Surface-enhanced Raman scattering effect in binary systems formed by graphene on aluminum plasmonic nanostructures

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Keywords: plasmonic, aluminum, SERS, GERS, nanostructures, hybrid systems, anodic aluminum oxide

Abstract

Binary systems (BS) formed by graphene (GR) deposited on top of aluminum (Al) nanoconcaves (Al-NC) and Al nanodomes (Al-ND) were synthesized by electrochemical anodization of Al. Using the plasmonic response of Al-NC and Al-ND and the distinctive physical and chemical properties of GR, these BS are proposed as Surface-Enhanced Raman Scattering (SERS) sensors using rhodamine 6G (R6G) as a proof molecule. As expected, the BS significantly enhances Raman signals of R6G molecules in comparison with substrates used as references, also suppressing the fluorescence background of R6G molecules.

1. Introduction

SERS is a powerful analytical technique with the capability of detecting and characterise analytes at the single-molecule level using the enhancement of the Raman signal in various orders of magnitude much larger than those obtained in traditional Raman [1–5].

The amplification of the signals in the SERS effect occurs through two mechanisms: Electromagnetic Mechanism (EM) and Chemical Mechanism (CM). The EM is mainly provided by plasmonic resonances present in metallic nanostructures [6, 7]. Gold (Au) and silver (Ag) are noble metals traditionally used for fabricating SERS substrates [8], but their plasmonic response are only tailored in to the visible range, extending into the infrared regions and their inherent drawbacks can limit their application. Comparatively, Al has plasmonic response in the ultraviolet–visible region of the electromagnetic spectrum [9–12]. Taking advantage of this beneficial property, Al has acquired great interest in detection applications and also as template for plasmonic metafilms [13, 14]. For example, Tian et al report the synthesis of Al nanocrystals as sustainable SERS substrates for single-stranded DNA phosphate backbones detection [15]. Although some of the main current problems for the fabrication of periodic plasmonic nanostructures are the expensive and sophisticated fabrication techniques [16–18]. The electrochemical anodization of Al is an alternative technique for synthesizing structurally well-controlled materials compared to other expensive techniques such as lithography, besides being low cost and highly scalable [19–21].

The CM results in the adsorption of the molecule in the substrate, inducing a modification of its electronic structure by means of a charge transfer between it and the substrate, resulting in a change in the polarizability of the molecule, and as a consequence, changes in its Raman signal [22]. The enhancement factors are much smaller (∼102) compared to those obtained by the EM.

On the other hand, it has been shown that GR is a good candidate as a substrate to enhance the Raman signal through CM, with enhancement factors of ~103 [23]. This effect is known as Graphene-Enhanced Raman Scattering (GERS) [24–26]. GR as SERS substrate has a superior adsorption capacity of molecules, and can effectively turn off the fluorescence background of molecules used as dyes [23]. For example, Zhao et al report GR on vertical arrays of Au nanorods as SERS hybrid substrate with high sensitivity to detect concentrations as low as 1 × 10−12 mol l−1 [27]. Hybrid systems formed of GR or other two dimensional (2D) nanomaterials and metal nanostructures are being extensively studied for potential SERS applications [28].
Combining the electromagnetic enhancement provided by the plasmonic response of Al nanostructures (electrical fields distributions pinned at the surface of the nanostructures) and the distinctive physical and chemical properties such as Charge-transfer or changes in Fermi level of GR, hybrid systems for the enhancement of the Raman signal can be obtained.

2. Experimental details

Figure 1 shows the schematic diagram of the synthesis process of the BS formed by GR deposited on Al-NC (GR/Al-NC) and Al-ND (GR/Al-ND).

For the synthesis of Al-NC and Al-ND, high-purity Al foils (Sigma-Aldrich 0.25 mm thick, 99.999% purity) were electropolished (see figure 1(a)) and anodized using mixtures of 90 ml of H₃PO₄ (0.01 M) + 10 ml of C₆H₄O₇ (1 M) for Al-NC and 70 ml of H₃PO₄ (0.1 M) + 30 ml of ethylene glycol for Al-ND, applying voltages of 227 V and 163 V at ambient temperature for 24 h, respectively. For more details of the clean process and pretreatments of Al foils, see [29] and [30].

