



Synthesis and Characterization of Reduced Graphene Oxide/Ag₂S nanocomposites by co-precipitation Method using Thiourea as Sulfur source and reducing agent

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Abstract : Graphene based nanocomposites are emerging as a new class of materials for many applications. Reduced graphene oxide/Ag₂S composites were synthesized through a simple co-precipitation method. The composite materials were characterized by X-ray diffractometer (XRD), Fourier transform infrared (FTIR), Ultraviolet – Visible (UV-Vis) and Raman spectroscopy measurements. The chemical state and its Binding Energy investigations of the rGO/Ag₂S were carried out by X-ray photoelectron spectroscopy (XPS). The surface morphology of the composite material was studied by Field emission- Scanning electron Microscope (FE-SEM) and Transmission electron Microscope (TEM) shows that the Ag₂S nanoparticles are heavily deposited on the surface of the reduced graphene Oxide layers.

Keywords : Reduced graphene oxide, Silver sulfide, Thiourea, Nanocomposite, and Co-precipitation.

Introduction

Graphene, thinnest and strongest material of single layer, two dimensional sheet of Sp² hybridized carbon has received great interest in recent years because of its excellent properties¹⁻³, leading to their potential application in different areas, such as Photovoltaics, sensors, batteries and nanoelectronics⁴⁻⁷. The study of decorating the graphene sheets with inorganic functional materials such as metals, metal oxides and metal sulfides is now becoming a promising and challenging area of research. Recently more effort has been focused to synthesis the inorganic materials on the graphene sheets by using the graphene oxide solution. The functional groups such as epoxide, hydroxyl, carboxyl and carbonyl groups were on the surface of the graphene oxide solution⁸. These functional groups offer the anchoring point of inorganic materials. So far, reduced graphene oxides (or) graphene/inorganic materials have been successfully synthesized. Such nanomaterials, metals (Ag, Au and Co), metal oxides (TiO₂, ZnO₂ and SnO₂) and metal sulfides (CdS and ZnS) were decorated on the surface of the reduced graphene oxide to make the composite material with excellent optical and photovoltaic properties were reported⁹⁻¹⁵.

In the past decade, the semiconductor nanoparticles have been investigated due to their potential applications in optic, electronic and catalytic properties. Among the semiconductors, silver sulfide is an important semiconducting material has been studied because of its applications widely used in electronic and optical devices, such as photo conducting cells and photovoltaic cells^{16, 17}. Semiconducting material properties are based on the silver sulfide nanoparticles; essentially it depends on the preparation methods. In this present work, we have studied the decoration of the silver sulfide nanoparticles on to the surface of the graphene oxide layers via an easy co-precipitation method. Thiourea is used as Sulfur source and reducing agent for the transformation of GO to rGO. An amine group, which helps to remove the oxygen containing functional groups and the studies, are discussed in detail.

Experimental

Graphite Oxide was synthesized from graphite powder by using Hummer's method¹⁸. 100 mg of graphite oxide (GO) was dispersed in 20 ml of ethanol by ultrasonication for 3 h. 339 mg of silver nitrate and 152 mg of thiourea is added to the solution under stirring. This solution is allowed to stir for four hours, and the reaction was performed at the temperature of 60 °C. The final product collected in the form of dry precipitate. Then the precipitate is centrifuged and washed with three times of ethanol followed by three times of water. Then the final product is dried in a vacuum oven at 60° C for 12 h.

Characterization

A little amount of the dried samples are dispersed in ethanol solution by ultrasonication for 30 mins and the resulting solution was used to UV and TEM measurements. For the TEM measurements, single drop of dispersed solution is dropped on the copper grid and the ethanol is allowed to evaporate in air atmosphere. The morphology of the samples was measured by Transmission Electron Microscope (TEM) using JEOL JEM-2010 and the Field emission Scanning Electron Microscope (FE-SEM) using HITACHI-S4800. X-ray diffraction patterns (XRD) were performed by RIGAKU RINTZ ULTIMA+. A Fourier Transform Infrared spectrum (FTIR) was recorded by PERKIN ELMER (Spectrum 100 FTIR spectrometer) using a KBr pellets. A Raman spectrum was recorded in Laser Raman Micro spectroscopy (Jobin-Yvon T64000 Raman Spectroscopy) with green laser of 514.532 nm excitation. UV-vis spectra are recorded by PERKIN ELMER (Lambda 750 UV-Vis spectrometer). The chemical state of the composite material was analyzed by X-ray photoelectron spectrometer (Theta Probe-Thermo Fisher Scientific Inc.).

