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Facile Synthesis of Graphene Based ZnO Nanocomposite

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ABSTRACT

Graphene is one of the best conductive materials for developing nanocomposites due to its outstanding electronic properties. Graphene is developed by modified Hummers' method. Zinc oxide (ZnO) based composites were developed by using different weight percentages (0.1%, 0.5% and 1%) as reinforcement. To enhance the dispersion of Graphene in ZnO matrix the synthesis was processed by ultrasonication process. The obtained graphene oxide, ZnO and composites were characterized by X-ray diffractometer (XRD), Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy (FESEM) techniques for structural information, band analysis and surface morphology respectively. The proposed nanocomposites were developed by varying loading percentages 0.1%, 0.5% and 1% weight of graphene. These materials are used in various applications like varistors, energy storage, sensors, super capacitors and so on.

1. Introduction

Nanoscience and nanotechnology primarily deal with the synthesis, characterization, exploration, and exploitation of nanomaterials. Carbon, one of the most common atoms on Earth, occurs naturally in many forms and as a component in countless substances which are called allotropes of carbon. Graphene, a "wonder material" is the world's thinnest, strongest, and stiffest material, as well as an excellent conductor of heat and electricity. It is the basic building block of other important allotropes. Graphite is of great interest due to its low cost, easy access, and widespread ability to convert to graphene. Scalability is also a much-desired feature [1-8]. Most common approach towards graphite exfoliation is the use of strong oxidizing agents to obtain graphene oxide (GO), a nonconductive hydrophilic carbon material [9, 10]. Although the exact structure of GO is difficult to determine, for GO the previously contiguous aromatic lattice of graphene is interrupted by epoxides, alcohols, ketone carbonyls, and carboxylic groups [11, 12]. Hummers reported an alternative method for the synthesis of graphene oxide by using $KMnO_4$ and $NaNO_3$ in concentrated H_2SO_4 [13]. GO prepared by this method could be used for preparing large graphitic film [14]. Zinc oxide (ZnO) is a semiconductor which is used in many applications in nanoscience field all around the world. This is often used to design electronic and optoelectronic devices [15] and it is an important electronic and photonic material because of its wide band gap of 3.37 eV and it has a relatively large exciton binding energy of 60 meV. Owing to its interesting properties such as optical transparency, electrical conductivity, piezoelectricity, near-UV emission [16-21] and various morphologies, ZnO has become one of the most attractive nanomaterials for research objectives. Its significant properties have made it applicable in UV-light emitters, varistors, transparent high-power electronics, hydrogen storage, electrically conductive fillers, surface acoustic wave devices, piezoelectric transducers, and gas sensors [22].

2. Experimental Methods

2.1 Materials

Graphite powder, sodium nitrate, potassium permanganate, hydrogen peroxide, sodium hydroxide, potassium hydroxide, ethylene glycol and zinc acetate were purchased from Sigma Aldrich. All the materials were used as received without any further purification.

2.2 Synthesis of ZnO Nanorods

In the synthesis process, zinc acetate dehydrate ($Zn(Ac)_2.2H_2O$) and 50 mL of hydrazine hydrate ($N_2H_4.H_2O$) were taken in round bottom flask, mixed well and stirred for about half an hour till a white colored precipitate appeared. The precipitate was refluxed for 6 hrs at 90 °C. At the end of reaction, a pure white colored precipitate (ZnO) appeared which was washed several times with methanol, filtered and collected after drying.

2.3 Synthesis of Graphene Oxide

Graphene oxide was synthesized from graphite using a modified Hummers' method. Concentrated H_2SO_4 (23 mL) was added to mixture of graphite flakes (1 g) and $NaNO_3$ (0.5 g). Mixture was kept at low temperature (ice bath) and then $KMnO_4$ was added drop wise to the above mixture by maintaining the reaction temperature below 20 °C. The reaction was warmed to 35 °C and the mixture was magnetically stirred for 30 min by slowly adding distilled water (46 mL). During oxidation process the color change was observed from dark purplish green to dark brown. After that the solution was cooled using a water bath for 10 min to stop the oxidation process and additional water (140 mL) and H_2O_2 (1 mL) was added. Consequently the color of the mixture changed to bright yellow indicating a high oxidation level of graphite. The solution was filtered and washed several times with water which resulted in thickening of the graphene oxide solution. The washing process was carried out using a simple decantation of the supernatant with centrifugation technique at 5000 rpm for 30 minutes which resulted in the formation of graphene oxide (GO).

