Asian Journal of Chemistry; Vol. 25, Supplementary Issue (2013), S194-S198

ASIAN JOURNAL OF CHEMISTRY

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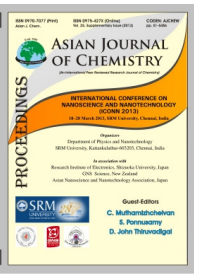

Optical and Structural Studies of Graphene Oxide-Zinc Oxide Blend Nanoparticles for Optoelectronics Application†

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AJC-12829

Nanomaterials are of particular interest as they combine the properties of two or more different materials with the possibility of possessing novel mechanical, electronic or chemical behaviour. The present work involves in understanding and turning such effects that could lead to hybrid devices based on such blends with improved optical properties. Graphene oxide is a significant material possessing high strength and good optical behaviour. Its optical behaviour is further enhanced on blending with zinc oxide nanoparticles. By the addition of zinc oxide into graphene oxide, it is possible to modify the required properties of our interest. The prepared nanocomposites were characterized by studying the morphology, chemical interaction and the absorption spectrum. The morphology of the nanoparticles were studied around using atomic force microscopy and scanning electron microscopy. The bonding nature of the functional groups of the prepared nanoparticles were analyzed using FTIR spectrum. Size and absorption spectra of the prepared nano-particles were studied 20 to 50 nm using X-ray diffraction and absorption peak at 370 nm for GO-ZnO blend which was attributed to the π-π^* transitions of the aromatic C-C bonds by using UV-visible respectively. The photoluminescence characters of ZnO, graphene oxide blend were studied by their emission spectra.

Key Words: Graphene oxide, Nanocomposites, Photoluminescence spectroscopy.

INTRODUCTION

Nanostructured materials are of great interest due to their various tunable nanostructures, phase transformations and quantum confinements, a need for a gamut of engineering usage. Among these nano-particles, wires, rings, combs, tetrapods of materials such as ZnO and graphene oxide are very much in demand for future electronic, optical and optoelectronic nano-devices[1-3]. These nanostructures elastically accommodate a high level of strain allowing remarkable structural flexibility and very high strength up to several tens of Gigapascals (GPa). Improved mechanical properties together with inherent slenderness (high aspect ratio) and its semiconductor characteristics predicts ideal proposition for the application of graphene oxide Blend ZnO to atomic force microscope probes, especially for measuring surfaces with higher degree of undulation[4]. Moreover various emission characteristics and shifting of luminescence bands can be attributed to the fine nanocrystalline structures leading to a large surface area and defects[4].

EXPERIMENTAL

Fourier transform infrared spectra were recorded (4000-500) wavelength using an Alpha Bruker spectrometer. Samples for infrared measurements were prepared by first removing the water out of the solution. X-ray diffraction pattern was recorded using an X-ray diffractometer (PANLYTICAL) using CuK_α radiation of wavelength $\lambda = 0.15406$ nm in the scan range $2\theta = 20\text{-}90^\circ$. Scanning electron microscopy (SEM with a Hitachi Japan, SU1510) and atomic force microscopy in dynamic force mode (Park System Korea, XE-70 (SPM)) were carried out to look into the morphology of various samples. For SEM, samples were drop-casted onto a silicon substrate and imaged in high vacuum mode. UV spectroscopy measurements were carried out Perkin Elmer Singapore, Lamda-25 using absorption peak of liquid samples are graphene oxide, ZnO and graphene oxide blends with ZnO. Photoluminescence spectra were recorded with a Perkin-Elmer model luminescence spectrometer with 320 nm excitation.

