

Green Synthesis of Graphene Oxide/Ag Nanocomposites via Laser Ablation in Water for SERS Applications

Parvathy Nancy¹, Anju K Nair², Jemy James², Nanda kumar Kalarikkal^{1, 2 a)}

¹*School of Pure and Applied Physics, Mahatma Gandhi University, Kottayam-686560, Kerala, India*

²*International and Inter University Centre for Nanoscience and Nanotechnology, Mahatma Gandhi University, Kottayam-686560, Kerala, India*

^{a)}*Corresponding author: nkkalarikkal@mgu.ac.in*

Abstract. The need for metallic nanoparticle decorated nanocomposites of graphene oxide finds much attention by reason of their technological applications. Unlike the traditional methods, herein, we present a laser-assisted synthesis of silver nanoparticles that are anchored onto the graphene oxide (GO) by a one-step reaction. Second harmonics of an Nd:YAG laser is used for the in situ generation of Ag nanoparticles (Ag NPs) from a silver target ablated in an aqueous suspension of graphene oxide and thereby to make GO/Ag nanocomposite. UV-Vis and fluorescent spectroscopy and HRTEM upholds the optical and morphological characteristics of GO/Ag nanocomposite. Particularly, the GO/Ag nanocomposites exhibit excellent Surface Enhanced Raman Scattering (SERS) performance.

INTRODUCTION

Pulsed Laser Ablation in Liquids (PLAL) is based on the irradiation of a focused pulsed laser beam onto the surface of a solid target surrounded by any kind of liquid¹. Herein, we detail the influence of laser radiation for the improvisation of graphene oxide (GO) sheets with Ag NPs by fine tuning the laser energy and SERS performance of the nanocomposite. The probe molecule used is Rhodamine to determine the enhancement performance of the as prepared SERS-active substrate. Natural graphite powder was used to synthesize graphene oxide (GO) with modified Hummers' method². A pure solid silver target is ablated in GO suspension in deionised water. During the laser ablation, Ag NPs were generated in the GO solution and spherical Ag NPs was strongly anchored onto the surface of GO sheets. The optical and morphological properties of the GO/Ag nanocomposite produced were studied by UV-Vis spectroscopy, fluorescent spectroscopy, and high-resolution transmission electron microscopy.

EXPERIMENTAL DETAILS

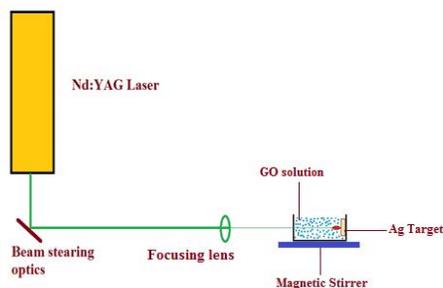


Figure 1 The experimental set up of production of Ag nanoparticle/GO composite

Figure 1 depicts the experimental arrangement of laser ablation. A pure solid silver target (SIGMA ALDRICH, 99.99% pure trace metal) of thickness 1mm is properly placed inside a glass cuvette which contained 30ml of graphene oxide solution. Second harmonic (532nm) of a Q-switched Nd-YAG Laser (Litron LPY 674G-10) beam having 8ns pulse width and 10Hz repetition rate was focused on to the silver target using a plano-convex lens of focal length 15 cm at room temperature. The Ag target is ablated for 15min at three different laser energies. The GO solution is kept under stirring with the help of a magnetic stirrer.

