Reduced graphene-ZnO hybrid: linear and nonlinear optical properties

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Abstract

The wonder kid in carbon family, Graphene[1] is single atom thick sheet of sp^2-bonded carbon atoms in a hexagonal two dimensional lattice. Compared to other carbon nanostructures like fullerenes, carbon nanotubes, graphite etc, the interest in graphene based materials has been exponentially increased due to its unique properties like high carrier mobility at room temperature, large specific surface area, good optical transparency and thermal conductivity. Single layer graphene is a zero band gap[1] material with one type of hole and electron whereas graphene nanoribbon[2] is a semiconductor in which one of the dimensions of 2D graphene is reduced to $<$10 nm. The tuning of bandgap by the modification of chemical structure makes graphene a good candidate for the fabrication of optoelectronic devices[3]. But solubility and processability are the two important criteria for the assembly of devices; this can be achieved by the functionalization of graphene. The two dimensional (2D) graphene structures offer two dimensions for chemical functionalisation[4] either on the 2D π-conjugated network or on its edges. By chemical functionalisation graphene may turn into semiconductor with tunable bandgap. Functionalisation also gives a way for the anchoring of nanoparticles and small molecules on graphene sheets. These functionalised graphene nanocomposites with tunable bandgap, have potential optoelectronic applications. Porphyrin[5-7] and fullerene are covalently functionalised with graphene sheets and it is found that nanohybrids offer nonlinear absorption superior to that of the individual moieties. Even though porphyrin, phthalocyanine have excellent nonlinear optical response, lack of proper stability against thermal and optical bleaching limit their potential applications. The fabrication of graphene based materials with Zinc oxide (ZnO) nanoparticles may expect to overcome this disadvantage, because ZnO nanoparticles have good stability. The option of such nanocomposites to fabricate optoelectronic devices may offer advantages like light weight, good stability and optical transparency.

ZnO nanostructures combining reduced Graphene oxide (rGO) and Zinc oxide (ZnO) is synthesized by hydrothermal method using Zinc acetate dehydrate, Graphene oxide (GO) Polyvinyl pyrrolidone (PVP) and Sodium hydroxide (NaOH) as raw materials. GO sheets are first prepared by chemical oxidation of graphite powder at low temperature by modifying modified Hummers method [4]. ZnO nanoparticles are then anchored on GO sheets via the reaction between Zn^{2+} and OH^- in aqueous solution in presence of PVP. The surface of GO sheets are covered with large number of hydroxyl, carboxyl and epoxy groups, and these functional groups act as anchoring sites for Zn^{2+} ions. After the addition of NaOH, the crystal growth units $Zn(OH)_4^{2-}$ may combine with functional groups on GO sheets by hydrogen bonds or coordination bonds[5]. While heating at 100^oC under hydrothermal condition, reduction of GO as well as hydrolysis of $Zn(OH)_4^{2-}$ will occur. The formation of ZnO nanoparticles lead to the exfoliation of graphene sheets and the as obtained rGO-ZnO is shown in Figure 1a.

The UV-vis absorption spectrum of rGO-ZnO hybrid is shown in Figure 1b. The pure ZnO shows a sharp absorption at 362 nm and the rGO-ZnO hybrid shows absorption in the whole visible region in addition to the absorption edge at 362 nm. The rGO-ZnO hybrid possesses an intense and broad range of absorption in the visible region due to the presence of graphene. Figure 1c shows the photoluminescence spectra of H-rGO-ZnO and S-rGO-ZnO respectively. The photoluminescence spectrum of pure ZnO shows a broad peak at 380 nm extending to 500 nm. When compared to pure ZnO there is a decrease in fluorescence yield of hybrid obtained by both the methods suggesting an additional pathway for the disappearance of charge carriers because of the interaction between excited ZnO nanoparticles and graphene sheets. This emission quenching represents the interfacial charge transfer process. We have employed Open Aperture (OA) Z-scan technique to measure the nonlinear absorption and optical limiting property of the colloids of pure ZnO and rGO-ZnO hybrid (1 mg/ml of water). Q-switched Nd: YAG laser (5ns, 532 nm, 10 Hz) was used as the source to induce nonlinearity in the sample. For an input fluence of 4 J/cm^2, the normalised transmittance as a function of distance for the nanopowder dispersed in water is shown in Figure 2. Compared to the bare ZnO and GO dispersions, the ZnO- graphene hybrid shows a 15 times enhancement in the nonlinear absorption

properties, because of the combination of nonlinear optical mechanism of reduced graphene oxide and ZnO.

References

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Figures

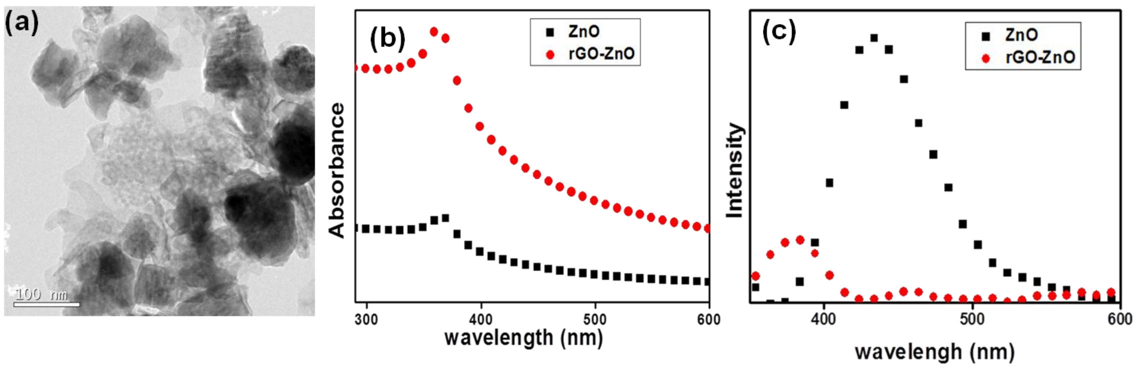

Figure 1. (a) TEM image of rGO-ZnO (b) UV-vis absorption of ZnO and rGO-ZnO
(c) Photoluminescence of ZnO and rGO-ZnO

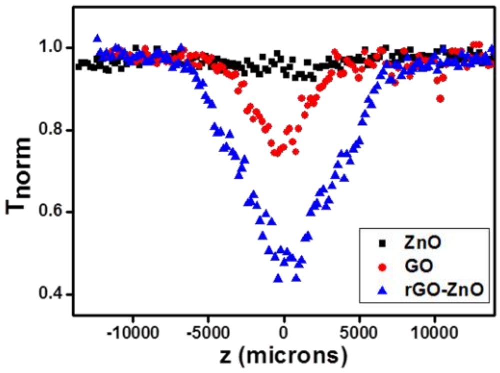

Figure 2. Normalized Transmittance curve of pure ZnO, GO and rGO-ZnO