Synthesis of metal oxide nanoparticles

Graphene/graphene oxide by Hummers method: Graphite oxide was synthesized from natural graphite by a modified Hummers method[1]. The graphite powder is put into conc. H_2SO_4 (46 mL). $KMnO_4$ (6 g) is added gradually with stirring in cooler condition, so that the temperature of the mixture is not allowed to reach beyond 25 ºC. The mixture is

†International Conference on Nanoscience & Nanotechnology, (ICONN 2013), 18-20 March 2013, SRM University, Kattankulathur, Chennai, India

then stirred at 35 ºC for 2 h and deionized water (92 mL) is added. After 1 h, the reaction is terminated by the addition of a large amount of deionized water 280 mL and 30 % H_2O_2 solution (5 mL) was added slowly, causing violent effervescence with an increase in temperature to 100 ºC, after which the colour of the suspension was changes to bright yellow (Fig. 1). The suspension washed with 1:10 HCl solution (50 mL) in order to remove the metal ions by filter paper and funnel. The paste collected from the filter paper is dried at 60 ºC, until it becomes agglomeration. The obtained paste was then dispersed into deionized water in static state for 2-3 h and slightly stirred by glass rod. The suspension is washed repeatedly with much deionized water atleast 5-7 times and filtered, until the pH of the supernatant becomes 7. The paste collected on the filter paper is dispersed into water by ultrasonication. The obtained brown dispersion is then centrifuged at 10000 rpm to remove any unexfoliated graphene oxide. The particles obtained after centrifuging was collected on a glass plate and dried at room temp for 2-3 days[1-5].

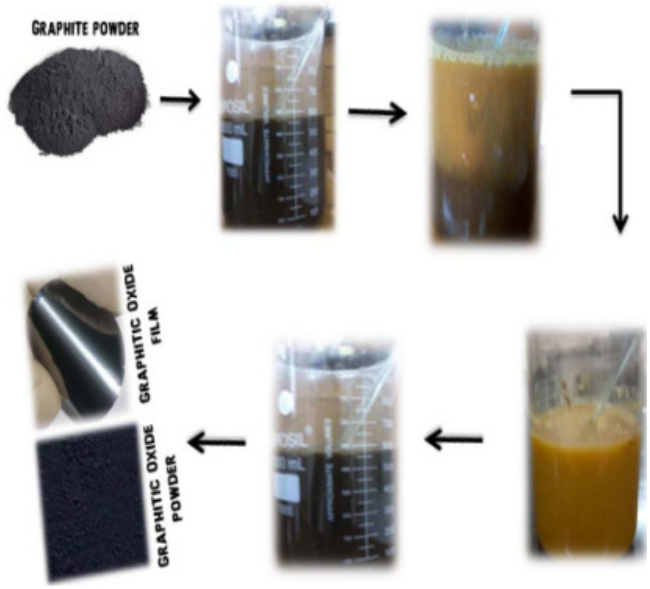


Fig. 1. Graphite to graphene oxide

Synthesis of zinc oxide by hydrothermal method: Zinc acetate (2.1 g) and ammonium oxalate (1.4 g) in 50 mL of water were mixed with stirring. To this ammonia solution was added dropwise till the pH reached to 8. A white precipitate of zinc oxalate obtained was filtered and washed thoroughly with distilled water. The white precipitate was dried at 110 ºC in a hot air oven for 1 h. The dried zinc oxalate was taken in silica crucible and kept inside the muffle furnace at 700 ºC for 3 h. The zinc oxide nano particles obtained are collected and stored in vacuum.

Preparation of graphene oxide blends with zinc oxide: Graphene oxide (0.01 g) and ZnO (0.01 g) nanoparticles are mixed in 50 mL of deionized water and thoroughly sonicated for 60 min. The resulting viscous syrup was then transferred into a glass plate or OHP sheet and kept it for 1 day. After evaporation of the solvent, leaving a thin film consists of graphene oxide and ZnO.

RESULTS AND DISCUSSION

FTIR analysis: Graphite is a material which consists of only C-C frame. It does not show any characteristic vibration in the finger print region shown in Fig. 2a. The oxidation of graphite into graphene oxide shows some specific vibration is the region around 2000-1000 cm^{-1}. On forming graphene oxide, the -OH group attached C of Graphite as -C-OH shows a peak at 1590 cm^{-1}. The FTIR spectra of graphene oxide is shown in Fig. 2b.

