IMPROVING THE ELECTRICAL CONDUCTIVITY OF GRAPHENE LAYER BY CHEMICAL DOPING OF SILVER NITRATE

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Abstract

In the present work, graphene oxides (GO) synthesized directly from graphite powder according to Hummers method were chemically reduced using ascorbic acid and ammonia achieving the reduced graphene oxide (rGO). The Ag-rGO nanocomposite was prepared by hydrothermal process using silver nitrate ($AgNO_3$) as a precursor. As synthesized GO, rGO and Ag-rGO nanocomposite were characterized with Fourier transform infrared spectrophotometer (FTIR), Scanning electron microscope (SEM), X-Ray Diffractometry (XRD) and Raman spectroscopy. The SEM micrographs show the ultrathin, wrinkled, layered flakes and paper-like morphology of graphene sheets. Raman and FTIR spectroscopic investigations provided the information about the number of graphene layers and structural properties. The conductivity measurement showed that the electrical conductivity is improved upon silver doping on graphene sheet.

Keywords: graphene oxide, reduced graphene oxide, Ag-rGO nanocomposite, electrical conductivity

Introduction

Graphene is a monolayer form of carbon with a two-dimensional (2D) honeycomb lattice structure. The most interesting electrical properties of single layer graphene is high electron mobility and ballistic conduction.

The mechanical exfoliation, micromechanical cleavage, epitaxial growth, exfoliation of graphite in the liquid phase through direct sonication, and chemical reduction are commonly used to develop graphene nanosheets (Dreyer *et al*, 2010). The disadvantage of mechanical exfoliation method is that it is not scalable and consequently not amendable for its mass production. Despite achieving pure monolayer graphene sheets by epitaxial growth, its transfer to insulating substrates is of great challenge. Hummers method, one of the chemical methods, has been the most popular approach for its simplicity and large scale production of graphene sheets with several in-plane oxygen-containing groups. In order to reduce it to rGO, chemical reduction or thermal annealing has been employed; the former one enables the exfoliated GO with poor electrical properties due to the presence of contaminates and structural defects, while the latter one would increase its electrical conductivity retaining its graphene structure (Galindo *et al*, 2014).

For the graphene based materials to be utilized as electrode, the electrical conductivity is of key importance. The electrical properties of graphene layers can be modulated by various doping techniques and it is noteworthy that doping is an especially striking approach to tailor and control the properties of graphene (Khan *et al*, 2014). However an extreme care is taken in selecting the doping method since most of doping methods cost degradation of structural uniqueness or electrical mobility (Farmer *et al*, 2009).

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Metal doping by chemical means is simple, easy and even applicable to a graphene device without disturbing the structural shape. Silver (Ag) is a noble metal with remarkable optical properties, excellent thermal and electrical conductivity (Rajeswari *et al*, 2017). The present work involves the synthesis of rGO by chemical reduction method and the Ag decoration on rGO by chemical doping. The optical, structural properties and surface morphology of rGO and Ag modified rGO nanocomposites were investigated. An enhancement in electrical conductivity of Ag-rGO nanocomposites upon Ag doping is illuminated in this work.

Experimental Details

2.1 Materials

Analytical grade graphite powder (99%), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4, 98%), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2, 30%), ascorbic acid (AA), ammonia (NH_3) and silver nitrate ($AgNO_3$) are purchased from Chemical Reagent Co, Ltd. Distilled water (DW) was used throughout the whole experiments. All chemicals were used without any purification.

