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Structural and Morphological Investigation of Functionalized Reduced Graphene Oxide-Multi Walled Carbon Nanotubes Nanocomposite

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ABSTRACT

2D materials like Graphene and its composite has emerged as most valuable and major concern because of their peculiar properties in field of nanotechnology in past few decades. Herein, we report the effective technique for the synthesis of functionalized rGO/MWCNTs nanocomposite through the solution phase mixing of rGO and MWCNTs assisted with probe sonication. The synthesized samples were tested via XRD, FESEM, FTIR and Raman Spectroscopy. X-ray diffraction technique was used for the structural analysis of the samples which revealed that most prominent peak was observed around 2θ~26.3°. Surface morphology of the samples were studied via FESEM, which revealed that rGO layers were wrapped around the MWCNTs. Raman spectra were recorded for the determination of quality of rGO and MWCNT via the position and intensity of D and G band. The various functionalities present on the samples were identified via FTIR spectra.

Introduction

Graphene belonging to the 2D materials category are widely known for its peculiar properties like excellent electrical conductivity, mechanical and chemical stability, high specific surface area [1-2] which makes it a good candidate for various applications such as

nanoelectronics [3-4], genetics [5], sensor [6], nano scale mechanical devices[7], energy harvesting and storage devices [8] etc. Graphite contains multiple sheets of graphene which is held and stacked via weak van der Waal forces. These individual layers can be separated out via mechanical exfoliation techniques as well as chemical process. There are several techniques for the synthesis of graphene like mechanical exfoliation by scotch tape, thermal exfoliation, chemical reduction method (Hummer's method and modified Hummer's method), chemical vapour deposition techniques, plasma exfoliation, etc [9-11]. The researchers around the globe are very much inclined towards the study of rGO. The reduced graphene oxide (rGO) is generally much popularly used for the research purposes as compared to the pure graphene, since it is quite easily synthesized via Hummer's method which is cheaper and its constituent precursors are easily available as compared to the other techniques. Besides this, reduced graphene oxides have properties almost similar to that of graphene but contain low conductivity due to presence of small quantities of oxides in it [10]. These oxides in trace amount are generally left out during the reducing process of GO in Hummers method. The major problem with the exfoliated layers of rGO is that they often restacked due to interaction of pi bonds which is a type of non-covalent interaction, hence resulting in pi stacking (π-π stacking). This pi stacking is mainly responsible for the poor electrical and electrochemical performances [12].

In the present work, we have tried to solve these challenges via insertion of functionalized MWCNTs between the exfoliated layers of rGO and making nanocomposite of rGO/MWCNTs. These insertions of MWCNTs are responsible for the further exfoliation and thus prevention from restacking of the rGO layers. We have synthesized the functionalized rGO/MWCNTs nanocomposite via solution phase mixing of commercial rGO and MWCNTs assisted with probe sonication and tested the samples for structural, morphological and Raman analysis. In experimental method section, detailed discussion of experiment related to materials used, sample preparation, the synthesis of nanocomposite and characterization techniques used has been discussed. Results and discussion section includes XRD, FESEM, FTIR and Raman analysis of the sample. Finally, the conclusion section includes the overall summary and the highlights of the presented research work.

Experimental Method

Materials Used:

All the glass beakers used in the experiments were washed in Aqua Regia for 3 hours followed by deionized water and acetone for the avoiding the involvement of organic and inorganic impurities in the sample. The following materials were used in the experiments. Multi walled carbon nanotubes, reduced graphene oxide, H_2SO_4, HNO_3, Ethanol and filter paper. All the chemicals used in the experiments were procured from Merck and used without further purification. DI water having extra purity obtained from Milli Q water purifier system was used for all the dilution purposes.

Exfoliation of rGO:
The reduced graphene oxide powder (rGO) were procured from Merck were used as a precursor material. The fine rGO powder is first annealed in a muffle furnace at 50°C for 1 hour. The stacked layers of 70 mg annealed rGO powder were dispersed in 10 ml of Ethanol and further exfoliated via probe sonication for 45 minutes. The obtained sample was vacuum filtered followed by vacuum dried at 50°C for the removal of moisture.