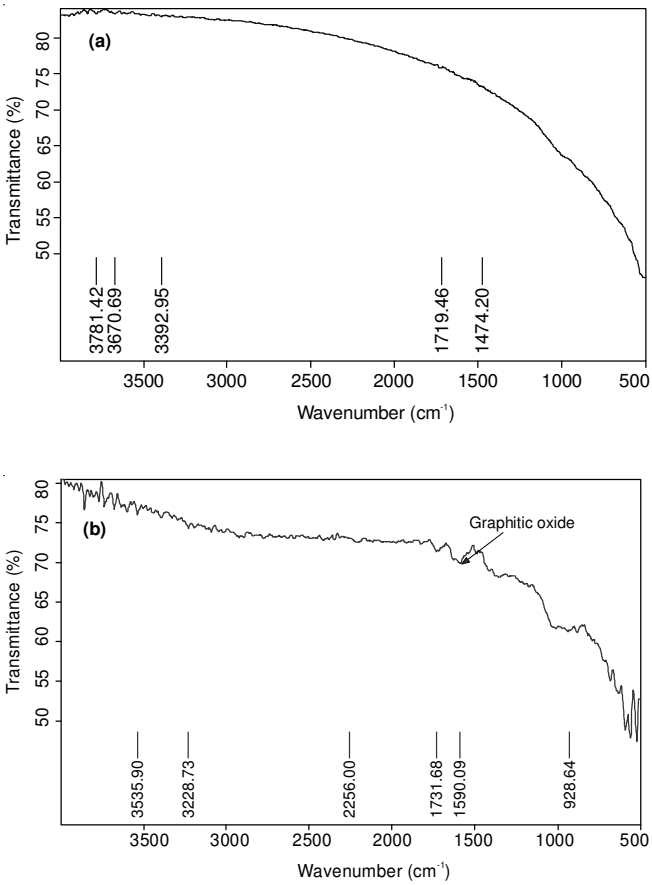


Fig. 2. a) Graphite; b) Graphene oxide

XRD results: The structural features of graphene oxide are explored from XRD data. Fig. 3a shows the one distinct diffraction peaks were observed at 2θ values of 12º respectively which were similar to found exactly those who reported in the literature[12]. The particle size was calculated using Debye-Scherer equation and found in the range of 20 nm. Fig. 3b shows X-ray diffraction pattern of ZnO nanoparticles the characteristic peaks for zinc oxide (2θ = 31.7º, 34.4º, 36.2º, 47.5º, 56.5º, 62.8º, 66.3º, 67.9º, 69º, 72.6º and 76.9º) corresponding to Miller indices (100), (002), (101), (103), (202), (212), (105), (204), (300), (106) and (214), are indexed to the hexagonal phase of ZnO (JCPDS file no. 36-1451). The obtained ZnO nanospherical are of wurtzite structure[6]. The mean particle size of ZnO nanoparticles has been calculated by Debye-Scherer formula are determined to be 40-45 nm.

The structural features of graphene oxide blend with ZnO are explored from XRD data. Fig. 3c shows the distinct diffraction peaks Predominant of graphene oxide were observed

respectively which were similar to found exactly those who reported in the literature. Apart from these major peaks, the corresponding ZnO show all of its peaks with lesser in intensity the particle size was calculated using Debye-Scherer equation and found in the range of 20, 46 and 27 nm respectively[7,8].

