Ag Nanoparticle Decorated Graphene Oxide: Fluorescence Quenching and Surface Enhanced Raman Scattering

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Abstract – The emission and Raman scattering properties of three dyes, Rhodamine 6G (R6G), Rhodamine B (RhB) and Sulforhodamine 101 (SR101), were characterised on graphene oxide (GO) and Ag nanoparticle (NP) decorated graphene oxide (AgGO) substrates to examine the impact of fluorescence quenching on Surface enhanced Raman scattering (SERS) detection. Strong correlation is found between the time-resolved fluorescence data and the Raman scattering peak signal-to-noise ratios (SNRs). The fluorescence quenching efficiency on GO is largest for R6G, while the fluorescence lifetime of SR101 is most strongly affected by the addition of the Ag NPs. R6G and SR101 demonstrate higher coupling efficiencies to the AgGO composite compared to RhB. The AgGO substrate yields significant improvements in the Raman scattering SNRs for all three dyes, which are again greatest for R6G and SR101.

I. INTRODUCTION

Raman spectroscopy is an extensively used tool for the study and characterization of molecular structures. However, the technique is limited by low sensitivity, with approximately $1/10^6$ of incident photons undergoing Raman scattering. With surface enhanced Raman scattering (SERS), large enhancements of the Raman scattered intensity can be achieved, thus allowing for high sensitivity detection of analytes at low concentrations. The origin of the SERS enhancement has been attributed to both chemical enhancement and enhanced local electromagnetic (EM) fields [1]. Analytes can experience large localised EM fields when they are in close proximity to a metallic surface, particularly roughened or nanostructured surfaces. This SERS enhancement by metallic nanostructures has been the subject of extensive research over the past decade [2]. Recently, the SERS activity of graphene, graphene oxide (GO) and reduced graphene oxide (rGO) substrates has been investigated. Due to the atomically flat nature of graphene substrates, analytes can be sufficiently close to the graphene substrate for chemical enhancement *via* efficient charge transfer to occur [3].

Graphene, GO and rGO have also been reported to demonstrate high fluorescence quenching efficiencies [4]. This fluorescence quenching is attributed to non-radiative energy transfer, which can occur *via* Förster resonance energy transfer (FRET) and charge transfer. Charge transfer has a stronger distance dependence, and consequently, FRET is the dominant mechanism at separations > 4 nm [5, 6]. Combining the fluorescence quenching properties of the graphene-based materials with the high local field generated by nanostructured metals paves the way for the formation of multipurpose SERS substrates. Herein we present complimentary studies of the impact of the various constituents of the AgGO composite substrate on the emission and Raman scattering spectra of Rhodamine 6G (R6G), Rhodamine B (RhB) and Sulforhodamine 101 (SR101). This study elucidates the extent of the influence of fluorescence quenching on the SERS sensitivity.

II. RESULTS

The AgGO composite material was synthesised according to [7], and was characterised using Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM), see Fig. 1(a-c). The TEM and SEM images illustrate the dense packing of the Ag NPs on the GO substrate, with a greater view of the surface morphology given in the SEM and AFM images in Fig. 1(b, c). From multiple TEM images, 340 Ag NPs were measured and the average diameter of the Ag NPs on the GO flakes was found to be 40 ± 16 nm, see Fig. 1(d) for size distribution. The AFM measurements gave the height of the AgGO flakes

Fig. 1. (a) TEM image of AgGO flake, (b) SEM image of AgGO flake, (c) AFM image of AgGO flake, (d) distribution of Ag NP diameters on the GO flakes, (e) normalised extinction spectra of AgGO (blue), GO (green) and Ag NPs (red) and (f) extinction (red), absorption (blue) and scattering (green) spectra of AgGO sample. The scale bar in (a, b) is 500 nm.