2.2 Preparation of Graphene Oxide and Reduced Graphene Oxide

Graphene oxides were synthesized directly from graphite according to Hummers method where 1.5 g of graphite powder was added to 35 ml of concentrated sulfuric acid and sodium nitrate while stirring in an ice bath. Potassium permanganate (4.5 g) was added slowly to keep the temperature of the suspension lower than 20 °C. This reaction system was transferred to a 40 °C oil bath and stirred for about 45 min. Distilled water (75 ml) was added and stirred for 20 min at 95 °C. Furthermore, 250 ml of DW was added in this solution. Hydrogen peroxide (30%)   (7.5 ml) was added slowly in the solution, it was changed from dark brown to yellow color. The mixture was filtered and washed with 1:10 HCl aqueous solution to remove metal ions. This solution is graphite oxide aqueous dispersion which was washed several times for neutralization to pH 6-7. And then, we need to put this solvent for overnight. Its precipitate was made by filtration method. The GO dispersion was centrifuged at 3000 rpm for 20 min (7 times) to remove the unexfoliated graphite. The GO aqueous dispersion was further sonicated for 1hr to exfoliate. The solution was absolutely graphene oxide. To reduce GO via a chemical treatment process, ascorbic acid (0.7 g) and the obtained GO suspension (250 ml, 0.3 g/ml) were mixed, and then ammonia solution (60 μl) was added to adjust the pH 8-10. Then the suspension was heated to 95 °C under vigorous stirring and kept for 2 hr. The resulting was reduced graphene oxide (rGO). The reaction mixture was allowed to cool down to the room temperature and was filtered by whatman paper. The filtrate was dried in vacuum at room temperature for 1-3 days.

2.3 Synthesis of Ag-rGO nanocomposites

In this work, silver nitrates ($AgNO_3$) with reduced graphene oxide composites were prepared by the following procedure. 5 ml of GO dispersion was allowed to sonicate for 30 min. Then, different ratio of $AgNO_3$ solution (30 mM, 50 mM and 70 mM) in DW was slowly added into the GO suspension under continuous stirring for 1 hr at room temperature. The obtained slurry was transferred into a 50 ml Teflon-lined stainless steel autoclave and heated to 120 °C for 24 hr. After the reaction, the superannuated liquid was discarded and the precipitate was cooled to room temperature washed with water, centrifuged and dried in an oven at 50 °C and labeled as Ag-rGO nanocomposites. Figure 1 shows the sample preparation of Ag-rGO nanocomposite.
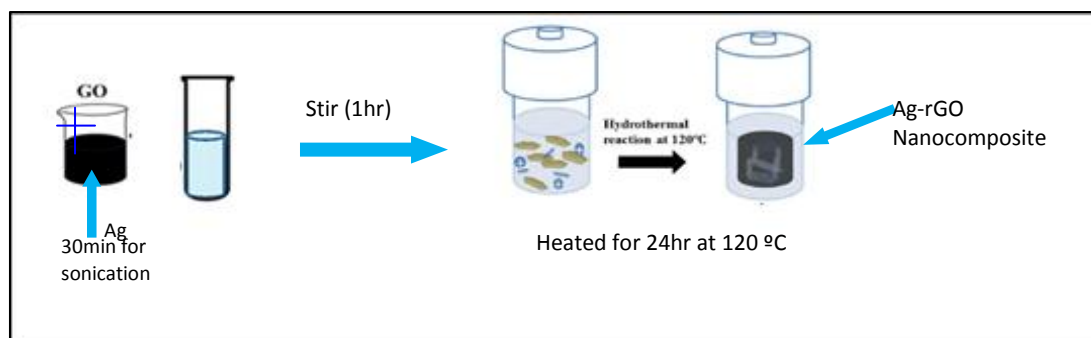
Figure 1 Schematic diagram of Ag-rGO nanocomposite by using hydrothermal method

2.4 Characterization

Centrifuge machine (Kokusan H-200 series) and Sonicator (AS ONE) were used to separate the layers by layers from the solution. GO dispersions were freeze- dried and used for morphological and structural characterizations. Scanning Electron Microscopic (SEM) images of GO, rGO and Ag-rGO composites were measured using Scanning Electron Microscope (JEOL-JSM 5610LV) with the accelerating voltage of 15kV. Fourier transform infrared (FTIR) spectra were taken out by the use of a FTIR-8400 SHIMADZU. The structural characterizations of GO, rGO and Ag-rGO were confirmed by X-ray powder diffractometer (Rigaku-RINT 2000). The solution of GO, rGO and Ag-rGO in DW were used for XRD analysis by filtration method on what man filter paper. Raman spectra were obtained on a nano-Raman Spectrometer employing a 532 nm laser beam using the dried powder mounted on the glass slide.