Results and Discussions

The Fig.1 Shows the phases of the as-obtained products were determined by X-ray diffraction (XRD) measurements of pristine graphite, as-prepared graphite oxide (GO) and rGO/Ag₂S composites. Fig.1a shows the XRD patterns of natural graphite powder. The fig.1b shows a sharp peak at $2\theta = 10.8^\circ$, corresponding to the (002) diffraction peak of graphite oxide^{15, 19}. The fig.1c shows the XRD patterns of rGO/Ag₂S composites. All the peaks in the pattern could be indexed to monoclinic Ag₂S (JCPDS 893840) and the cell constants are calculated to be $a = 4.23031$ nm, $b = 6.91958$ nm and $c = 7.87222$ nm. No impurities phase is detected in these composites. These diffraction peaks indicates that the sample is nanosized. The crystalline size of the sample is estimated to be 14 nm from the Scherrer equation. In the low angle range (below 12°), the XRD pattern does not show any diffraction peaks resulted from the graphite oxide that would be formed by self-restacking of the graphene oxide sheets. When increase in the load of nanoparticles on to the layers, the intensity of the graphene oxide decreases²⁰.

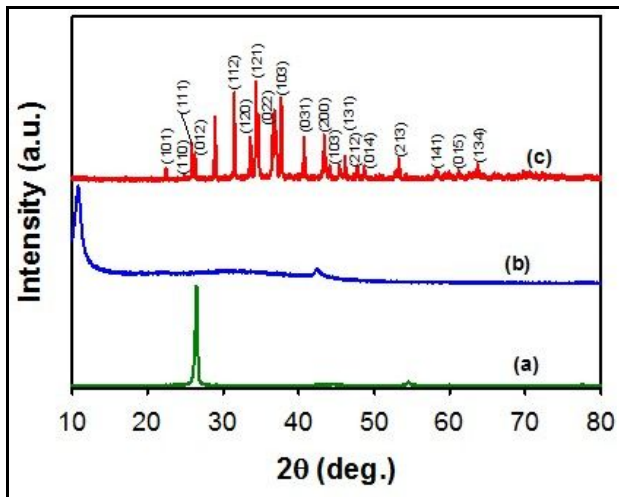


Fig.1. XRD patterns of (a) Graphite powder, (b) Graphite Oxide (c) rGO/Ag₂S nanocomposites