Purification of MWCNTs:
Prior utilization of the commercial MWCNT for making the composite it very essential to eradicate the catalytic particles which are responsible for hinder the experimental results. First of all, the MWCNT powder is annealed at 450°C for 1 hour in a muffle furnace for removing the moisture. The dried MWCNTs were refluxed in 3 M H_2SO_4 and 1 M HNO_3 via probe sonication for 45 minutes at 40°C, followed by DI water washing intensively. The obtained solution was vacuum filtered using nylon membrane having pore size 0.45 µm. The obtained residue solid was dried in oven at 50°C which results in purified and functionalized MWCNTs powder.

Synthesis of rGO/MWCNTs Nanocomposite:
For the synthesis of rGO/MWCNT nanocomposite, 50 mg of exfoliated r-GO and 40 mg of purified functionalized MWCNTs is taken and both are mixed in 10 ml each of ethanol separately. Both the solutions were probe sonicated for 30 minutes. After the sonication, both solutions were mixed with each other in a single container and further probe sonicated for 45 minutes. The obtained mixture solution was vacuum filtered and left overnight at room temperature. The filtered sample is kept at 90° C in a muffle furnace for 1 hour for the removal of residual moisture attached on the composite powder to obtain the final rGO/MWCNTs nanocomposite.

Characterization Techniques:
The physical characterizations of synthesized nanocomposite powder samples were carried out via following techniques. The structural and phase analysis were done via powder XRD (RIKAGU, Smart lab). The XRD patterns of the powder sample were recorded from angle ranging 5° to 90° using X-ray diffractometer having Cu k_α radiation. (λ=1.54Å). The morphological studies were done by Field Emission Scanning Electron Microscope (SEM, Sigma and ZEISS). Confocal Raman Microscope (WITEC alpha 300R Raman spectrometer with a 532 nm Nd-YAG laser with 1800 line mm^{-1} grating) was used to check the quality of rGO/MWCNT nanocomposite. To identify the attached functionalities present within the nanocomposite sample, Fourier Transform Infrared (FT-IR BRUKER OPTICS) spectra were recorded.

Result and Discussion

The structural properties of r-GO and r-GO/MWCNTs nanocomposite have been investigated by XRD analysis. The recorded XRD spectra at room temperature provide the intrinsic crystallographic information like average crystallite size and interplanar spacing of

the samples being tested. Figure 1 shows X-ray diffraction spectra of exfoliated rGO and rGO/MWCNT nanocomposite, clearly showing two peaks. The most prominent peak is observed around 2θ =26.3° which corresponds to (002) plane. The prominent peak seems to be slight shifted towards left side for the case of composite sample. This might be due to the increment of interplanar spacing due to the further exfoliation of rGO while composite formation. The average crystallite size (D) of the samples has been calculated using Scherrer equation given in equation (1)

$$\mathbf{D} = \frac{\mathbf{k\lambda}}{\boldsymbol{\beta}\,\mathbf{cos\theta}} \tag{1}$$

Where λ represents the wavelength (1.54 Å) of X-ray, θ is the Bragg's angle, β is the full width at half maxima (FWHM) of the peak and k is a constant known as shape factor of particle. The average crystallite size of rGO and rGO/MWCNT was 11.21 nm and 8.62 nm as shown in table 1. The decrease in the crystallite size of the composite also reveals that the rGO sheets were wrapped due to the non-covalent interaction among the carbon atoms of the aromatic rings. The interplanar spacing (d) is calculated via Bragg's law given in equation (2).

$$\mathbf{n\lambda = 2d\ sin\theta} \tag{2}$$

Where, n represents order of diffraction and λ and θ have the usual meaning. The values of d were found to be slightly increased from 3.37 Å (for rGO) to slightly higher value i.e. 3.45 Å in case of composite samples. This increment in the interplanar spacing may be due to the insertion of MWCNTs within the exfoliated layers, thus resulting extra exfoliation of rGO.

Table 1. The XRD analysis of the as-synthesized samples is shown in below.

Sample	Avg. Crystallite size (nm)	Interplanar spacing (Å)
Reduced Graphene Oxide (rGO)	11.21	3.37
rGO/MWCNT Nanocomposite	8.62	3.45

The surface morphology of the as-synthesized composite samples is analyzed through FESEM. The figure 2 (a-b) illustrates the FESEM micrographs of reduced graphene oxide and its composite with MWCNTs. The first image representing the surface topography of rGO sample revealed the uniformity throughout the surface with slight crumpled and ruptures. These deformations may be due to the exfoliation and restacking process as well as generation of air pockets between the layers which is might also be responsible for entangled layers. It is clearly seen in the second image representing the rGO and MWCNTs nanocomposites, the rGO layers is uniformly wrapped around the MWCNTs via π-π interaction of aromatic carbon atoms of rGO and MWCNTs. This may results in the increased diameter of the MWCNTs.