Results and Discussions

3.1. FTIR Analysis of GO, rGO and Ag-rGO composites

FTIR spectra of GO and rGO (Figure 2a) show the characteristic functional groups of GO which are C-O-C (round about 1047 cm^{-1}), C-O (1213 cm^{-1}), carboxyl C=O stretching band at 1722 cm^{-1}, and O-H deformation band at 1417cm^{-1}. The carbon-carbon double bonds (C=C), can be observed round about 1585 cm^{-1}. The O-H stretching vibrations in the region of 3600-3000 cm^{-1} are attributed to the hydroxyl and carboxyl groups of GO and residual water between GO sheets. As expected, due to the reduction reaction by Ascorbic acid (AA) these characteristic bands of GO are relatively weaker (lower transmittance after the reduction) or completely removed in the FTIR spectra of rGO. The majority of carbonyl and epoxy groups can be changed into hydroxyl groups in the GO by chemical reduction. This result indicates that rGO was successfully obtained after reduction reaction.

These spectral changes indicate the presence of carbonyl, ether and hydroxyl groups in the chemical structure of the treated graphite, implying that graphene oxide has been produced. The spectrum of the Ag-rGO nanocomposites given in Figure 2b can be observed the absorption peaks at 1514 cm^{-1}, 1415 cm^{-1} (C–H bending vibrations) and 1016cm^{-1} and those are represented the C–OH stretching vibrations. The peak at 1585 cm^{-1} in the GO sample shifted to a lower frequency at 1514 cm^{-1} in the Ag-rGO nanocomposite. It is attributed to the skeletal vibration of the graphene sheets, which is different from the spectrum of rGO sample without the addition of Ag+. The FTIR results demonstrate that Ag+ contributes to the reduction of GO to graphene,

which is consistent with XRD results. And strong interaction may exist between silver nanoparticles and the remaining surface hydroxyl groups on rGO sheet.

As a result, Ag-rGO nanocomposite was formed finally. The overall reaction can be described by the following equations:

$$Ag^+ + OH^{-1} \rightarrow AgOH$$

$$GO + AgOH \xrightarrow{\text{hydrothermally}} rGO\text{-}Ag + H_2O$$
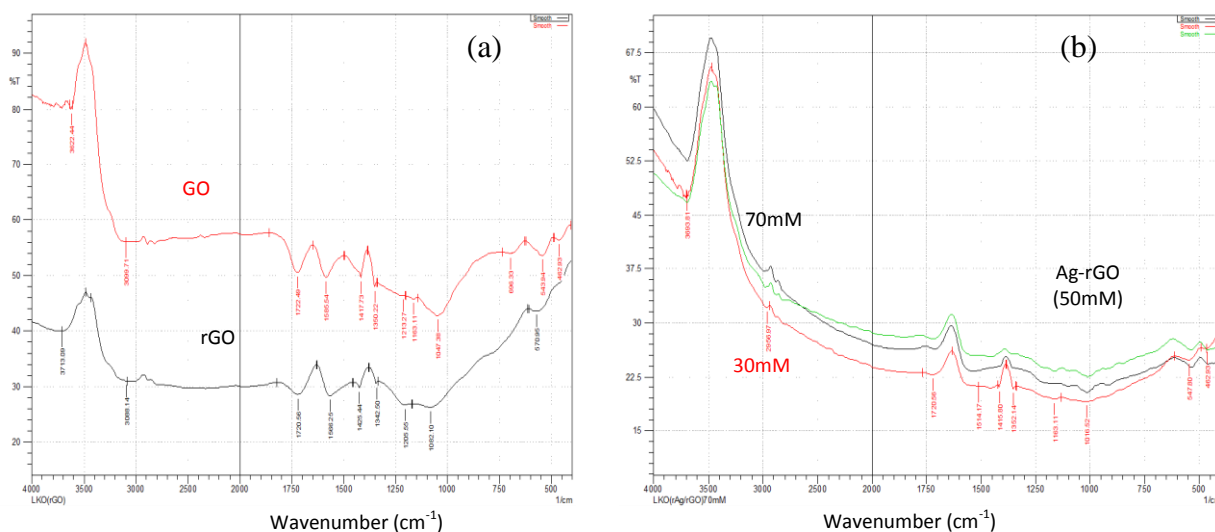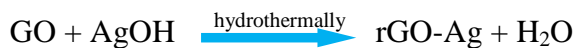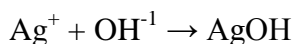
Figure 2 FTIR spectra of (a) graphene oxide and reduced graphene oxide (b) Ag-rGO nanocomposites (30 mM, 50 mM, 70 mM)

