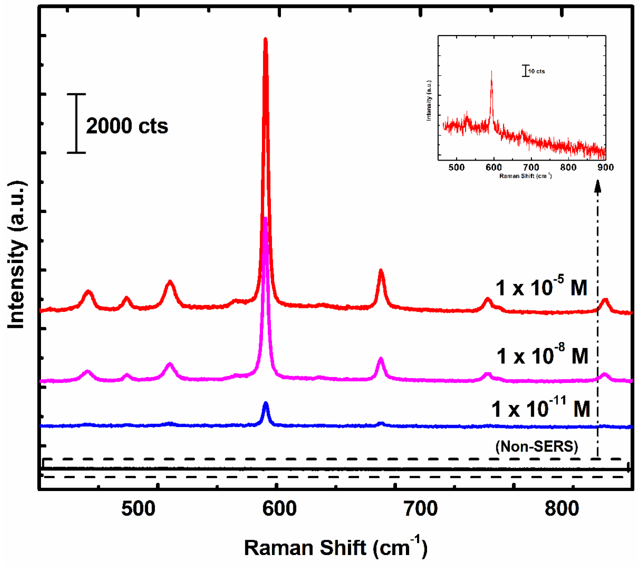

Figure 4 – SERS Spectrum of CV at different concentrations.

SERS Mapping

SERS measurements of CV on the dried GNR/GO thin film substrate showed a high increase of Raman signal. However, the quality and uniformity of the SERS substrate are fundamental for the development of a commercial SERS substrate. SERS mapping was performed. The substrate was dipped for about 20 seconds in a solution of 10^{-7} M of CV. Then Raman mapping measurements were made using the 591 cm^{-1} peak as a reference. Figure 5a shows an optical image of GNR/GO film as substrate and the Figure 5b shows the SERS mapping. This figure shows the variation of Raman signal depending on the position on the substrate; the yellow range is the intensity of the CV SERS Raman signal peak at 591 cm^{-1}. The variation of intensity is mainly due the molecules distribution on the substrate and by depth of focus. Figure S4 shows the same mapping SERS measurements at two different focal distances.

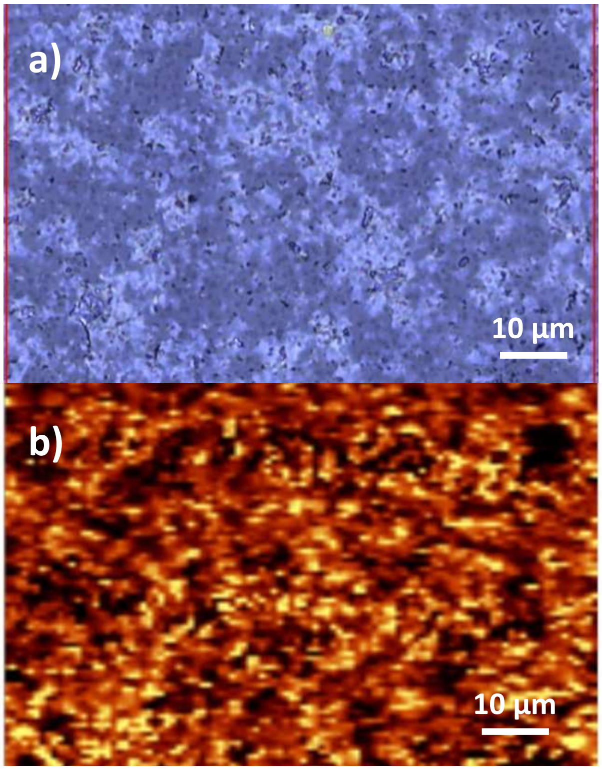

Figure 5 – SERS mapping of the GNR/GO hybrid film. A) Optical image of GNR/GO film as substrate b) SERS mapping.

Substrate enhancement factors (SEFs) were calculated according to the methodology proposed by Le Ruet *et al*[41]. We assume that all of the SERS molecules were uniformly adsorbed for all the samples, due to the dilute concentration of the SERS molecules (10^{-7} M). The results of our calculations indicate an enhancement factor of the order of ~10^6.

GO/GNR film features high SERS enhancement factors with detection limits near picomolar concentrations for the aromatic dye used. Other authors have reported work with hybrids between GO and metallic nanoparticles[42]. However, gold nanorods are better for SERS than spherical nanoparticles as demonstrated by El-Sayed et al[42] due to high curvature and well-developed tunability of the surface plasmon resonance. Spherical nanoparticles only have a peak of plasmon resonance (~520 nm). On the other hand, the gold nanorods have two plasmon modes one transverse (~520 nm) and another longitudinal (~640-1000 nm), where both of them are active, though the longitudinal plasmon mode is the most intense, as shown in Figures 3 and S3. Other studies published in the literature have achieved enhancement of about 10^4-10^5 and detection limits of nanomolar concentrations[25, 42, 44-45]. The detection limits and enhancement factors obtained in our experiment is comparable or higher to the ones recently reported in the literature.

Conclusions

We have developed a simple method for the synthesis of nanocomposite between graphene oxide and gold nanorods. The process was carried out through the photochemical synthesis of gold nanorods by irradiation of ultraviolet light and their growth on graphene oxide. The synthesis shows excellent distribution of nanorods in aqueous solution as characterized by images of transmission electron microscopy (TEM). A thin film was formed with the hybrids on a glass substrate, showing high detection sensitivity, easy preparation and high enhancement in the Raman signal, while SERS mapping showed great uniformity and high magnification factor (10^6).

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