After anodization (see figure 1(b)), porous anodic alumina (PAA) was selectively dissolve using a mixture of CrO₃ (1.8% wt.) + H₃PO₄ (6% wt.) at 60 °C for 24 h, with this procedure the Al-NC are observed in the remaining Al surface corresponding to the negative shape of the bottom of the PAA (see figure 1(c)). For the case of Al-ND, the Al was dissolved using a mixture of HCl (20% wt.) + CuCl₂ (0.5 M) after the anodization. With this process nanodomes were obtained (see figure 1(d)). Subsequently, Al film of ~50 nm thickness was deposited by thermal evaporation on top of nanodomes using 5 × 10⁻⁶ torr working pressures (see figure 1(e)).

Carbon films were synthesized by chemical vapor deposition (CVD) method [31, 32]. Under these conditions of synthesis carbon films which are a mixture of GR and few layer GR (from two to five layers) were obtained. Carbon films were transferred on top of Al-NC and Al-ND (see figures 1(f) and (g), respectively). GR zones were selected for this study.

Finally, GR/Al-NC and GR/Al-ND were immersed in a R6G proof solution at a concentration of 1 × 10⁻⁶ mol l⁻¹ for 18 h for a better adsorption of molecules (see figures 1(h) and (i)).

The morphology of Al-NC and Al-ND was evidenced by using field-emission scanning electron microscope (SEM) JEOL 7600 F equipped with energy dispersive x-ray spectrometer (EDS). The geometric parameters were evaluated directly from SEM images by using Image J software [33].

Reflectance measurement was performed using UV–vis spectrophotometer (UV-2600 Shimadzu Corporation). The probe was set at 8° angle and reflectance spectra were collected using integrating sphere in the 190–1400 nm wavelength range. Raman spectroscopy was made using Nicolet Almega XR Spectrometer and AFM Alpha 300AR-WITec confocal Raman microscope. All the measurements were performed using an excitation laser wavelength of 532 nm, with a 100X objective (spot size ~4 μm) and ~3.85 mW incident power.
3. Results and discussion

Figures 2(a) and (b) show SEM micrographs of Al-NC and Al-ND, respectively. In both cases, it is observed that the nanostructures present a hexagonal structure, and their size depends on the anodized voltage.

The characteristic geometric parameters, the interconcave and interdome distance ($D_c$) (see figures 1(c) and (d)), of these nanostructures were estimated from SEM micrographs. The statistical analysis of typical size distributions of $D_c$ for Al-NC and Al-ND are shown in figures 2(c) and (d), respectively. The $D_c$ value of Al-NC is $696.8 \pm 77.0$ nm, and $438.8 \pm 56.4$ nm for Al-ND.

These nanostructures can support surface plasmon resonances (SPR) manifested as minima in reflectance spectra or maxima in absorbance spectra in the UV-visible region, and their positions depend on the periodicity $D_c$ of the arrays and on the optical properties of Al. The excitation of SPR in nanostructures with hexagonal geometry can be studied using as first approximation the coupling model of SPR and photons in a 2-dimensional hexagonal periodic array [34, 35].

Studies show that when the SPR wavelength ($\lambda_{\text{SPR}}$) match or is near to the wavelength of the excitation laser probe of the Raman system ($\lambda_{\text{exc}}$), in our case $\lambda_{\text{exc}} = 532$ nm, the obtained SERS signal is the strongest [29, 36].

However, achieving the matching of $\lambda_{\text{SPR}}$ around the position of $\lambda_{\text{exc}}$ still remains a problem due to effective methods for synthesizing nanostructures with well-controlled plasmonic resonances. With electrochemical anodization of Al, the size of Al nanostructures can be modified (in this case $D_c$, see figure 3(a)) and in turn $\lambda_{\text{SPR}}$ can be changed (see figure 3(b)) through the appropriate electrolytes and anodization voltages. Considering this fact, in this work the appropriate experimental conditions were chosen to tune $\lambda_{\text{SPR}}$ and looking for a value as near as possible to $\lambda_{\text{exc}}$ to secure the maximum Raman enhancement: anodization voltages of 227 V and 163 V for Al-NC and Al-ND, respectively, (see figure 3(b)).