3.2 SEM Analysis

The detailed surface morphology of graphene oxide and reduced graphene oxide were carried out by using Scanning Electron Microscope (SEM). Figure 3(a) reveals the existence of crumple structure for graphene oxide. This is due to the exfoliation of graphite to become oxide and results in deformation upon the exfoliation and restacking. Figure 3(b) shows the image of reduced graphene oxide (rGO), thin sheets of folded and wrinkled structure has been observed by using ascorbic acid as reducing agent.

The morphology of the synthesized composites were also observed by Scanning electron microscope (SEM). Fig 3(c,d,e) display the SEM images different molarity (AgNO$_3$ 30 mM, 50 mM and 70 mM) of the Ag-rGO nanocomposites. It exhibits a uniform decoration of AgNPs on the rGO sheets. The average particle size is round about 420-550 nm. The restacking property of rGO sheets was prevented by the uniform distribution of AgNPs (Li *et al,* 2012).
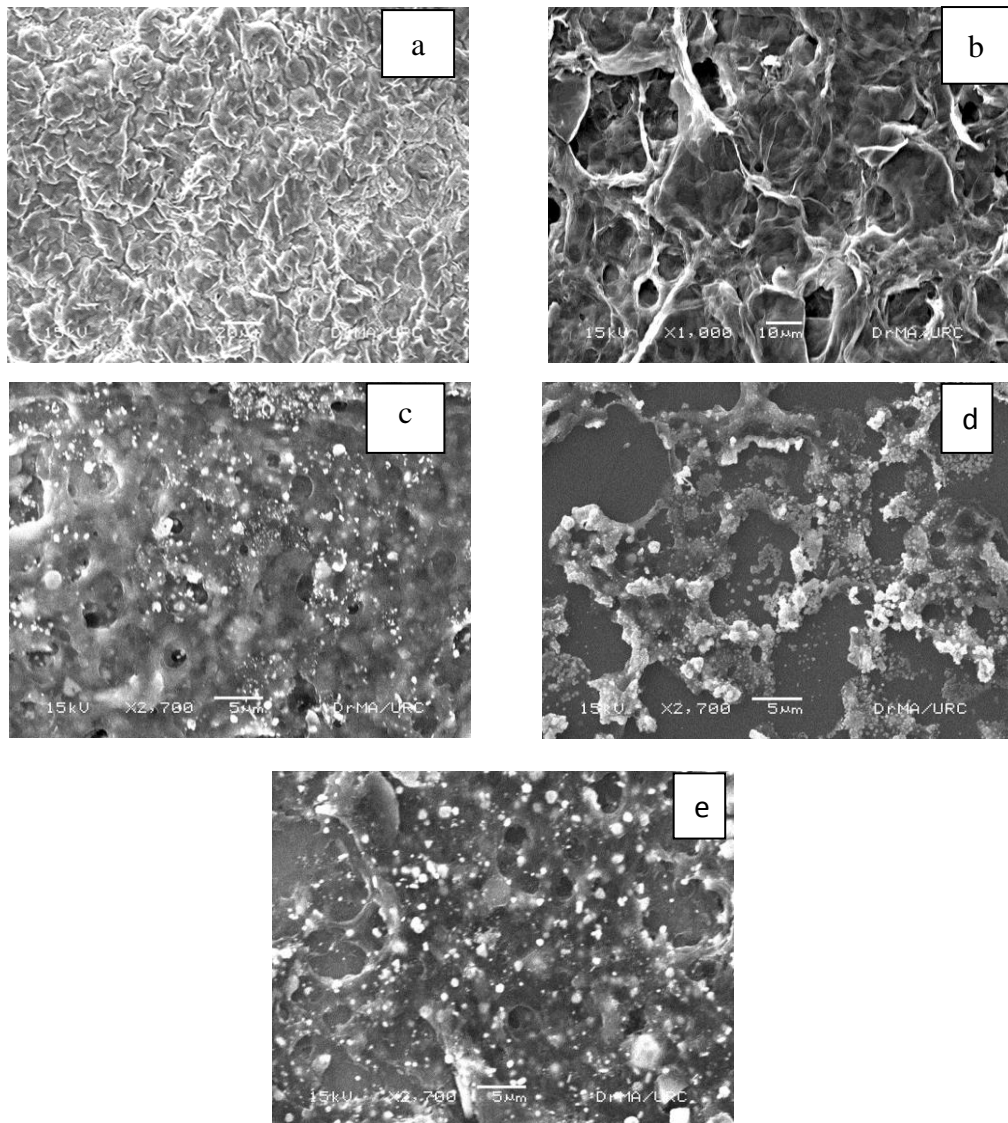
Figure 3 SEM images of (a) graphene oxide (b) reduced graphene oxide (c) Ag-rGO nanocomposites for 30 mM of silver nitrate (d) 50 mM and (e) 70 mM

