
Synthesis and Structural Characterization of ZnO-Graphene Nanocomposite by Chemical Co-Precipitation Method

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Abstract

Graphene has attracted the scientific research community due to its unique two-dimensional structure, high conductivity, large surface area, superior charge carrier mobility, superior thermal and mechanical properties etc. To obtain graphene by chemical route, graphite oxide (GO) is used as a medium which is obtained from graphite. There is large amount of hydroxyl, carboxyl, carbonyl, epoxide etc. functional groups attached onto the basal or edge plane of GO making it strongly hydrophilic and easily exfoliated in water. Further reduction of GO get rids of unwanted accessory functional groups results in formation of reduced graphene oxide (r-GO) having desired properties. Further its properties can be manipulated by synthesis of graphene/r-GO-metal/metal oxide composites according to the applications to be drawn. These composites can be used in various applications, such as, in energy storage devices like anode materials in lithium ion batteries (LIBs), supercapacitors, photocatalysts, sensors, removal of organic pollutants etc. In the present study, Graphene Oxide-ZnO composites are synthesised by a simple chemical precipitation method. Further the structural characterizations of the samples prepared are done by X-Ray Diffraction (XRD), UV-Visible Spectrophotometry, Fourier Transform Infrared Spectroscopy and Raman spectroscopy.

Keywords: *Reduced- grapheme oxide, ZnO-graphenenano composites, chemical co-precipitation, structural characterization*

1. Introduction

In the present era whether it is diamond, graphite, fullerene, CNTs or the thin layer graphene, carbon is the centre of attraction in the scientific research. These forms of carbon have many fascinating applications due to their exceptional properties. Graphene, greatest smart material of the present time [1] is an atom thick layer of sp² hybridised carbon atoms tightly packed in 2-Dimensional honeycomb lattice [2,3]. It is a revolutionary material as it is less toxic [4] which can be chemically optimised, and it is biodegradable [5].

Graphene exhibits excellent electronic & mechanical properties such as a superior charge carrier mobility of $2.5 \times 10^5 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$ at rooms temperature [6,7], with a young's modulus of 1TPa, and strength of 130 GPa, single layer graphene is the strongest material ever measured [8], an electrical conductivity of up to 6000 s/cm [9], a thermal conductivity of $5000 \text{ Wm}^{-1}\text{K}^{-1}$ [10], a larger theoretical specific surface area of 2630 m²/g [11,12]. In addition to this graphene has high transparency with absorption of less than 2.3% towards visible light [13]. Due to its fabulous properties' graphene have numerous applications in different fields, viz. electronics, biological and chemical fields. It is used as a flexible transparent

conductor in making LED, OLED and LCD[14], as an ideal electrode material in flexible organic field effect transistors[15], as supercapacitors[16], in Biological application as used in tissue engineering application & regenerative medicines, to facilitate the differentiation of stem cells [17], development of bio devices which can detect a single bacteria & sense DNA[18], used as electrodes in Li-ion batteries[19], GNR used in FET[20], as gas sensors [21], as a distillation agent[22], in optical modulator[23], as a piezoelectric material [24], as a photocatalyst [25] and in solar cells [26].

The first method reported for preparation of graphene is traced in back 1970s [27], but the first single monolayer of graphene is produced by A.K Geim& K.S. Novselov in 2004 by the micromechanical exfoliation (the Scotch tape) method [28]. Though this route is good for precise device assembly but it's not favourable for large scale production. Thus, for solving the problem of scalability chemical route is preferred. Graphene is produced by chemical reduction of graphite oxide (GO) which is readily synthesized by oxidation of graphite powder [29]. The previously contiguous aromatic lattice of graphene is modified by the various functional groups such as epoxides, alcohols, ketones, carboxylic groups and hydroxyl groups [30]. Further GO can be reduced to reduced graphene oxide(rGO) to remove the unnecessary functional groups for better practical purposes by chemical reduction by using reducing agents such as hydrazine, sodium borohydride, or by heat treatment etc [31]. Thus, graphene sheets can be synthesized by reducing GO or rGO chemically according to the desirable applications. Primarily two approaches are applied for preparation of graphene using carbon materials: the top-down chemical approaches (as reduction of GO and graphitic fluoride by thermal or chemical method) in which graphitic material are used as starting material & the bottom up approaches (like CVD, arc discharge and epitaxial growth) in which small carbon based molecules are used as precursor for synthesis of graphene [32].