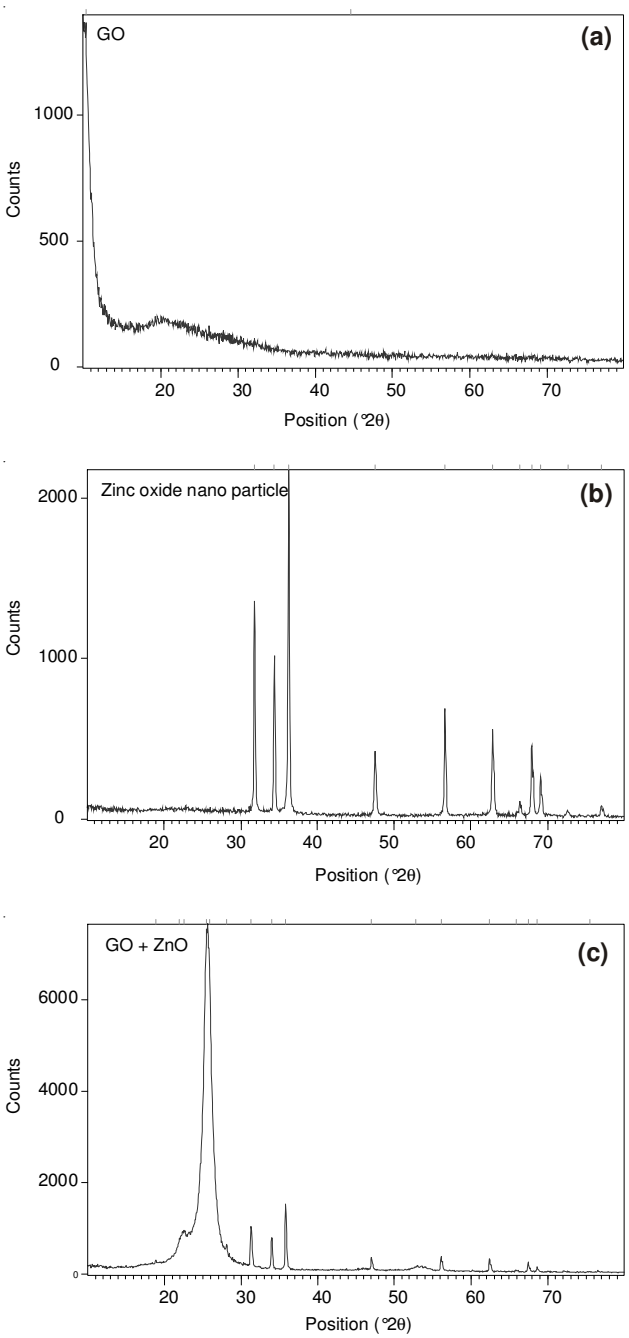


Fig. 3. a) GO NPS; b) ZnO NPS; c) GO blend with ZnO NPS

Analysis of atomic force microscopy: The surface topography of the materials prepared here are recorded at ambient conditions in non-contact mode using XE70 scanning probe microscope PARK system, South Korea. Surface morphology, particle size in length, height, *etc*. is performed by using XEI software, supplied by PARK system. The 3D image of different metal oxide nanoparticles and Graphene oxide blend with Zinc oxide nanoparticles are shown. In Fig. 4a, 4b and 4c represents the 3D-atomic force microscopy image of the graphene oxide, zinc oxide. The size of particle, distribution of particles on the surface, height up to which the particles are found *etc*., have been determined from the scale given in the left. Graphene oxide is around 75 nm (Fig. 4a), zinc oxide is around 100-120 nm (Fig. 4b).

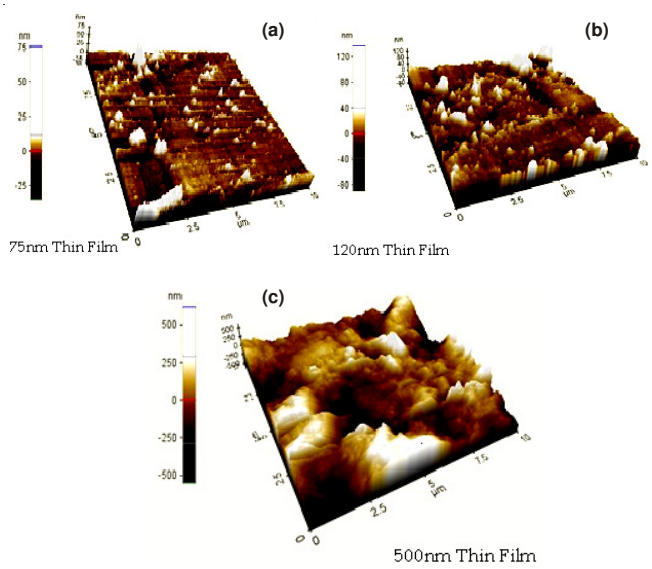
On making a composite by blending the zinc oxide with graphene oxide the particle size found are higher in comparison with plain materials. Fig. 4c represents the 3D atomic force microscopy images of the graphene oxide blended with zinc oxide respectively. From the particle height scale it is clear that the increase in particle size has been found. From the Fig. 4c the particle size noticed is 500nm are for graphene oxide with ZnO. Such increase in particle size is because of the entrapment of ZnO oxide nanoparticles into graphene oxide network.

