Suppression of the surfactant-induced SERS blinking in a graphene oxide/gold nanorod nanocomposite

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Abstract: *We demonstrate a graphene oxide/gold nanorod nanocomposite as a surface-enhanced Raman spectroscopy (SERS) substrate that suppresses the usual temporal intensity fluctuations, commonly referred to as blinking. We demonstrate that the presence of graphene oxide improves the temporal stability compared to gold nanorods alone, which is attributed to the removal of the nanorod's surfactant from plasmonic hot spots, via the graphene oxide−surfactant interaction. The nanocomposite is, then, used as a SERS substrate for the detection of Rhodamine 640.*

Key-Words*: graphene oxide; gold nanorods; nanocomposite; SERS; blinking.*

Introduction: By confining light to nanometer length scales using plasmonic nanostructures, the scattering cross section of a molecule can be enhanced a billion-fold, providing a platform to enable efficient chemical and biological detection through surface enhanced Raman spectroscopy (SERS). However, thermal fluctuations and charge transfer dynamics can lead to strong temporal fluctuation in the SERS spectrum, which may be an obstacle for precise molecular recognition and has largely prevented the widespread practical application of SERS in areas that require high accuracy standards, such as chemical sensing and medical diagnosis. While the blinking dynamics has not yet been fully understood, a variety of physical and chemical processes has been suggested [1]. Molecular diffusion and adsorption/desorption cycles within a hot spot are among the most accepted pictures. In such cases, the surfactant on the metallic nanocrystals can play a significant role. In this work, we demonstrate blinking suppression in a nanocomposite consisting of graphene oxide (GO) and gold nanorods (AuNRs) [2]. While the SERS spectra obtained with AuNRs without GO or analyte molecules exhibited strong blinking attributed to cetyltrimethylammonium Bromide (CTAB), the surfactant used in the AuNRs' synthesis, the GO/AuNR nanocomposite was found to suppress the CTAB signal and its temporal instability. The nanocomposite was then used as a SERS substrate for the detection of Rhodamine 640 (RH640) at concentrations as low as 10^{-10}M.

Experimental: Graphene oxide was synthesized by a modified Hummers method and AuNRs by a seed mediated method [2]. Samples were prepared on Si substrates with a 300-nm thick SiO_2 top layer. AuNR samples were prepared by dipping the substrate in the AuNR suspension for approximately 12 h and then drying it under gentle N_2 gas flow. For the GO/AuNR nanocomposite preparation, the substrate was first dipped in the GO suspension for 12 h and dried under N_2 flow, and then immersed in the AuNR suspension for another 12 h, finally being dried in the same manner. Samples containing RH640 as the probe molecule (AuNR/RH640 and GO/AuNR/RH640) were prepared by first following the preparation routes described above and then depositing a 20 μL droplet of a RH640 solution (10^{-6}M to10^{-10}M) in deionized water.

Results and discussion: We studied the stability of the SERS signal in four different samples, described above. The AuNR sample was found to exhibit strong temporal oscillation (blinking), attributed to CTAB. Figure 1a shows a time-averaged SERS spectrum in which the marked peaks (asterisks) refer to the tentative assignment to known CTAB Raman modes (also visible in the Raman spectrum of pure CTAB powder). The peak at 179 cm^{-1} (red asterisk) is attributed to the Au−Br stretching mode, indicating a chemical bond between CTAB and the AuNRs. Figure 1b shows a SERS spectrum time series for the AuNRs sample, in which CTAB blinking can clearly be observed. In contrast, temporally stable spectra are shown in Figure 1c, for the GO/AuNR sample. While the 179 cm^{-1} Au−Br band is still visible, all other CTAB peaks do not appear. In fact, CTAB is known to self-assemble on GO's surface either through van der Waals forces or via electrostatic attraction between the negatively charged GO and the cationic CTAB polar head groups [3]. We then speculate that CTA^+ is electrostatically attracted by and displaced toward GO, while the bromide remains in the AuNRs' surface due to its high affinity to gold atoms. The absence of CTA^+ Raman bands indicates its removal from the plasmonic hot spots at the AuNRs' surface, which leads to a more stable spectrum.