2.4 Synthesis of Graphene based ZnO Nanocomposite

The GO was prepared using modified Hummers' method in the presence of the ultrasonic process. The graphene-ZnO nanocomposite was synthesized by an Ultrasonic Qsonica Sonicator (Model no: Q500, 20 KHz

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frequency, 500 W). In this process different loadings of 0.1%, 0.5% and 1% wt. GO was dispersed in 100 mL ethanol to get a dark brown color solution by stirring for 30 min, then 30µL of hydrazine monohydrate solution was added for reduction. 0.2 M Zinc acetate dehydrate was added to the resulting solution and then transferred into a 500 mL vessel and placed in an ultrasonic chamber for 2 hrs sonication. The mixture was stirred for 3 hrs at 80 °C. Finally, the solution was filtered and washed several times with distilled water and dried in hot air oven at 90 °C for 5 hrs to evaporate the solvents. The subsequent powder was calcinated at 450 °C for 4 hrs in a muffle furnace.

2.5 Characterization Techniques

Powder X-ray diffraction (XRD) patterns were recorded using a BrukerAXS-D8 diffractometer operating with Cu-Kα radiation (λ=0.15406nm) in the 2θ range 5° – 80° with a scanning speed of 1 degree per minute. A Thermo Nicolet Nexus Fourier FTIR spectrometer in the range 4000–400 cm^{-1} was used for recording IR spectra using KBr disk method. The field emission scanning electron microscope (FE-SEM, FEIQuanta200F) operating at an accelerating voltage of 20 kV was used for obtaining clearer images with good spatial resolution.

3. Results and Discussion

3.1 Structural Analysis

XRD pattern of graphene oxide, ZnO and G-ZnO composite (with weight percentages 0.1%, 0.5% and 1%) are shown in Fig. 1. The major peak of graphite is seen at 2θ = 25.5° with an interlayer distance of 3.4 Å. After oxidation, the peak was observed at 2θ = 10° in GO showing the perfect oxidation and the interlayer distance of graphene is 8.8 Å. The increased interlayer distance is due to the intercalation of oxygen functional groups during oxidation process. There are five major peaks in G-ZnO composite at 2θ value 31.8°, 34.4°, 36.2°, 47.5°and 56.5° which correspond to (100), (002), (101), (102) and (110) crystalline plane of ZnO respectively.

These crystalline planes are indexed to the wurtzite structure of ZnO particles matched with the JCPDS No.36-1451. The average ZnO crystalline size as calculated from Debye-Scherrer's formula that was 14 nm. Apart from the ZnO peaks graphene peak could be seen at 2θ =24.5°. It shows that the inter layer distance between the graphene sheet is 3.6 Å, which is slightly larger than the layer distance of natural graphite indicating small amount of oxygen functional groups may be present in the graphene sheets [23-25].

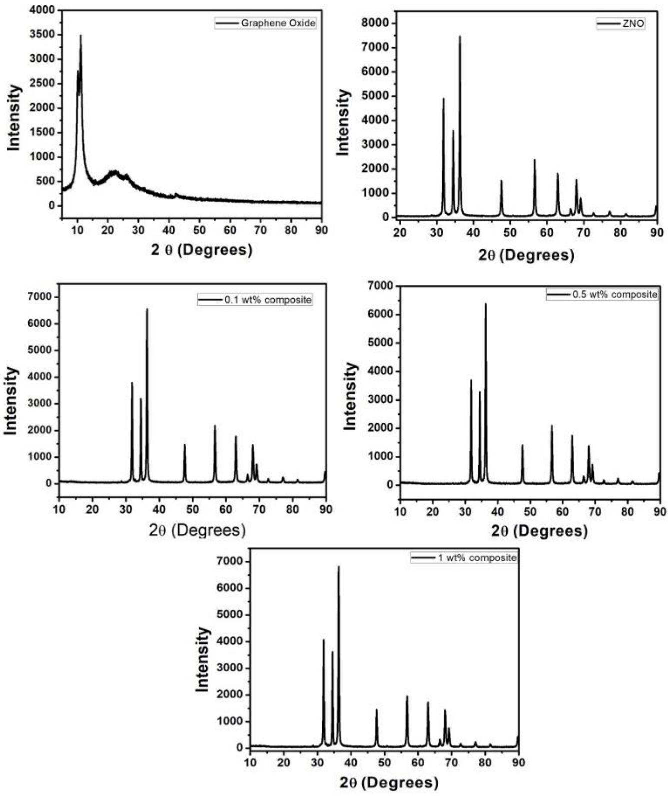

Fig. 1 XRD pattern of graphene oxide, ZnO and G-ZnO composite with weight percentages 0.1%, 0.5% and 1%

3.2 Fourier Transform Infrared Spectroscopy

The FTIR spectra of GO and G-ZnO composite are shown in Figs. 2 and 3. It is observed that the oxygen functional groups of GO are revealed by the peaks at 1726 cm^{-1}, 1217 cm^{-1} and 1055 cm^{-1} corresponding to C=O stretching, C-O stretching and C-O bending respectively. These oxygen functional groups are generated during the oxidation process of the graphite by Hummers' method.

In the case of G-ZnO composite, it could be observed that the oxygen functional groups were almost reduced, which is indicating the reduction of GO during the reaction process. The absorption peak at 1581 cm^{-1} and 450 cm^{-1} indicated the skeletal vibration of graphene sheets and stretching vibration of Zn-O [26-28].