3.3 X-Ray Diffraction Analysis

In addition, X-ray diffraction can also be used to characterize the crystal structure of GO, rGO and Ag-rGO nanocomposites. The XRD spectrum of resulting powder and sheets of GO and rGO sample were shown in Figure 4(a). A sharp peak at $2\theta \sim 10.85°$, corresponds to the reflection from the (111) plane, was observed in XRD spectra of GO. The pattern reveals that the phase precipitated out in the sample is hexagonal structure. The interplaner spacing d (002) between individual graphene layers (3.35Å) can be used as an indicator of the degree of graphitization. Reduced graphene oxide has a peak around $2\theta \sim 26.32°$ for LAA and NH_3 Figure 4(a). This change in peak position and FWHM of the peak could be due to the exfoliation of GO sheets after removal of the intercalated carboxylic groups. These XRD results are closely related to the exfoliation and reduction processes of GO.

After the hydrothermal process, the diffraction peaks of the Ag-rGO nanocomposites (Figure 4b) with 30 mM, 50 mM and 70 mM of silver nitrate are indicated at 38.02°, 44.2° and

$64.3°$, corresponding to the crystal planes (111), (200) and (220) shown the presence of Ag metal in the composites (Panbo *et al,* 2013).
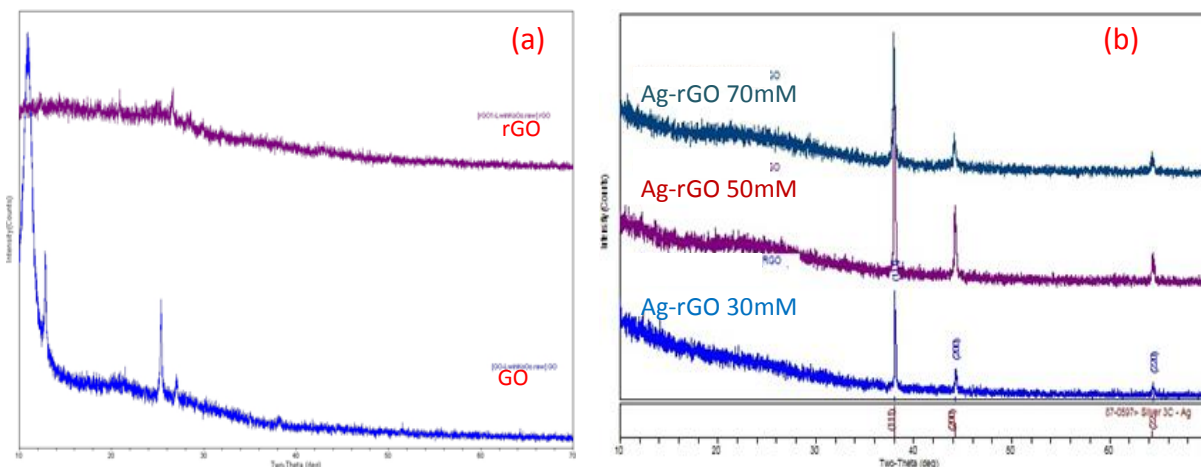