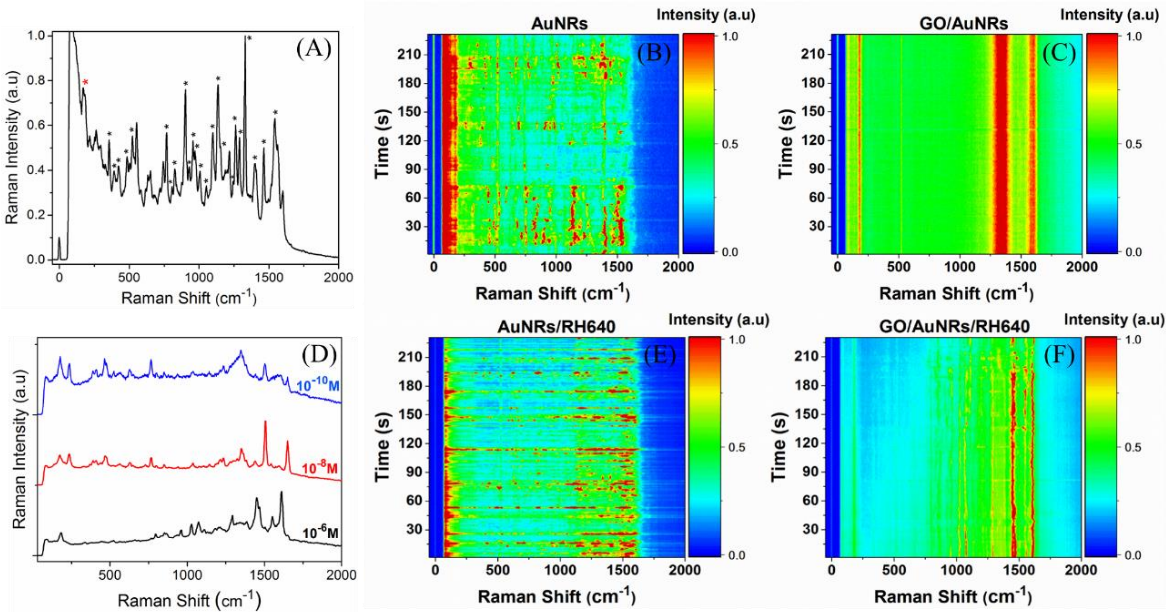

Figure 1. (a) SERS spectrum of the AuNR sample. The asterisks indicate the modes that are successfully assigned to CTAB. The red asterisk denotes the Au−Br stretching mode. SERS spectra time series for the (b) AuNR sample and (c) GO/AuNR nanocomposite sample. (d) Spectral comparison for different RH640 concentrations on the GO/AuNR nanocomposite. SERS spectra time series for (e) the AuNR/RH640 sample and (f) the GO/AuNR/RH640 sample

Since GO inhibits CTAB blinking on AuNRs, the nanocomposite is proposed as a SERS substrate with improved stability. In a proof-of-principle experiment, RH640 was used as a probe molecule. The spectra obtained with concentrations of 10^{-6}, 10^{-8}, and 10^{-10} M are shown in Figure 1d, with clearly visible RH640 bands. However, when RH640 (10^{-6} M) is added to an AuNR sample, blinking continues and seems to slightly increase relative to the AuNR-only case (Figure 1e). Such an increase is possibly connected to the dynamics of adsorption/desorption of both CTA+ and RH640 molecules within plasmonic hot spots, as Raman peaks of both molecules could be identified along a spectral time series. In contrast, a significantly more stable spectrum is achieved with RH640 (10^{-6}M) on the GO/AuNR substrate, as shown in Figure 1f. Simultaneous high sensitivity and high-stability operation is unusual in SERS and is a major asset of the demonstrated nanocomposite substrate. We speculate that AuNRs in the nanocomposite, which are negatively charged due to the adsorption of the Br^{-} ions, attract and attach to the positively charged RH640 molecules promoting the stable and intense SERS signal.

Conclusion: We presented a study of the use of GO/AuNR nanocomposites for highly sensitive and stable SERS. We showed that the electrostatic attraction between GO and CTAB head groups, as well as the van der Waals interaction between the nonpolar CTAB tails and the GO sheets, remove CTA+ from the AuNRs' plasmonic hotspots. As a consequence, SERS blinking, which is found to be rather strong in AuNR samples due to the CTA^{+} dynamics, is suppressed in GO/AuNR samples. As a proof-of-principle SERS experiment, Rhodamine 640 was successfully detected down to 10^{-10}M concentrations, with minimal temporal instabilities, on the GO/AuNR substrate. Our results, therefore, contribute toward a more widespread use of SERS, by demonstrating a blinking free, stable and reproducible SERS substrate. The nanocomposite can also be used for the modification of the inner walls of capillary fibers, work that is now being conducted to test the platform as an optofluidic SERS substrate.

References and acknowledgements:

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