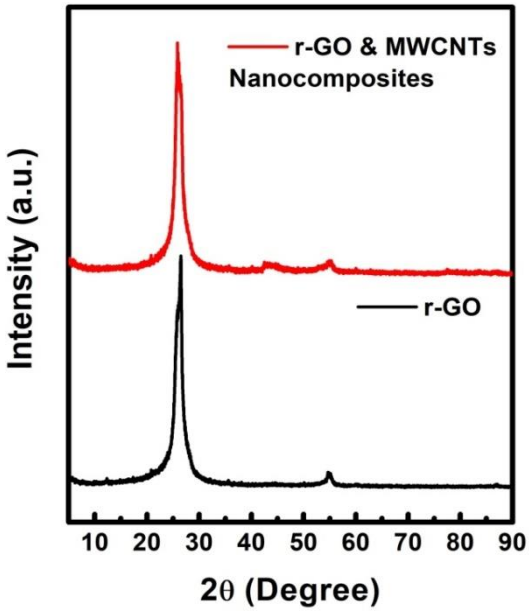

Figure 1. XRD spectra reduced graphene oxide (rGO) and rGO/MWCNTs nanocomposites.

The degree of defects and disorders induced during functionalization process of rGO and its composites with MWCNTs during the synthesis process is analyzed via Raman spectra. Figure 3 illustrates the first and second orders Raman spectra of rGO and rGO/MWCNT nanocomposites. From the figure 3, the D, G and 2D peaks for rGO are appearing around 1346, 1576 and 2683 cm^{-1} respectively; whereas in case of nanocomposites these D, G and 2D peaks appears to be slightly shifted to higher values i.e. towards right side. The D-peak is typically ascribed to defects states and disorder of the carbon crystallites. It is mainly arises due to the breathing mode of six carbon atoms in the hexagonal ring structure. On the contrary, G-peak is arises due to E_{2g} mode symmetry of C-C bond stretching vibrations which generally corresponds to the crystallinity of the carbonaceous materials.

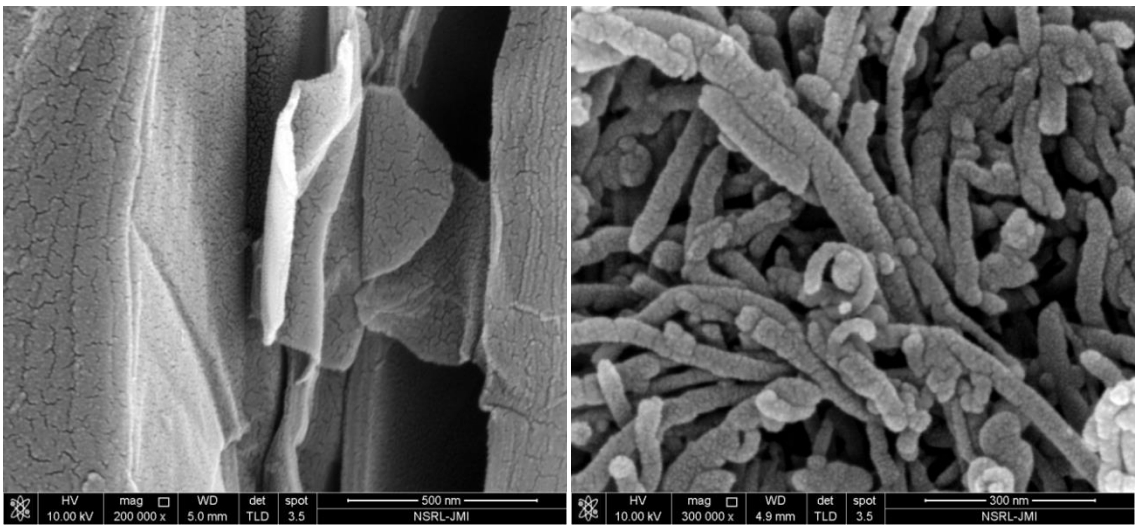

Figure 2. FESEM pictograph of reduced graphene oxide (rGO) and rGO/MWCNTs nanocomposites in the left and right hand side respectively.