The particle size distribution in the entire scan area *i.e.*, 0-10 μm or 0-2.5 μm *etc*., can be well assessed from the line profile drawn either horizontally or vertically over the 2D atomic force microscopy image after the scanning process.

Line profile analysis: Fig. 4d represents the 2D atomic force microscopy image of graphene oxide. A horizontal line is drawn at 8μm and a vertical line drawn at 2.5 μm using XEI software. The curves shown in the right and the line profile for vertical and horizontal lines which gave the information about the distribution of particles with size height *etc*., the right top curve shows a maximum particle height found around 30-32 nm. The bottom right display exhibit a maximum particle height about 60 nm. These data suggests that the particle size of graphene oxide obtained here is about 40-60 nm.

Zinc oxide: The line profile data is also explored for the zinc oxide nano particles. The 2D atomic force microscopy image and their details are given in the Fig. 4e. From the maximum peak height, the particle size is found around 120-125nm.

Graphene oxide blend with zinc oxide: On impregnating the metal oxide into the matrix of graphene oxide, the particle size was found to be increased, most of the graphene oxide blend were appeared in the region around 200-300 nm. After blending zinc oxide with graphene oxide, the atomic force microscopy images were recorded and the 2D image and its line profile in given in Fig. 4f. The maximum peak height from this image is found around 400-450 nm.



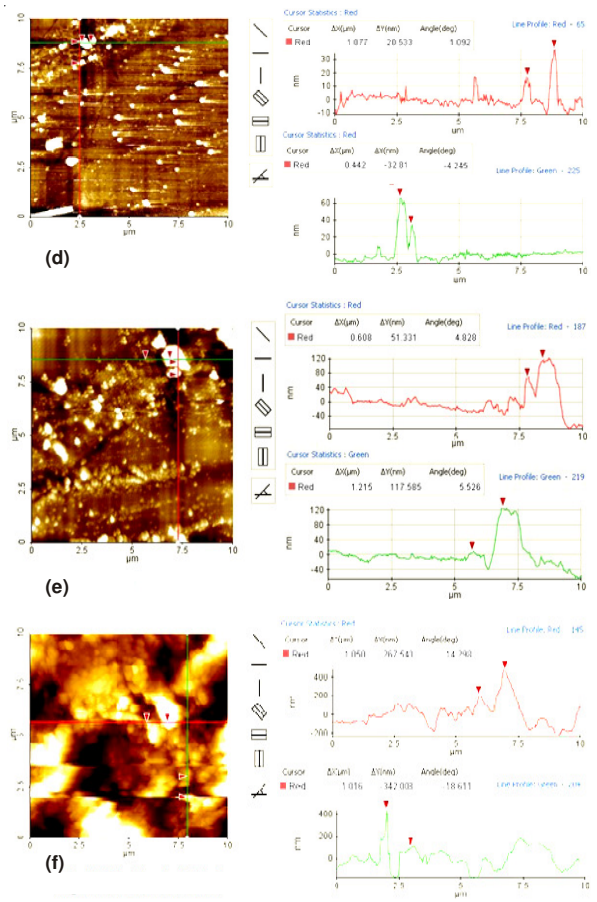


Fig. 4. a) Graphene oxide; b) Zinc oxide; c) Go blend ZnO; d) GO; e) ZnO; f) Go blend with ZnO

SEM results: SEM is used to determine the morphology of the surfaces. Fig. 5a represents the SEM image of graphene oxide nanoparticles prepared by Hummers method. The SEM micrograph confirms the graphite oxide layer formation. The wrinkles observed were probably caused by the oxygen functionalization and the resultant defects during the preparation of graphene oxide.

Fig. 5b shows the SEM image of as grown ZnO film deposited on glass substrate. The film deposited in the optimized condition is smooth, dark gray in colour and uniformly covering the substrate with good adherence. The overall surface structure shows grains of spherical shape uniformly covering the substrate without any cracks and pores.

Fig. 5c SEM images shows that the graphene oxide sheets were covered by densely packed and irregularly shaped ZnO grains, spreading in a large scale.