Further to prove the efficiency of graphene, graphitic oxide (GO) and rGO in different applications, their nanocomposites are prepared by anchoring them with specific functional groups & various metal/metal oxides, such as ZnO, TiO₂, Mn₂O, Ag₃PO₄, BiVO₄, CuO, Ag/ZnO, SnO₂, La₂Ti₂O₇, etc. which can be employed in photocatalysis, fuel cells, sensors, transistors, electronics, photonics, bioengineering, energy production & energy storage etc [33-41]. Graphene/GO/rGO/ based composites also show great improvements in their performance towards adsorption capacity, catalytic, photocatalytic/electrocatalytic/photoelectrocatalytic activity & disinfection & desalination ability in water purification application [42]. Among the metal oxides ZnO& TiO₂, SnO₂ and CdS are most extensively used UV-Light- Driven photocatalysts due to their large bandgap (3-3.32 eV) [43].

In the present study, Graphene Oxide-ZnO composites are synthesised by a simple chemical precipitation method. In the first step, graphitic oxide (GO) is prepared by using Hummers-Offeman [29] method using the graphite fine powder as the precursor. Then in the second step, using graphitic oxide as the precursor and is mixed with reducing agent hydrazine hydrate and zinc acetate dihydrate, ZnO-Graphenenanocomposites are synthesized having different concentrations of zinc. Here the amount of graphitic oxide and of hydrazine hydrate are kept as constant while varying the concentrations of zinc acetate dihydrate.

2. Experimental

a. Materials

Graphite fine powder (Central Drug House, min assay 99.5%), sodium nitrate (Fisher Scientific), Potassium Permanganate Purified (CDH), Phosphoric acid, H₂SO₄, H₂O₂(30%), zinc acetate dihydrate extra pure

(SiscoResearch Laboratory Pvt. Ltd. Min assay 99.5%), Hydrazine Hydrate (CDH), sodium hydroxide. Millipore water is used throughout the synthesis procedure.

b. Synthesis Of Zno Nanoparticles

ZnO nanoparticles were synthesized by dissolving 4mM zinc acetate dihydrate and 20 mM of NaOH in water. Initially both solutions were cooled in ice bath and the NaOH added dropwise to zinc acetate dehydrate solution while stirring. Then the turbid solution was heated at 75°C for 30 minutes in a water bath. The precipitate obtained was washed thrice and dried at room temperature [44].

c. Synthesis Of Graphitic Oxide (Go)

GO was synthesized by modified Hummers method [29,45]. In details, 5g graphite powder and 2.5 g sodium nitrate were mixed with 108ml of H₂SO₄ and 12ml of H₃PO₄ and stirred in an ice bath for 10 minutes. Then 15g KMnO₄ was slowly added to the mixture so that the temp remains below 5°C. The suspension was reacted for two hours in ice bath and then placed in room temperature for 42 hours. Then it was stirred for 1 hour followed by stirring in water bath for another 1hour at 40°C. Then temperature was adjusted to 80°C for 1 hour while water as added continuously till the volume of suspension became 400ml. Then 15ml of H₂O₂ was added after 5 minutes. The reaction product was centrifuged (4000 rpm) for 15 minutes and washed with water and 5% HCL several times. Finally, the product was dried at 60°C.

d. Synthesis Of GZ Composites

GZ composites were prepared with a simple chemical route [46]. Firstly, dried GO powder was dispersed in 90ml water (0.3g in 90ml) andsonicated for 30 minutes. Then 0.1g Zinc Acetate added and stirred for 3 hours. Then 20µl of N₂H₄ was added and the mixture was stirred for another 3 hours at 80°C. The precipitate was centrifuged (3000rpm) for 30 minutes and washed with water and alcohol several times. The obtained powder was dried at 100°C in water bath for 2 hours followed by annealing the dried powder at 450°C for 4 hours. The final powder was designated as GZ-1. The process was repeated with varying mass of Zinc Acetate as 0.2g and 0.3g and the product were designated as GZ-2 and GZ-3 respectively

e. Characterizations

Powder XRD patterns of the prepared sample were recorded by RigakuUltima in single phase as 40kV with Cu-K α Radiation. FTIR of the sample was recorded by Bruker.UV-Vis spectroscopy was recorded on a Systronics double beam UV-Vis Spectrophotometer:2202.Raman mapping measurements were performed at room temp in 180 back scattering geometry.