Figure 4 XRD patterns of (a) GO and rGO (b) Ag-rGO Nanocomposites with 30 mM, 50 mM and 70 mM of silver nitrate ($AgNO_3$)

3.4 Raman Analysis

Raman spectra are powerful tools to characterize carbonaceous materials. The reduction of GO to rGO was confirmed by this spectra. Raman spectra of synthesized GO is presented in Figure 5(a). In the Raman spectra of GO, the band at 1579 cm^{-1} is called G band, this band arise from the first order scattering of the (E2g) stretching mode. The band at 1348 cm^{-1} is the D band that corresponded to decrease of the size of in plane sp^2 domains. GO and rGO have both D and G bands. In the Raman spectrum of graphene and other sp^2 carbon samples containing defects, several additional symmetry-breaking features are found. After reduction reaction D/G intensity ratio (I_D/I_G) of rGO (at 1337 cm^{-1} of D band) (Figure 5b) increases from 0.97 (intensity ratio of GO) to 1.08 (intensity ratio of rGO). This increase is due to formation of domains that are numerous in number and smaller in size with respect to ones present in GO.

Figure 5c-e shows the Raman spectra of Ag-rGO nanocomposites with treatment of $AgNO_3$ for different reaction ratios (30 mM, 50 mM and 70 mM). It is noted that the composites exhibit for 30 mM (D band at 1342 cm^{-1} and G band at 1586 cm^{-1}), 50 mM (D band at 1337 cm^{-1} and G band at 1585 cm^{-1}) and 70 mM (D band at 1343 cm^{-1} and G band at 1589 cm^{-1}). The intensity disorder ratio are changed after hydrothermal treatment ($I_D/I_{G=}$1.09, 1.07, 1.11) (Moon *et al*, 2010). Raman spectra confirmed the formation of crystalline Ag with rGO during hydrothermal treatment. The Raman spectra recorded in 2680-2720 cm^{-1} (2D band) region for all samples is presented in Figure 5. The number of layers can be predicted from the shape and position of the 2D band. The estimated layers of prepared sample are 5.
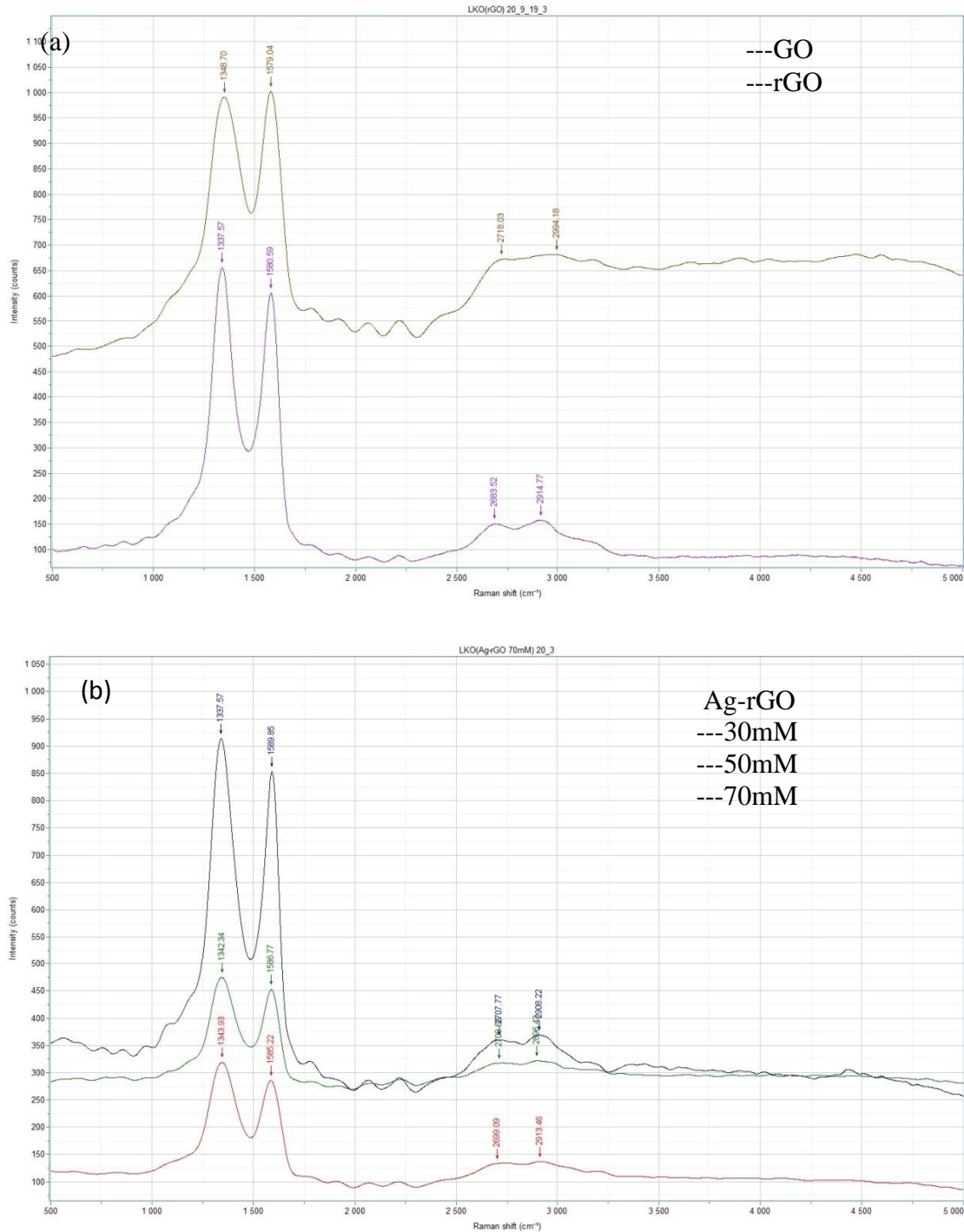
Figure 5 Raman spectra of (a) graphene oxide and reduced graphene oxide (b) Ag-rGO nanocomposites (30 mM, 50 mM and 70 mM)

