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RGO-Ag nanocomposite as active SERS substrate

Heena Wadhwa, Devender Kumar, Suman Mahendia*, Shyam Kumar
Department of Physics, Kurukshetra University, Kurukshetra-136119, INDIA
Email: mahendia@gmail.com

ABSTRACT: In the present study, reduced graphene oxide - silver (RGO-Ag) nanocomposites were prepared by employing in-situ reduction of graphene oxide (GO) and metal salt. RGO-Ag composites were characterized using transmission electron microscopy (TEM). TEM images confirm the presence of Ag nanoparticles on the surface of RGO with average size of 44 nm. Further optical properties of RGO-Ag nanocomposites were studied using UV-Visible absorption spectroscopy. Further, the potential of RGO-Ag nanocomposites as active surface enhanced raman scattering (SERS) substrate has been studied with rhodamine 6G chloride (R6G) as probe molecule with the detection limit of 1µM. Also the fluorescence quenching has been observed in Raman spectrum of R6G which further helps in retaining the desired information.

Keywords: Reduced graphene oxide; transmission electron microscopy; UV-visible spectroscopy.

INTRODUCTION: Surface Enhanced Raman Scattering (SERS) analysis is one of the most widely explored analytical tools especially in the fields of biological and chemical sensors [1]. SERS enhances the Raman signals by several orders of magnitude which are the possible cause for the high sensitivity for SERS. The Electromagnetic (EM) and Chemical (CM) enhancement are the major factors responsible for the SERS enhancement [2]. Traditionally rough metallic surfaces or metal nanoparticles are employed as SERS substrate. These have combined advantages of Raman fingerprints of probe molecules along with biocompatibility for detection of proteins in cells and tissues, DNA and other biomoleules [3]. But the control over their size and morphology, aggregation, packing of nanoparticles assembly and stability are still occurring as major obstacles in the fabrication of reliable SERS substrate [4-5]. Therefore, there is a need for SERS substrate with high enhancement factor, stability and homogeneity.

On the other hand, graphene; the 2-d wonder material, has shown its potential for SERS substrate which may be owned to its large surface area and luminescence quenching efficiency [6-7] and also some graphene based metal composites have been fabricated as active SERS substrate [8]. Further two dimensional nature of graphene supports the uniform distribution of noble metal nanoparticles, leading to SERS signals with high stability and homogeneity [9].

In this work, reduced graphene oxide decorated with silver nanoparticles (RGO-Ag nanocomposites) were synthesized employing in-situ reduction method and the formation of nanocomposites were confirmed by characteristic SPR peak observed in UV Visible absorption spectra along with Transmission electron microscopy (TEM) images. Also their potential as active SERS substrate has been tested for Rhodamine 6G chloride (R6G) and observed detection limit is 1µM.

EXPERIMENTAL

Materials: In the present work, chemicals like Graphite powder, Sulphuric acid (H_2SO_4), Sodium Nitrate ($NaNO_3$), Potassium permanganate ($KMnO_4$), Hydrazine monohydrate (35 wt.%), Hydrogen-peroxide (H_2O_2) (30 wt.%), Hydrochloric acid (HCl), Ammonia solution (25wt.%), tri sodium citrate dehydrate ($C_6H_5Na_3O_7H_2O$), Silver Nitrate ($AgNO_3$) and Rhodamine 6G (R6G) were used as it is as they procured.

Methods: The synthesis of RGO-Ag nanocomposites was employed using in-situ reduction of metal salt precursor in presence of reduced graphene oxide stock solution. In a typical synthesis process, graphene oxide (GO) was prepared using modified Hummers method from graphite powder [10]. After that exfoliated GO solution (1 mg/10 ml) was prepared using ultra-sonication for 45 minutes followed by dropwise addition of 35 wt.% ammonia solution to make pH of resultant solution to 10. Afterwards, 35 µl of hydrazine monohydrate was added and solution was transferred to oil bath at 80^0 C for 2 hours and the resulting solution was named as Reduced Graphene Oxide (RGO) stock solution. Meanwhile 1 mM silver nitrate solution was prepared and mixed in equal volume with that of RGO stock solution. Further, 1 (wt/v%) of sodium citrate solution was added and stirring was continued for next 15 minutes to obtain desired RGO-Ag nanocomposites.