RESULTS AND DISCUSSION

UV-Vis absorption spectra

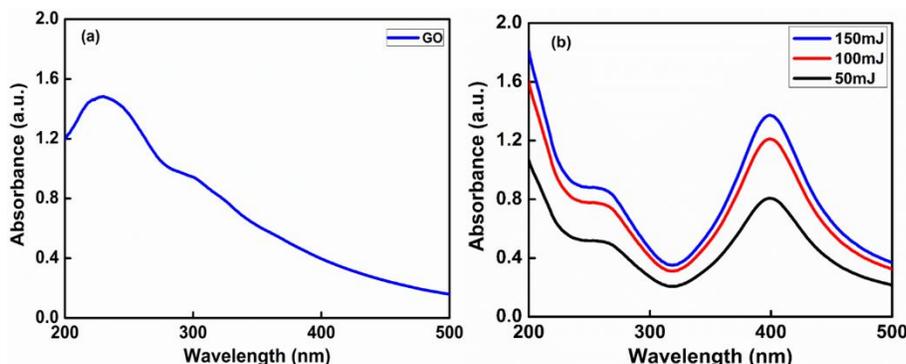


Figure 2 UV-Vis Absorption spectrum of (a) GO & (b) GO/Ag nanocomposite

Figure 2(a) represents the UV-Vis absorption spectrum of GO sheets. The GO sheets displays an absorption peak at 234 nm corresponding to $\pi \rightarrow \pi^*$ interaction of C-C bonds and a small shoulder peak at 304 nm attributed to $n \rightarrow \pi^*$ interaction of C=O bonds. Figure 2(b) shows the UV-Vis absorption spectra of GO/Ag nanocomposites. After the laser ablation with different laser energies (50mJ, 100mJ and 150mJ), the absorption peak of GO in all the samples gradually shift to 255nm, which indicates that some of the GO sheets have been reduced due to the interaction of GO with high laser energy (Figure 2(b)). Along with this, the entire GO/Ag samples exhibit a broad absorption peak at ~ 400 nm, which is ascribed to the surface plasmon resonance (SPR) of Ag NPs^{3, 4}. That means, the Ag NPs have been formed successfully on the surface of GO sheets. The results illustrates that laser energy is the key tuning parameters for enhancing the concentration and size of Ag NPs onto the GO sheets.

Photoluminescence spectra

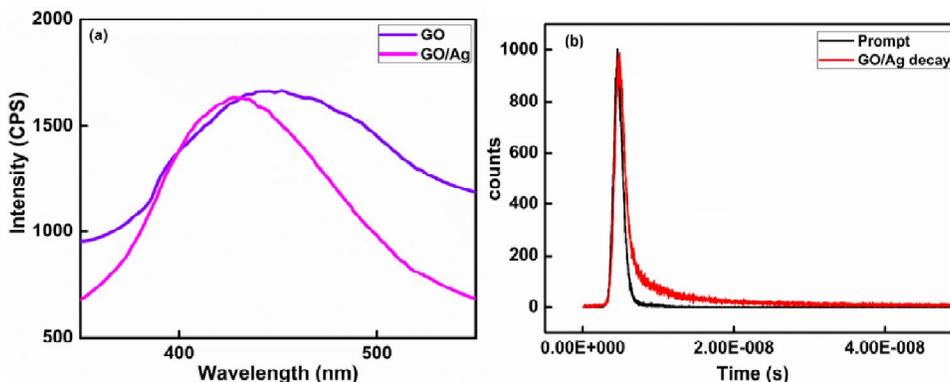


Figure 3 Photoluminescence spectra of (a) GO and GO/Ag nanocomposite (b) Fluorescence decay curve of GO/Ag nanocomposite

The as prepared samples were excited at a wavelength of 300nm. Both GO and GO/Ag nanocomposite exhibit broad emission peaks at 440nm and 425nm respectively as shown in figure 3. In the laser assisted synthesis of GO/Ag nanocomposite, Ag NPs are formed in-situ and it is decorated especially on the region around defects of the surface of GO so that there may be a chance of luminescence quenching. A small luminescence quenching has been observed with a little reduction in intensity in the case of GO/Ag nanocomposite compared to GO. This is an indication of an increase of charge carries due to the effective interaction between Ag NPs and the GO sheets.

The fluorescence lifetime of the GO/Ag nanocomposite (Figure 3(b)) were investigated. The decay curves were fitted to multi-exponential functions. Here, GO/Ag nanocompositerequires three time constants for satisfactory fits.They are $T_1 = 2.429222E-09s$, $T_2 = 8.636833E-09s$, $T_3 = 1.764924E-10s$. The mean life time value can be calculated using equation (1)⁵

$$T_m = a_1T_1 + a_2T_2 + a_3T_3 \quad (1)$$

Where a_1 , a_2 , a_3 , T_1 , T_2 , and T_3 are the amplitudes and decay times of the multi exponential components of the fluorescence decay. The mean life time of GO/Ag nanocomposite obtained from the time resolved measurement is 375.86ns.

TEM and HRTEM Analysis

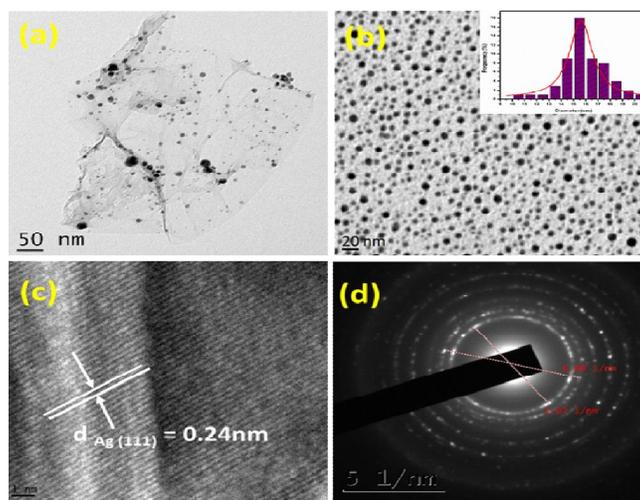


Figure 4(a) & (b) –TEM: (c) - HRTEM image and (d) SAED pattern of GO/Ag nanocomposite. Particle distribution diagram is in the inset