3.5 Electrical Conductivity

Electrical resistivity is a measure of how strongly a material opposes the flow of electric current. It is represented by ρ and the unit is Ohm-meters (Ωm). It is defined as the ratio of the electric field inside a material to the electrical current density through it. The material with lower electrical resistivity more readily conducts a flow of electrical charge. Electrical conductivity is the reciprocal of electrical resistivity. It is represented by σ and the unit is Siemens per meter

(S/m). The electrical resistance for a uniform material with known geometry can be measured in a direct way and electrical resistivity can be calculated by the following equation:

$$R= \rho L/A \text{ (or) } \rho = RA/L$$

The method is simple and straight forward, but the contact resistance is usually involved. Two-point probe and four-point probe are commonly used to measure the resistance of thin films (Zhao *et al,* 2019). In two-point probe measurement, it is difficult to accurately separate either contact resistance R_c between probes and sample surface or spreading resistance R_{sp} from the material resistance or interest. Four-point probe method in the Figure 6 can avoid the influence from the wirings and contacts, which is a key advantage. One configuration is that the probes are arranged in-line with equal spacing (s), in which the two outer probes apply a constant current and the two inner probes measure the potential difference between them. With an ultrahigh internal resistance, almost no current flows through the sense loop. The typical probe radius ranges from 30 to 500 μm and probe spacing is in the range of 0.5-1.5 mm. In order to eliminate the size effect of finite geometry in four-point probe, the sample width should generally be forty times larger than probe spacing (Smits *et al,* 1958). Sample thickness is one of the correction factors in the data processing. Most of the samples measured using four-point probe. The outer probe and inner probe voltage will then be used to calculate the sheet resistance.

$$R_s = \frac{\pi}{\ln 2} \frac{V}{I} = 4.53236 \frac{V}{I}$$

where,

     Rs = sheet resistance (ohm per square)

     V = the voltage measured between the inner probes

   I   = the current applied between the outer probes

Figure 6 Four-point probe symbol and machine

The conductivity measurement of samples of GO, rGO and Ag-rGO nanocomposites thin film are conducted by linear four- point probe method. According to the Table 1, the electrical conductivity of nanocomposites is significantly improved for higher concentrations Ag. In this work, it was found that the value of the conductivity for Ag concentration of 30mM of Ag-rGO nanocomposite is increased by ~ 97.6 % compared with the GO film in the Figure 7.