between 50 – 100 nm thus verifying the adhesion of Ag NPs on both sides of the GO flakes. The extinction spectra of the AgGO composite, GO flakes and Ag NPs in aqueous solution are shown in Fig. 1(e). The localised surface plasmon resonance can be seen in the Ag NPs extinction spectrum and it is noted that the extinction spectrum for the AgGO composite is much broader and the peak has red-shifted relative to that of the Ag NPs alone. The broadening of the extinction spectrum and the red-shift of the peak is mainly attributed to the increased interaction between the Ag NPs as they are now densely packed on the GO scaffold. This increased interaction can result in a collective behavior, increasing the scattering contribution to the overall extinction spectrum, particularly at longer wavelengths [8]. This was confirmed with UV-Vis measurements using an integrating sphere. The extinction, scattering and absorption spectra of the AgGO composite are shown in Fig. 1(f), where it is apparent that scattering makes a significant contribution to the overall extinction spectrum, most notably at longer wavelengths.

Fig. 2. (a) Fluorescence decays for R6G alone (black), on GO (blue) and on AgGO (red). (b) Raman spectra of R6G on Ag NPs (green), AgGO (red) and GO (blue). (c) SNR as a function of concentration for R6G, RhB and SR101 on AgGO substrates.

The fluorescence decay curves for R6G alone and in the presence of GO and AgGO can be seen in Fig. 2(a). There is a large reduction in the average lifetime in the presence of GO with a further reduction in the presence of AgGO. This trend in lifetime reduction in the presence of GO and AgGO is seen for each dye. The interaction between the dyes and the substrates can be quantified in terms of an efficiency, η , which is given by

$$\eta = 1 - (\tau_{DS}/\tau_D) \quad (1)$$

where τ_D is the lifetime of the dye alone and τ_{DS} is the lifetime of the dye on the GO or AgGO substrate.

We find the largest lifetime reduction for R6G on both GO and AgGO, while SR101 shows the largest increase in the efficiency on AgGO compared to GO, indicating a stronger interaction with the Ag NPs. RhB is least influenced by the presence of the AgGO substrate. Single Raman spectra for R6G at a concentration of 10^{-4} M on Ag NPs, GO and AgGO substrates are shown in Fig. 2(b). The spectra show large fluorescence background with low Raman peak intensities in the presence of Ag NPs, whereas the spectra on the AgGO substrate show well defined peaks over a reduced background. The visibility of the Raman peaks and thus the performance of the AgGO composite as a SERS substrate can be quantified in terms of a signal-to-noise ratio (SNR). The SNR is given by

$$SNR = S/N/\sqrt{N} \quad (2)$$

where S is the signal intensity at a given peak and N is the noise value at the base of the peak. The detection limits for each of the dyes on the AgGO substrate were identified from a concentration dependence study, the SNR at each concentration is shown in Fig. 2(c). R6G and SR101 show the largest SNR values, while RhB demonstrates the weakest performance on the AgGO composite substrate. This finding mirrors the time-resolved data, which also showed that RhB had a weaker interaction with the composite. The large SNR for R6G is expected due to its higher fluorescence, arising from a high quantum yield and better the spectral overlap between the Raman excitation wavelength and the dye absorption maximum compared with the other two dyes.

III. CONCLUSION

We have examined the impact of a AgGO composite substrate on the fluorescence and Raman scattering signals of three dyes, R6G, RhB and SR101. Time-resolved fluorescence measurements indicate a stronger interaction between the dyes and the AgGO composite compared with undecorated GO. Coupling efficiencies of over 70% are measured for R6G and SR101. In the case of R6G the change in the fluorescence lifetime is dominated by the presence of the GO, whereas the lifetime of SR101 is most strongly influenced by the addition of the Ag NPs. The results have also shown that components of the AgGO composite have competing effects on the dye fluorescence; fluorescence quenching by the GO and fluorescence enhancement by the Ag NPs. However, an overall reduction of the fluorescence background in the Raman spectra is produced in all cases, contributing to higher SNR values on the AgGO composite than with the Ag NPs alone.

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