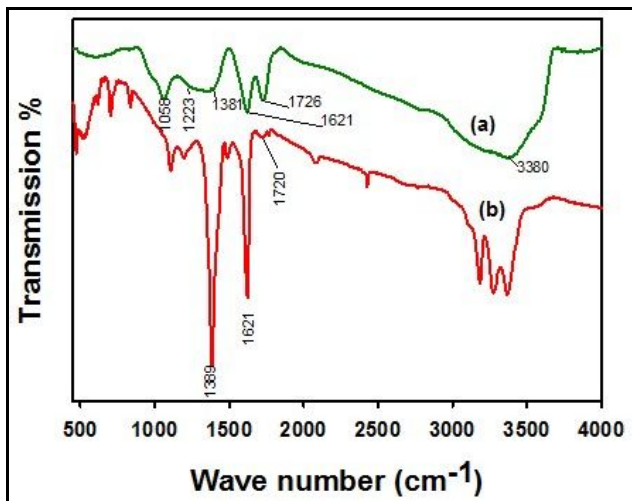


Fig. 2 FTIR spectra of (a) Graphite oxide, (b) rGO/Ag₂S nanocomposites

The formation of graphite oxide and reduced graphene oxide/Ag₂S nanocomposites were characterized by FT-IR and the spectrum is as shown in Fig.2. The FTIR spectra of graphite oxide shows a strong peak around 1621 cm⁻¹ due to aromatic C=C. The stretching vibrations of the hydroxyl groups of GO are observed around 3380 cm⁻¹. It also exhibits peak at 1726cm⁻¹ due to the C=O stretching as well as peaks due to carboxyl (1381cm⁻¹), epoxy (1223cm⁻¹), and alkoxy (1058cm⁻¹) groups situated at the edges of graphite oxide layers as shown in fig 2a²¹. However, all the bands are related with the oxygen-containing functional groups, some of the peaks become very weak and the peaks at 1389cm⁻¹ and 1621cm⁻¹ becomes very sharp in the FT-IR spectra of the rGO/Ag₂S composite Fig 2b. The new peak at 1551 cm⁻¹ is due to the skeletal vibrations of reduced graphene oxide sheets.

The XPS spectra of rGO/Ag₂S composites were detected from the range 0 to 800eV and as shown in Fig. 3a. For the composite material, the band at 284.9 eV is in good agreement with the Sp² bonded carbon groups. The peaks at 286.3 eV and 288.4 eV are hydroxyls/ epoxy and carboxyl groups respectively (Fig. 3b). The XPS peak of O1s is shown in the Fig.3c, two peaks at 531.7 eV and 533.5 eV which corresponds to the C=O and C-O (C-O-C) groups²². The binding energies of Ag 3d appears at 368.4 eV and 374.4 eV is assigned to the Ag 3d_{5/2} and Ag 3d_{3/2} respectively (Fig. 3d)²³. The binding energies S2p peaks appears at 161.4 eV and 162.6 eV is assigned to the S 2p_{3/2} and S 2p_{1/2} respectively (Fig. 3e)²³. The binding energy at 399.8 eV is assigned to the N1s (Fig. 3f). The binding energies of Ag 3d and S2p confirms the presence of Ag₂S nanoparticles and the carbon content in this composite material.

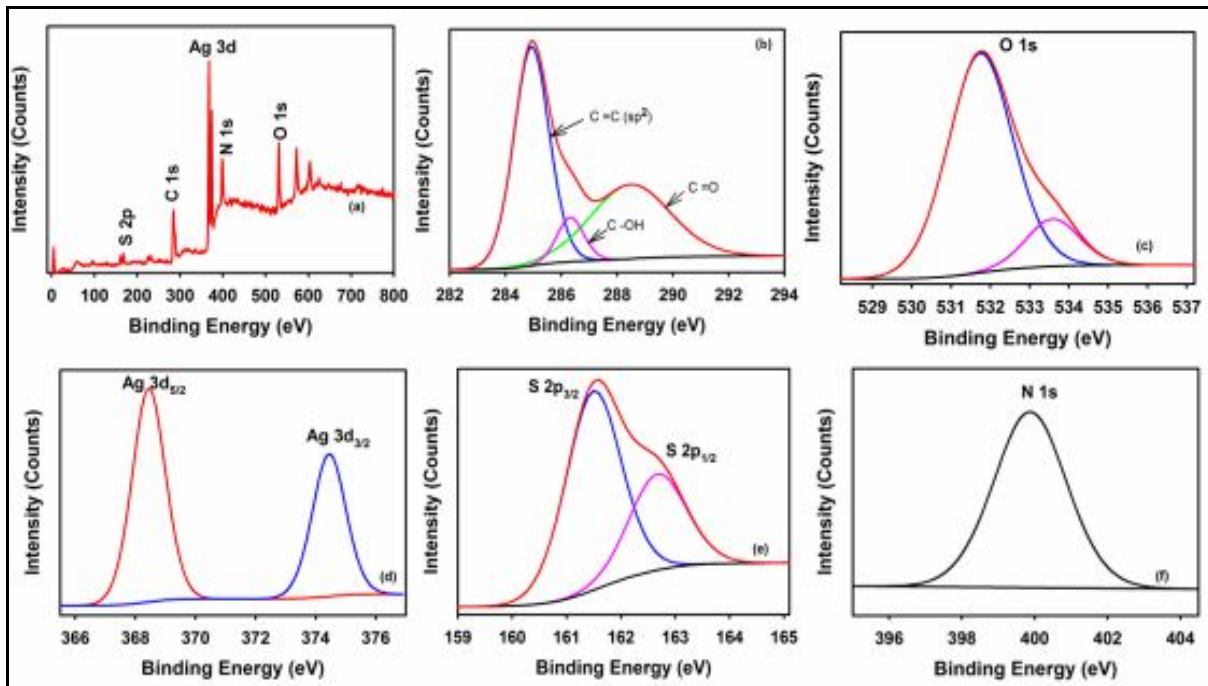


Fig. 3 XPS spectrum of (a) Survey, (b) C 1s, (c) O 1s, (d) Ag 3d, (e) S 2p and (f) N 1s