3. Results & Discussion

XRD patterns of GO and GZ composites are shown in figure 1. The sharp and intense peaks of the samples prepared indicate good crystallinity of the samples. The XRD peaks of GO as shown in figure are in good agreement with the literature [46,47]. XRD results show the typical (002) and (101) peaks at ~ 26 ° and ~ 42° of graphene in all of the samples. In addition to that in GZ series the peaks at 31.8° (100), 34.4° (002), 36.1° (101) 56.85° (110) are also appearing with increasing concentration of ZnO precursor. Hence XRD results confirmed the formation of ZnO on Graphenenanocomposites.

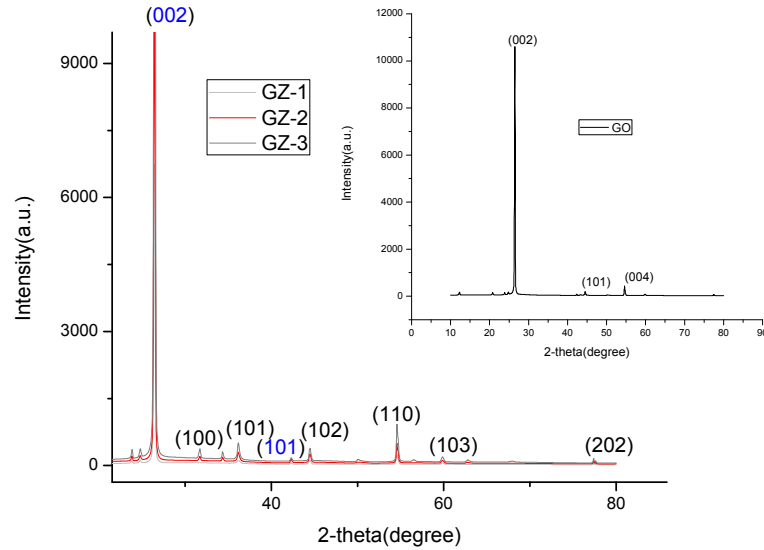


Fig 1.XRD patterns of GO (inset)and GZ composites.

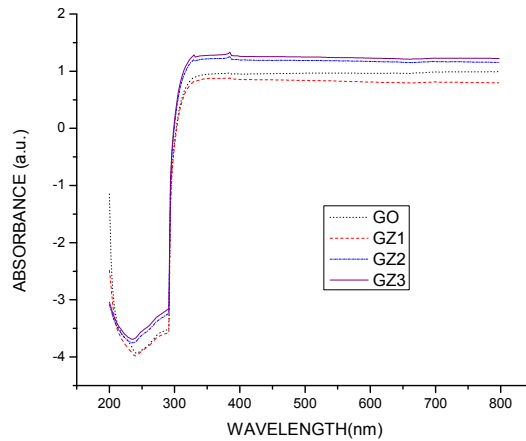


Fig 2. UV-Vis spectra of GO and GZ composites.

Figure 2 shows the UV-Vis spectra of different samples prepared. All the samples show good absorbance in visible region. The as calculated band gaps of prepared samples are shown in table 1.

Table 1. Estimated band gap of synthesized samples

Samples	ZnO	GO	GZ-1	GZ-2	GZ-3
Band Gap(eV)	3.71	2.76	2.76	2.82	2.99

The FTIR and Raman study is ongoing along with the photocatalytic activity.

4. Conclusion

ZnO anchored reduced graphene oxide sheets were successfully synthesized by facile chemical route (modified Hummers-Offeman method) and characterized by XRD, UV-Vis spectra, FTIR etc. XRD results show the typical (002) and (101) peaks at $\sim 26^\circ$ and $\sim 43^\circ$ of graphene in all of the samples. The formation of ZnO on graphene had increased the band gap from 2.76 eV to 2.99 eV.

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