SERS substrate: R6G was employed as probe molecule for SERS measurements (with different concentrations from 1mM to 0.1 µM). For sample preparations, first 2 µl of as prepared RGO and RGO-Ag nanocomposite solution were drop casted on clean glass substrate and dried at 40^0 C afterwards 2 µl of R6G solution was dropped on same substrates and dried.

Characterization: Shimandzu Double Beam Double monochromator UV–Visible Spectrophotometer (UV–Visible 2550) with integrating sphere assembly ISR-240A operating in wavelength range 190–900 nm with the resolution of 0.5 nm was employed to study the UV-Visible absorption spectra in solution form. TEM measurements were carried out using a Tecnai-G^2-20 TEM facility operating at 200 kV, equipped with a LaB_6 filament and a charge-coupled device camera having point resolution of 2.04 Å.

RESULTS AND DISCUSSIONS

Absorption Spectroscopy: UV-Visible absorption spectrum of GO (Figure 1, curve ‘a’) shows a peak at 233 nm and belonging to the π to π* transition of C-C, C=C bonds in sp^2 region. Also a shoulder at 300 nm belongs to the n to π* transition of C=O bond in sp^2 hybrid region of GO, respectively. Further, curve ‘b’ representing the absorption spectrum of RGO, contains a single absorption peak at 260 nm which belongs to characteristic π to π* transition of RGO. The red shifting of this peak from 233 nm to 260 nm in RGO indicates the restoration of graphitic like structure of GO and also the disappearance of 300 nm peak in curve ‘b’ clearly indicates the removal of oxygen functionality [11]. Further, the absorption spectrum of RGO-Ag nanocomposite (curve ‘c’) contains two peaks at 260 nm and 420 nm respectively belonging to RGO and characteristic surface plasmon resonance (SPR) peak of entangled Ag nanoparticles [12], thereby confirming the reduction of GO along with the formation of Ag nanoparticles.

TEM Analysis: Figure 2 (i) present the TEM image of RGO-Ag nanocomposite in which RGO sheet contains many folds which are the signature of multi-layer planer type morphology of graphene nanosheets [13]. Also the morphology of attached Ag nanoparticles is not limited to spherical shape, but silver nanoparticles of various shapes are formed (inset of Figure 2(i)). The histogram of entangled Ag nanoparticles to RGO surface (shown in Figure 2 (ii)) shows that silver particle of various size ranging from 10-100 nm are formed with average size 44 nm are formed.

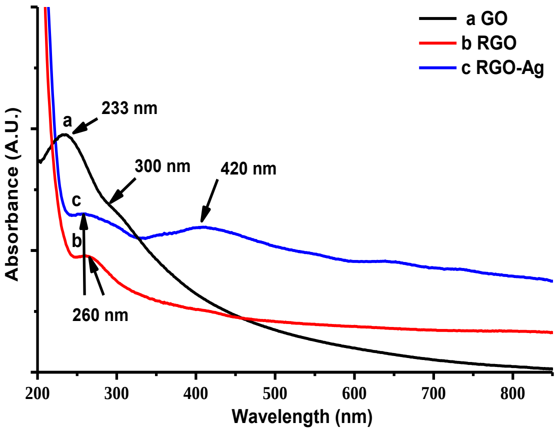

Figure 1: UV-Visible absorption spectra of (a) GO, (b) RGO and (c) RGO-Ag nanocomposite.

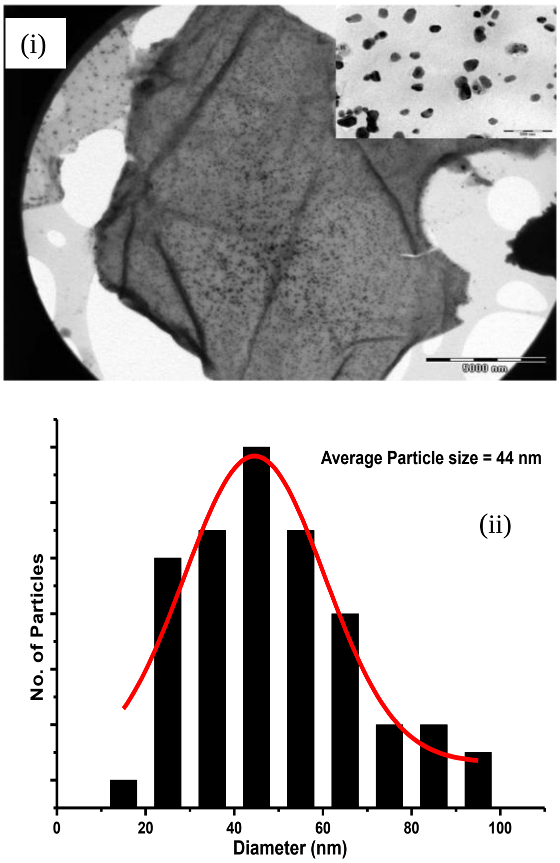

Figure 2: (i) TEM images of RGO-Ag nanocomposite with inset showing magnified view and (ii) Histogram showing the particle size distribution of entangled Ag nanoparticles on RGO surface.