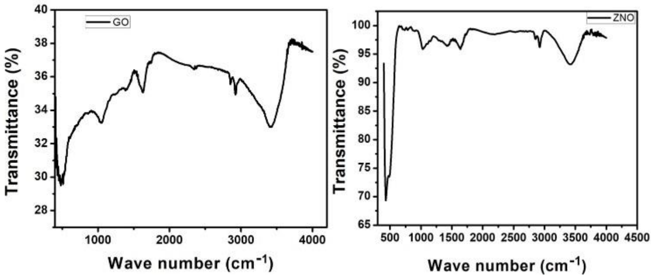

Fig. 2 FTIR spectra of graphene oxide and ZnO

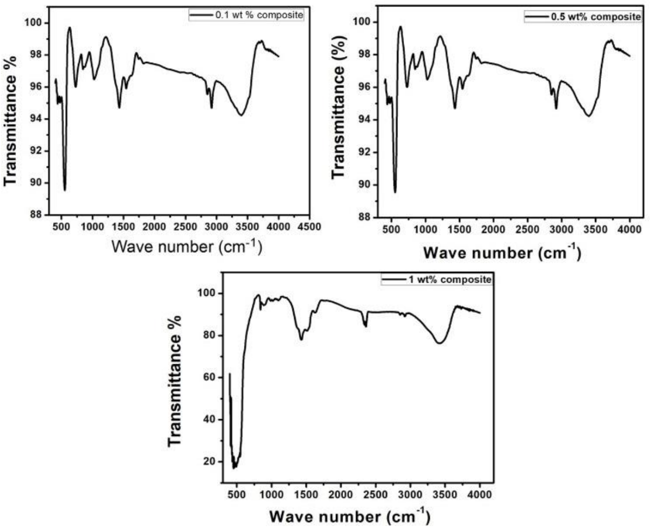

Fig. 3 FTIR spectra of G-ZnO composite with weight percentages 0.1%, 0.5% and 1%

3.3 Field Emission Scanning Electron Microscopy

FESEM images of G-ZnO composite with weight percentages 0.1%, 0.5% and 1% are shown in Figs. 4(a), (b) and (c) respectively. These results indicate the formation of ZnO on graphene matrix. The wrinkled structure of graphene sheets was well decorated with ZnO nanoparticles with an average particle size of 150 nm along with a few nanorods. These data again suggest, but do not prove, the presence of individual sheets in our reduced GO materials.

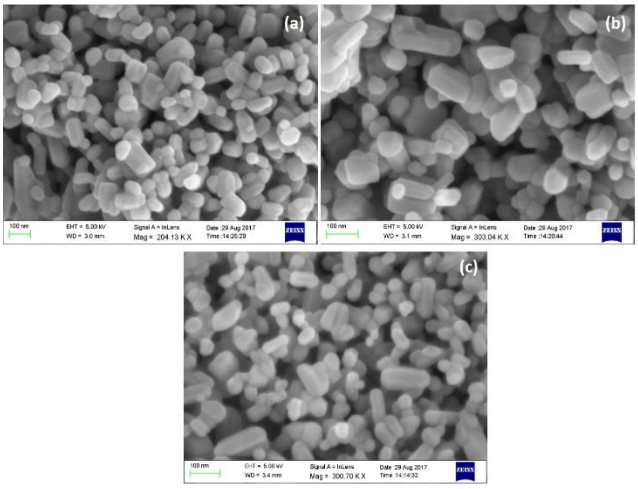

Fig. 4 FESEM images of G-ZnO (with (a) 0.1%, (b) 0.5% and (c) 1%)

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The absence of charging during the FESEM imaging indicates that the network of graphene-based sheets and the individual sheets are electrically conductive. The obtained composite rods length is around 150 nm and the diameter is around 30 nm. It indicates that these G-ZnO with various weight percentages are suitable for super capacitor applications because of rods structure which is in nano range [29].

4. Conclusion

In summary, XRD shows wurtzite structure of ZnO and the G-ZnO composite forms nano sized rods with length around 150 nm and diameter around 30 nm as evident from FESEM. FTIR spectra confirm Graphitic and Zn-O stretching vibration bands. This suggests that the G-ZnO composite electrode is a promising material for electronic applications. In conclusion, reduction of exfoliated graphene oxide sheets in water with hydrazine results in a material with graphitic characteristics that are comparable to those of pristine graphite. This nanoscale carbon-based material consists of thin graphene-based sheets and possesses a high specific surface area. The characterization of the graphene oxide indicates that the hydrazine treatment results in the formation of unsaturated and conjugated carbon atoms, which in turn imparts electrical conductivity. As such, graphene based ZnO sheets may find use in a variety of applications such as batteries, sensors, and as an electrically conductive filler material in supercapacitors.

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