The UV–vis spectrum of GO exhibits two characteristic peaks, the peak at 230 nm shows the $\pi \rightarrow \pi^*$ transitions of aromatic C–C bonds, and a peak at 303 nm is attributed to $n \rightarrow \pi^*$ transitions of C=O bonds of the graphene oxide (Fig. 4a)²⁴. The Fig. 4b shows the absorbance intensity of the rGO/Ag₂S is in the range of 300 – 350 nm is greatly increased by comparing with the GO spectrum Fig (4a), which can be attributed to the strong absorption of Ag₂S nanoparticles.

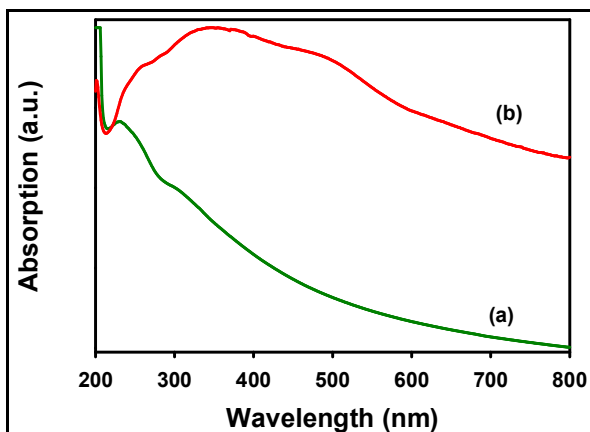


Fig. 4. UV spectrum of (a) graphite oxide and (b) rGO/Ag₂S nanocomposites

The Raman spectra of graphene oxide and rGO/Ag₂S shows the D and G bands structure of carbon and it suggests that the structure of carbon is maintained in the composite material as shown in the Fig.5. The Raman spectrum of the graphite shows the weak D band at 1338 cm⁻¹ and G band at 1563 cm⁻¹. The D/G intensity ratio of the graphite is 0.89 (Fig 5a). In the Raman spectrum of GO (Fig.5b), the D band shifts to 1346 cm⁻¹ and the G band is broadened and shifts to 1587 cm⁻¹. The D/G intensity ratio is increased to 0.99. In the rGO/Ag₂S composite spectrum

(Fig.5c), the peaks of D and G band is at 1350 cm⁻¹ and 1584 cm⁻¹, and the D/G intensity is slightly increased to 1.01 as compared to the D/G intensity value of GO. With comparison of the GO, in the composite material the D band is red shifted by 4 cm⁻¹ and the G band is blue shifted by 3 cm⁻¹. Increase in the D/G intensity ratio, GO is successfully transformed to rGO.

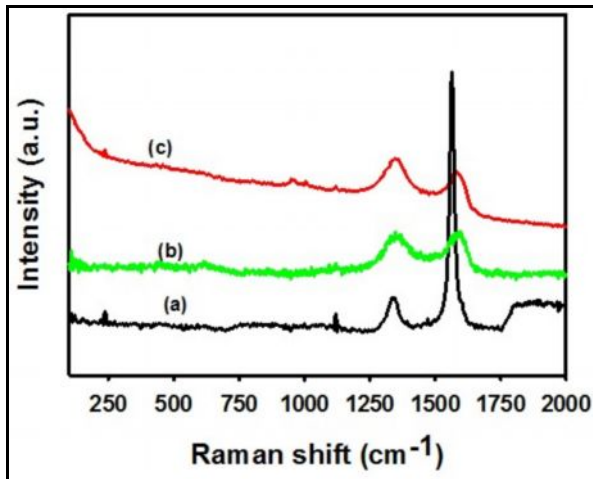


Fig. 5. Raman Spectrum of (a) graphite powder, (b) graphite oxide and (c) rGO/Ag₂S nanocomposites.