Reflectance spectra of the Al-NC and Al-ND as a function of light wavelength are shown in figures 3(c) and (d) respectively. A dip in the reflectance intensity at $\sim 826$ nm ($\sim 1.5$ eV) is observed in both cases (pink colour arrow), this feature is related to interband transitions (IT) of the crystalline bulk Al. In addition other minima in $\sim 532$ nm adjudicated to SPR are observed (blue colour arrow) [29, 30].

Figures 4(a) and (b) show Raman spectra of GR/Al-NC and GR/Al-ND, respectively. We observe that Raman signal intensity of the characteristic G and 2D bands of GR significantly increases in both cases in comparison with substrates used as references (SiO$_2$ (306 nm)/Si and electropolished Al). In the case of GR/Al-NC (see figure 4(a)), the enhancement factors obtained were: $\sim 32$-fold for the G band and $\sim 21$-fold for the...
2D band compared to GR on electropolished Al, and ~19-fold for the G band and ~20-fold for the 2D band compared to GR on SiO2 (306 nm)/Si. For the case of GR/Al-ND (see figure 4(b)), the enhancement factors obtained were: ~40-fold for the G band and ~48-fold for the 2D band compared to GR on electropolished Al, and ~44-fold for the G band and ~50-fold for the 2D band compared to GR on SiO2 (306 nm)/Si.

Figures 4(c) and (d) show Raman spectra of R6G solution (1 × 10^-6 mol l^-1) detected in GR/Al-NC and GR/Al-ND, respectively, as well as on substrates used as references. For R6G on electropolished Al (black curve), SiO2 (306 nm)/Si (red curve), Al-NC (blue curve) and Al-ND (orange curve) characteristic bands are not observed due to their high fluorescence; while for R6G on GR/electropolished Al (pink curve) and GR/SiO2 (306 nm)/Si (purple curve) characteristic Raman bands [37–39] (see table 1) were observed in both cases. In these latter cases, GR quenches R6G fluorescence, allowing some of its characteristic bands to be observed.

Finally, in the case of R6G molecules deposited on GR/Al-NC (see figure 4(c)), the enhancement factors of the band located at 1647 cm^-1 was ~14-fold with respect to GR on electropolished Al, and ~5-fold with respect to GR/SiO2 (306 nm)/Si; while for R6G molecules on GR/Al-ND (see figure 4(d)), the enhancement factors of the band located at 1570 cm^-1 was ~7-fold with respect to GR on electropolished Al, and ~13-fold with respect to GR on SiO2 (306 nm)/Si.

The obtained results demonstrate the good sensitivity of the BS proposed here for SERS proofs, mainly due to SPR in Al nanostructures, and in addition to physical and chemical properties provided by GR. Additionally, GR can effectively suppress fluorescence, allowing detection of the Raman signal from highly fluorescent molecules; also isolates molecules from the metallic nanostructures greatly preventing photoinduced damage such as photocarbonization, as well as chemical absorption and deformation [40].

Particularly, using the plasmonic properties of Al nanostructures (Al-NC and Al-ND), it is possible to design SERS substrates formed by the combination of GR and metal nanostructures called graphene-mediated SERS substrates (G-SERS substrates) with superior characteristics compared to other traditional SERS substrates.

4. Conclusions

In summary, we have demonstrated that BS based on Al nanostructures and GR can be used as SERS substrates using R6G as the analyte at concentration of 1 × 10^-6 mol l^-1. We find significant enhancement of the
characteristic Raman signal of GR of ∼32 times on Al-NC and ∼50 times on Al-ND in comparison with substrates used as references; for the R6G on BS the enhancement was ∼14 times and the fluorescence background was successfully suppressed. The BS proposed here can significantly improve the detection sensitivity and can be useful on the detection of biological and chemical molecules.

**Acknowledgments**

We thank Josué E. Romero and Omar Novelo of the Laboratorio Universitario de Microscopía Electrónica (LUME-IIM-UNAM) for the SEM images; Miguel A. Canseco for his assistance with the UV–vis equipment, Carlos D. Ramos for his help with the evaporation system, Raúl Reyes for his technical support (all of them at IIM-UNAM), Prof. J. M. Saniger of ICAT-UNAM for his useful comments, and finally the Laboratorio
Universitario de Caracterización Espectroscópica (LUCE-ICAT- UNAM) for the facilities for Raman measurements.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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