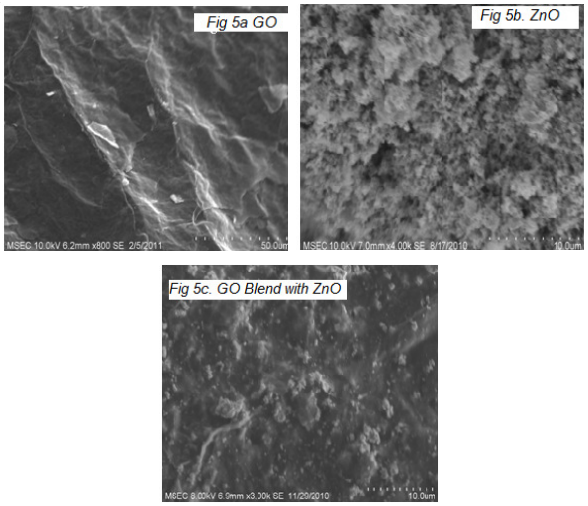


Fig. 5. a) GO; b) ZnO; c) GO blend with ZnO

UV-visible spectroscopy analysis: The ultraviolet-visible spectra of graphene oxide, ZnO and graphene oxide blend ZnO is represented in Fig. 6. It shows the maximum absorption peak at 370 nm for graphene oxide blend with ZnO and which was attributed to the π-π^* transitions of the aromatic C-C bonds. The band gap energy calculated from the UV-visible absorption spectra is 3.26 eV. When the graphene oxide blend with different concentration ratio of ZnO nanoparticles in that 3:1 is gives the best result of the UV spectrum analysis[9].

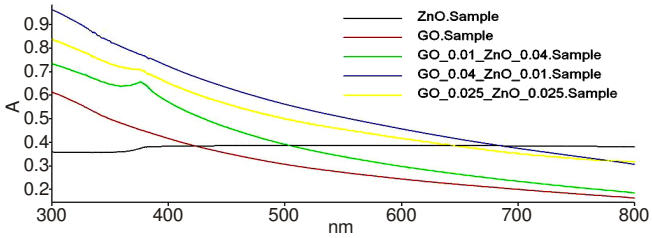


Fig. 6. UV visible spectra of ZnO, graphene oxide and blended samples

Conclusion

Here, we report the synthesis of graphene oxide and ZnO nanoparticle through chemical method, The nanostructures of the prepared graphene oxide and ZnO particles have been confirmed using UV-visible absorbance, XRD and TEM analysis. A model equation using the effective mass model has been developed in this work to calculate the particle size as a function of the peak absorbance wavelength. Photoluminescence emissions from the prepared graphene oxide and ZnO nanoparticles are observed at excitation wavelengths of 320 nm. The maximum photoluminescence emission takes place in 400-700 nm wavelength range, covering the whole visible region of the electromagnetic spectrum, from the prepared graphene oxide blend ZnO nanoparticles at 320 nm excitation (Fig. 7.)

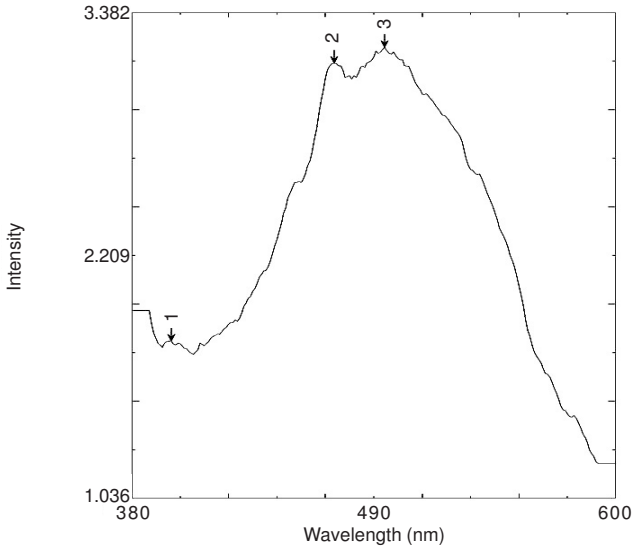


Fig. 7.

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