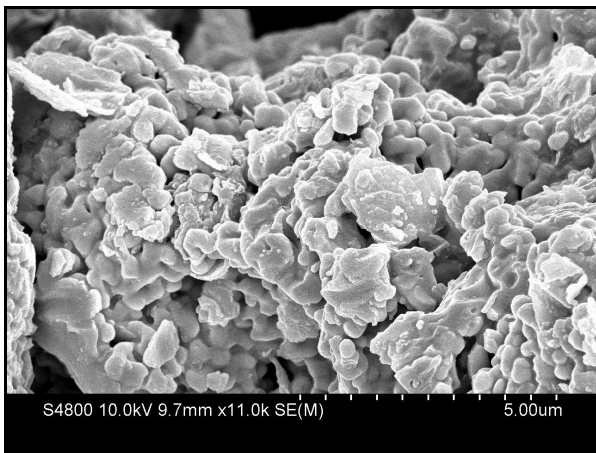


Fig. 6. The FE-SEM image of the rGO/Ag₂S nanocomposites

The surface morphology of the synthesized rGO/Ag₂S composites under a field emission scanning electron microscope (FE-SEM) as shown in the Fig.6. In the surface morphology, that the rGO layers are heavily covered by the silver sulfide nanoparticles. In the rGO, that the particles are deposited on the top of the layers and as well as underneath of the graphene oxide layer. However, the size of the graphene oxide does not show its influence of the structure of the composite material. Here, the graphene oxide sheets are having a large radius and thickness when compared to the diameter of the silver sulfide nanoparticles.

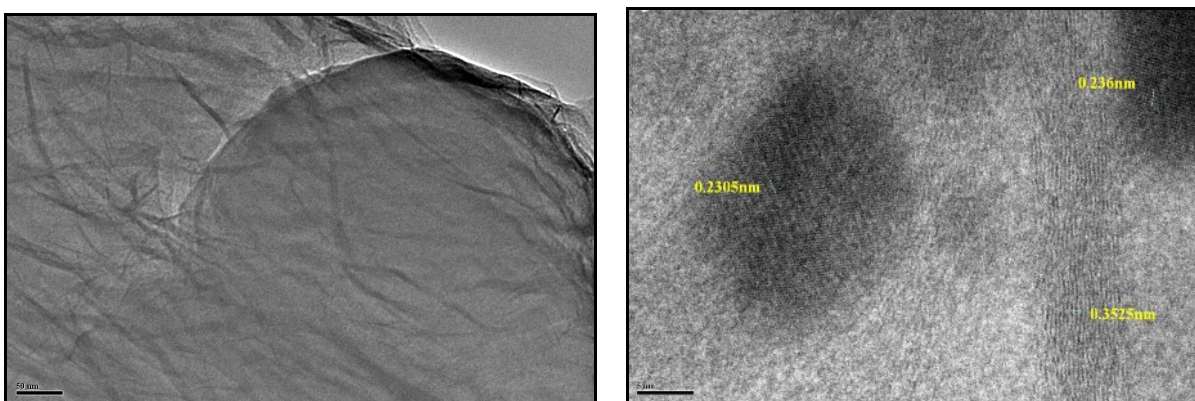


Fig. 7. TEM images of (a) graphite oxide and (b) rGO / Ag₂S nanocomposites

The Fig.7 Shows the TEM images of GO and rGO/Ag₂S composites. The sheet like structure of the graphite oxide was observed and it is shown in the Fig.7a. TEM image of the rGO/Ag₂S composites shows that the material is composed of graphene oxide sheets and silver sulfide nanoparticles. The dark color was found in the composite material, which can be attributed to the overlapping of the silver sulfide nanoparticles Fig.7b. The inter planner distance of the silver sulfide nanoparticles on the graphene oxide sheets is 0.23nm and the inter planner distance of the rGO layers is 0.35nm.