TEM observations suggest that individual GO sheets are densely coated with nanoparticles, exhibiting a hierarchical micro/nanostructure. Figure 4(c) shows the HRTEM image of the interface between Ag NPs and GO sheets. An inter-planar distance of 0.24 nm, which corresponds to the 111 plane of Ag NPs, is clearly seen in the HRTEM image. Figure 4(d) shows the selected area electron diffraction (SAED) pattern, which reveals that these nanoparticles exhibit high crystallinity. The Ag NPs are nearly spherical with average particle size 15nm. Particle distribution diagram is shown in the inset of figure 4. Overall, GO sheets act as a planar substrate to fix 0D Ag nanoparticles, while the nanoparticles separate the sheets as spacers. For such a structure, aggregation of both GO sheets and Ag NPs are effectively avoided, which enables the active surface to be maintained and open channels left for mass transport.

SERS Performance

SERS is a powerful analytic technique in which weak Raman signals of analytemolecules are greatly enhanced when they are very close to the surface of plasmonicnanoparticles⁶. Figure 5(a) shows the comparative SERS spectra of Rhodamine 6G (R6G) with GO/ Ag nanocomposites prepared at three different laser energies. The GO/Ag sandwich nanocomposite exhibits a strong SERS effect using R6G as a probe molecule. A confocal Raman

spectrometer (with 523nm excitation) is used for the SERS measurements. The integration time was set to be 10s for the detection of analyte molecule. The peak vibrations at 1186, 1313, 1509 and 1651 cm^{-1} are attributed to C-H in-plane bending, C-O-C stretching and C-C stretching of the aromatic ring respectively⁷. The detection limit of GO/Ag nanocomposites on R6G probe molecule was about $1 \times 10^{-12} \text{M}$.

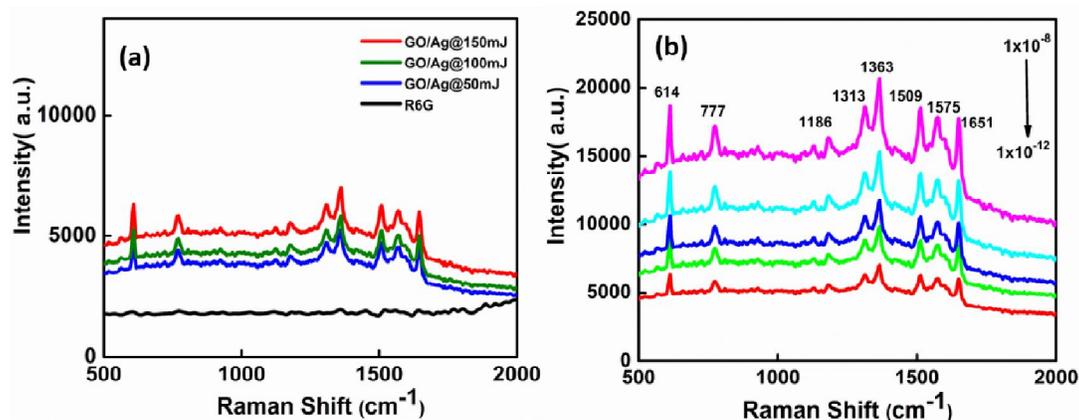


Figure 5 SERS spectra of (a) $1 \times 10^{-7} \text{M}$ R6G adsorbed GO/Ag nanocomposite prepared at different laser energies & (b) R6G with different concentrations from $1 \times 10^{-8} \text{M}$ to $1 \times 10^{-12} \text{M}$ on GO/Ag nanocomposite substrate

The enhancement factor (EF) for GO/Ag nanocomposite at 150mJ laser energy is estimated to be as high as 3.5×10^7 compared to other two samples (The EF can be roughly calculated as $I_{1363, \text{SERS}} / I_{1363, \text{NR}} \times C_{\text{NR}} / C_{\text{SERS}}$, where $I_{1363, \text{SERS}}$ and $I_{1363, \text{NR}}$ represent the intensities of the SERS peak at 1363 cm^{-1} of the GO/Ag nanocomposite and clean R6G, respectively, C_{NR} and C_{SERS} denote the corresponding R6G concentrations for normal Raman and SERS substrates. These results indicate that the GO/Ag nanocomposites are promising SERS substrates for the highly sensitive detection of chemical analyte molecule, R6G.

CONCLUSION

Ag NPs have been successfully anchored on GO sheets by laser ablation of Ag targets in GO aqueous solution. The PL shows the GO/Ag nanocomposite is fluorescent in nature and shows faster decay. It makes them a good candidate for potential applications in optoelectronics and biomedicine. It can also act as building blocks for three-dimensional structures. Our results signified that the built GO/Ag nanocomposites have excellent SERS performance for sensing R6G with an enhancement factor of 3.5×10^7 . Also the proposed synthesis strategy provides a sample scope for the production of different functional materials for SERS applications.

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