SERS Analysis: Figure 3(i), depicting the Raman spectrum of RGO-Ag composites; contains two peaks at 1348 cm^{-1} and 1587 cm^{-1} belonging to characteristic D and G band of carboneous materials [14]. The SERS Spectrum of RGO-Ag nanocomposites are shown in Figure 3(ii) with different concentration of R6G (1 mM-0.1 µM). R6G is organic dye which is generally employed as probe molecule in SERS. The Raman spectrum of R6G (curve ‘g’, Figure 3) contains large amount of fluorescence which generally hinders the useful information. R6G spectrum is showing peaks at 1641, 1569, 1527, 1358 cm^{-1} due to in plane C-C stretching, the 765 cm^{-1} is due to C-H out of plane bending vibrations and that of 606 cm^{-1} is due to in-plane bending vibrations of CCC ring of R6G [15].

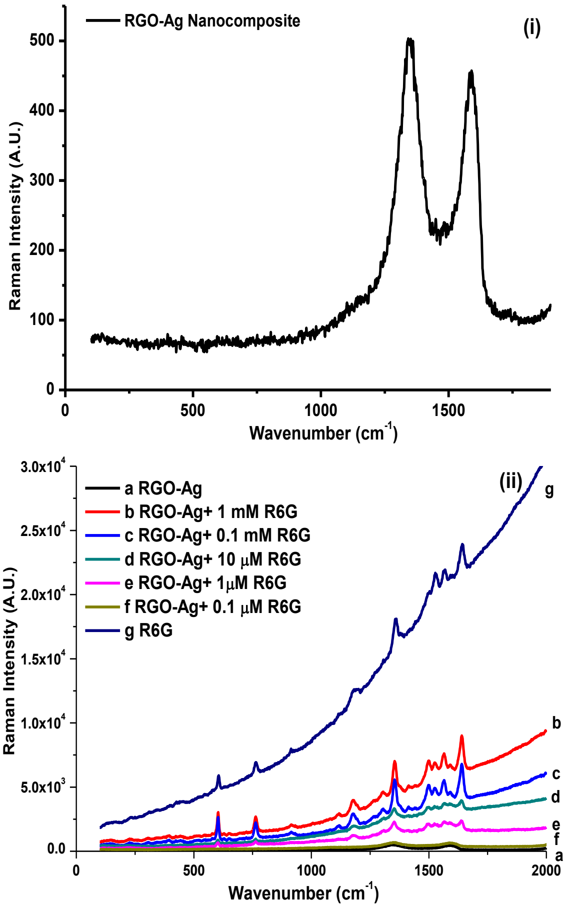

Figure 3: (i) Raman spectra of RGO-Ag nanocomposite and (ii) SERS spectra of RGO-Ag nanocomposites with different concentrations of R6G (1mM- 0.1 µM).

While depositing R6G on RGO-Ag nanocomposites, the SERS intensity decreases, which may be attributed to the fluorescence quenching ability of RGO. The charge transfer between hexagonal rings of R6G and RGO is the possible cause behind the observed behaviour. Also the Raman shifts at 1174 and 1303 cm^{-1} belonging to in plane C-C stretching are observed. With decreasing concentration of R6G, the SERS intensity also decreases and at concentrations of R6G below 1 µM, no characteristic peaks of R6G is observed, thereby setting detection limit to 1 µM. The possible cause for such type of behaviour may be understood by considering the mechanism responsible for SERS enhancement. The Electromagnetic mode (EM) mode governs the SERS enhancement of metal nanoparticles while Chemical mode (CM) is major governing mechanism for RGO. On observing the results for RGO-Ag nanocomposites, it can be inferred that both mechanisms are competitive in nature. At concentration below 1 µM, the SERS behavior of RGO dominates and for the higher concentration, that of metal nanoparticles dominates.