Conclusion

In summary, we have successfully synthesized the rGO/Ag₂S composites by a simple co precipitation method. On the basis of obtained data using SEM, TEM and Raman spectroscopy, the Ag₂S nanoparticles are deposited on the surface of the graphene oxide sheets. The XRD pattern of the composite material exhibits the monoclinic system with the average size of 14 nm. The presence of oxygen containing functional groups was confirmed in the composite material through FTIR and XPS. The π system of the graphene oxide is confirmed by UV-Vis- Spectrometer. It is to be expected that the synthesized composite materials could be very useful to the development of novel optical devices.

References

1. Novoselov K.S. Geim A.K, Morozov S.V, Jiang D, Zhang Y, Dubonos S.V, Grigorieva I.V and Firsov A.A., Science., 2004, 306, 666-669.
2. Geim A.K and Novoselov K.S., Nat. Mater., 2007, 6, 183-191.
3. Zhu Y, Murali S, Cai W, Li X, Suk J. W, Potts J. R and Ruoff R. S., Adv. Mater., 2010, 22, 3906-3924.
4. Stankovich S, Dikin DA, Dommett GHB, A.Kohlhaas K, Zimney EJ and Stach EA., Nature 2006., 442, 282-286.
5. Xu C.H, Wang X.B, Wang J.C and Hu H.T., Chem. Phys. Lett., 2010, 498, 162
6. Wang C.Y, Li D, Too C.O and G.G. Wallace., Chem. Mater., 2009, 21, 2604
7. Vivekchand SRC, Rout CS, Subrahmanyam KS, Govindaraj A and Rao CNR. J Chem Sci., 2008, 120, 9-13.
8. Gao W, Alemany L.B, Ci L.J and Ajayan P.M., Nature Chemistry., 2009, 1, 403.
9. Tang X. Z, Cao Z, Zhang H. B, Liu J and Yu Z. Z., Chem. Commun., 2011, 47, 3084-3086.
10. Vinodgopal K, Neppolian B, Lightcap I. V, Grieser F, Ashokkumar M and Kamat P. V., J. Phys. Chem. Lett., 2010, 1, 1987-1993
11. Ji Z, Shena X, Song Y and Zhu G., Materials Science and Engineering B., 2011, 176, 711-715
12. Akhavan O and Ghaderi E., J. Phys. Chem. C., 2009, 113, 20214-20220.
13. Akhavan. O, Carbon., 2011, 49, 11 -18.
14. Song H, Zhang L, He C, Qu Y, Tian Y and Lv Y., J. Mater. Chem., 2011, 21, 5972-5977.
15. Jia L, Wang D. H, Huang Y. X, Xu A. W and Yu H. Q., J. Phys. Chem. C., 2011, 115, 11466-11473.
16. Wysk H and Schmalzried H., Solid State Ionics., 1997, 96, 41-47.
17. Omeiri S, Hadjarab B and Trari M., Thin Solid Films., 2011, 519, 4277-4281.
18. Hummers W.S and Offeman R.E., J.Am. Chem. Soc., 1958, 80, 1339.
19. Wu J, Shen X, Jiang L, Wang K and Chen K., Appl. Surf. Sci., 2010, 256, 2826-2830.
20. Liu Y. J, Wang Z. M, Aizawa M, Peng W.Q and Hirotsu T., Mater. Lett., 2009, 63, 260- 262.
21. Ji Z , Shena X, Song Y and Zhu G., Mater. Sci. and Eng.B., 2011, 176, 711-715.
22. Wang H. L, Hao Q. L, Yang X. J, Lu L. D, Wang X., Appl Mater. Inter., 2010, 2, 821-828.
23. Shukla S, Seal S and Mishra S.R, Journal of Sol-Gel Sci. and Technol., 2002, 23, 151-164.
24. Paredes J. I, Rodil S. V, Alonso A. M and Tasco'n J. M. D, Langmuir 2008, 24, 10560- 10564.
25. Mani Jayanthi, Thirugnanam Lavanya, SriRangarajan Chenthamarai, Kaveri Satheesh, Synthesis, Optical Characterization And Electrochemical Properties Of Cd_(1-x)Ni_(x) S/ Reduced Graphene Oxide Nanocomposites, International Journal of ChemTech Research ,2016, Vol.9, No.02 pp 156-164.

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