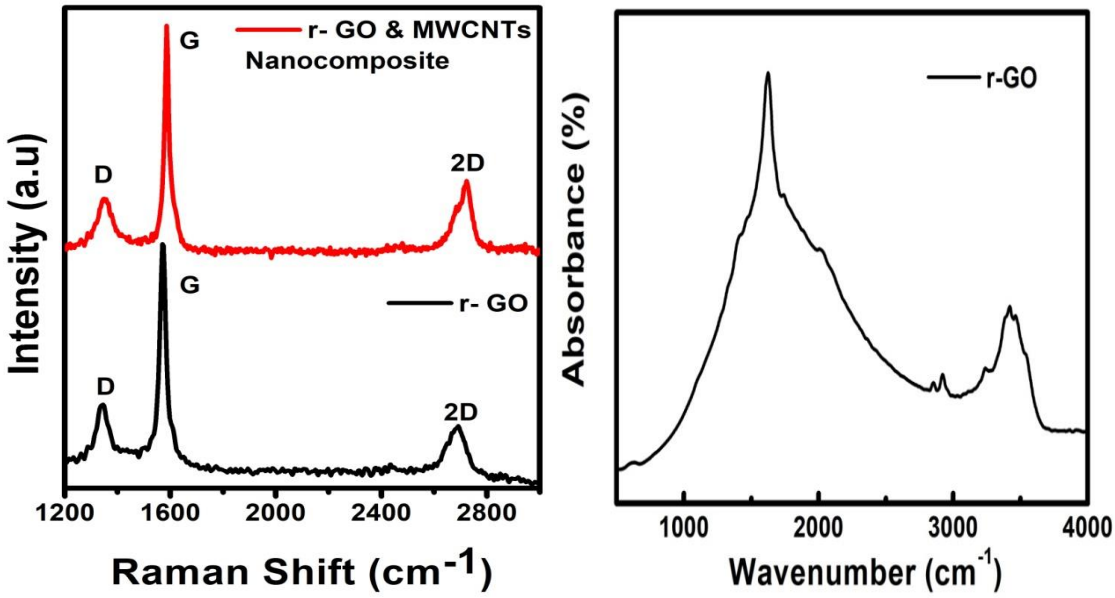

Figure 3. Raman spectra of reduced graphene oxide (rGO) and rGO/MWCNTs nanocomposites in the left hand side whereas the spectra on the right side represent the FTIR spectra of rGO sample.

A Fourier transform infrared (FTIR) spectrum of reduced graphene oxide is recorded at room temperature in the wave number range of 500-4000 cm^{-1} for investigating the different functionalities present in the powder sample. The powder samples were first binded with Potassium Bromide (KBr) for pellet formation before the FTIR spectra was recorded. Due to the stretching vibration of C=C and bending mode of water associated with Potassium Bromide used for the preparation of FT-IR sample, the spectra shows sharp intense peak at 1629 and 3409 cm^{-1} and show prominent peak at 3409, 1722 and 1629 cm^{-1} due to O-H, C=O and C=C stretching vibrations, respectively. The stretching bands C-O (epoxy) and C-O (alkoxy) are attributed at 1617 cm^{-1}.

Conclusion

Graphene based nanocomposite has emerged as most valuable nanomaterials due to the excellent properties of graphene acting as filler in nanocomposite. It is concluded that the synthesis of rGO/MWCNT nanocomposite via probe sonication was successfully accomplished. FESEM images confirm that during the formation of nanocomposite, the layers of rGO were further exfoliated due to insertion of MWCNTs and that those layers of rGO get wrapped along the MWCNT due to π-π interaction. The structural analysis performed via XRD reveals that the most prominent characteristic peaks were obtained near 2θ~26°. The position get slight shifted towards the lower values in the case of nanocomposite when compared to that of rGO. An FTIR spectrum was recorded to identify the functional groups attached to the sample. Raman analysis revealed that no significant shift was observed in D and G bands after the addition MWCNT for the formation of rGO/MWCNT nanocomposite. The G band appears higher in intensity as compared to D band which significantly indicates that the purity and better crystallinity in the sample.

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