Table 1 Electrical conductivity for GO, rGO and Ag-rGO nanocomposites thin film

Type of Samples	Sheet Resistance R_s (MΩ/sq)	Electrical Conductivity $\sigma = 1/\rho$ (m S/m)
GO	179.50	1.393
rGO	157.07	1.592
Ag-rGO (30 mM)	90.83	2.752
Ag-rGO (50 mM)	81.01	3.086
Ag-rGO (70 mM)	61.99	4.033
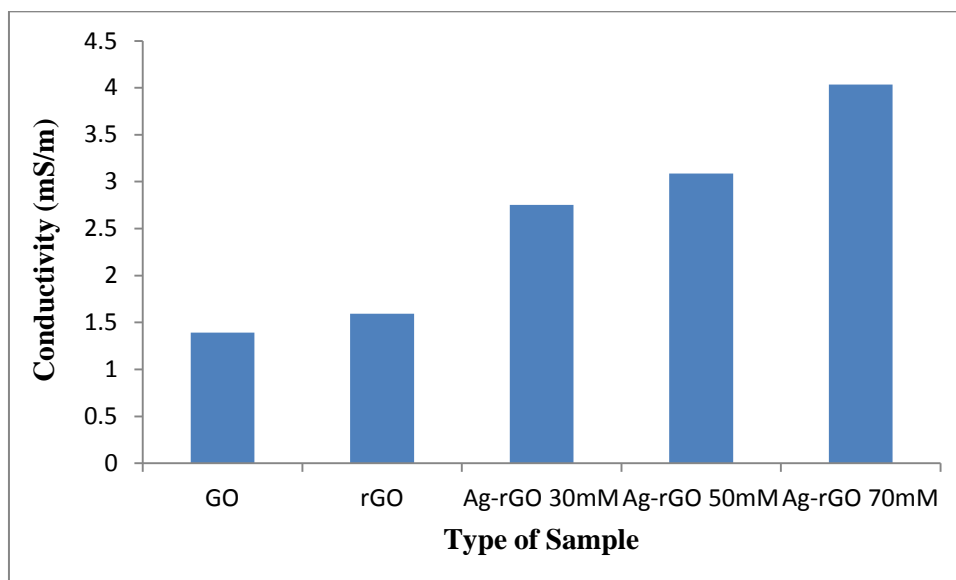
Figure 7 Comparison of conductivity with GO and Ag-rGO

Conclusion

In this study, graphene oxide, reduced graphene oxide and Ag-rGO nanocomposite were synthesized by Hummers method, chemical reduction method and hydrothermal method respectively. The effect of reducing agents on the structure and morphology of GO, rGO and Ag-rGO nanocomposites are investigated by SEM, XRD, Raman spectrometer and FTIR spectroscopic techniques. rGO sheets with a high degree of reduction and low sheet stacking were obtained using ascrobic acid as the reducing agent. The preparation of Ag-rGO nanocomposites were successfully investigated by hydrothermal synthesis. Hydrothermal method plays an important role in reduction of graphene oxide to rGO. Ag+ contributed to restoring of sp^2 structure of rGO. Effect of chemical doping treatment after finishing the hydrothermal process, the conductivity of Ag-rGO nanocomposites (30mM, 50mM, 70mM) is enhanced 97.5 %, 121.53 % and 189.52 % (1.9 times, 2.2 times and 2.8 times) than the GO film. The graphene (Ag-rGO composite) is a promising material to improve the electrical conductivity for electronic devices such as supercapacitor electrodes, memory devices.

Acknowledgements

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