CONCLUSIONS: In this study, RGO-Ag nanocomposites have been synthesized and confirmed by their characteristic SPR peak observed in UV-Visible absorption spectrum. Also TEM analysis governs that RGO sheets are of multilayer nature and entangled Ag nanoparticles have average size 44 nm. The RGO-Ag nanocomposites have also been employed as active SERS substrate for RGO with detection limit 1 µM. Such a simple method for SERS detection is strength of our technique and can found applications in biosensors. This technique is fast, cost effective and suitable for large scale synthesis.

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REFERENCES:

1. Zhang Y., Liu S., Wang L., Qin X., Tian J., Lu W., Changa G. and Sun X. (2012), “One-pot green synthesis of Ag nanoparticles-

graphene nanocomposites and their applications in SERS, H_2O_2, and glucose sensing", *RSC Advances*, 2, 538–545.

2. Netzer N. L., Tanaka Z., Chen B. and Jiang C. (2013), "Tailoring the SERS Enhancement Mechanisms of Silver Nanowire Langmuir–Blodgett Films via Galvanic Replacement Reaction", *The Journal of Physical Chemistry C,* 117, 16187-16194.

3. Schlücker S. (2009), "SERS microscopy: nanoparticle probes and biomedical applications" *ChemPhysChem*, 10, 1344-1354.

4. Liu Y., Zhang Y., Ding H., Xu S., Li M., Kong F., Luo Y. and Li G. (2013), "Self-assembly of noble metallic spherical aggregates from monodisperse nanoparticles: their synthesis and pronounced SERS and catalytic properties", *Journal of Materials Chemistry A.* 1, 3362-3371.

5. Liao F., Cheng L., Li J., Shao M. W., Wang Z. H. and Lee S. T. (2013), "An effective oxide shell protected surface-enhanced Raman scattering (SERS) substrate: the easy route to Ag@AgxO-silicon nanowire films via surface doping", *J Mater Chem C,* 1, 1628–1632.

6. Xie L., Ling X., Fang Y., Zhang J. and Liu, Z. (2009), "Graphene as a substrate to suppress fluorescence in resonance Raman spectroscopy', *Journal of the American Chemical Society,* 131, 9890-9891.

7. Qiu C., Zhou H., Yang H., Chen M., Guo Y., and Sun L. (2011), "Investigation of n-layer graphenes as substrates for Raman enhancement of crystal violet", *The Journal of Physical Chemistry C,* 115, 10019-10025.

8. Hu C., Liu Y., Qin J., Nie G., Lei B., Xiao Y., Zheng M., Rong J. (2013), "Fabrication of reduced graphene oxide and sliver nanoparticle hybrids for Raman detection of absorbed folic acid: a potential cancer diagnostic probe" *ACS Appl Mater Interface,* 5, 4760–4768.

9. Hsu K. C. and Chen D. H. (2014), "Microwave-assisted green synthesis of Ag/reduced graphene oxide nanocomposite as a surface-enhanced Raman scattering substrate with high uniformity", *Nanoscale research letters*, 9, 1-9.

10. Hummers W. (1958), "Preparation of graphitic oxide", *J. Am. Chem. Soc.,* 80, 1339.

11. Lai Q., Zhu S., Luo X., Zou M. and Huang S. (2012), "Ultraviolet-visible spectroscopy of graphene oxides", *AIP ADVANCES* 2, 1-5.

12. Zainy M., Huang N. M., Kumar S. V., Lim H. N., Chia C.H. and I. Harrison, (2012) "Simple and scalable preparation of reduced graphene oxide–silver nanocomposites via rapid thermal treatment", *Materials Letters* 89, 180–183.

13. Paredes J. I., Villar-Rodil S., Martínez-Alonso A. and Tascon J. M. D. (2008), Graphene oxide dispersions in organic solvents, *Langmuir*, 24, 10560-10564.

14. Tian J., Liu S., Zhang Y., Li H., Wang L., Luo Y., Asiri A.M., Al-Youbi A.O., Sun X. (2012), "Environmentally Friendly, One-Pot Synthesis of Ag Nanoparticle- Decorated Reduced Graphene Oxide Composites and Their Application to Photocurrent Generation", *Inorg. Chem.*, 51, 4742−4746.

15. Hildebrandt P., Stockburger M. (1984), "Surface-enhanced resonance Raman spectroscopy of rhodamine 6G adsorbed on colloidal silver", *J. Phys Chem.* 88, 5935–5944.