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Multifunctionality in graphene decorated with cobalt nanorods

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ABSTRACT

Creating multifunctionality is always fascinating and required for various advance applications. We have prepared cobalt-graphene nanocomposite by co-reduction of graphite oxide and a divalent cobalt salt in water, at room temperature, by sodium borohydride. Microstructural study by high resolution transmission electron microscope (HRTEM) delineates that the nanocomposites consists of few layer of graphene sheets decorated by cobalt nanorods. The composite shows unusual photoluminescence in visible range due to defect decoration by cobalt nanorods, in spite of showing expected absorbance and magnetic properties. Functional nanomaterials with both magnetic and luminescence properties are important for application in biological systems.

1. Introduction

Graphene is an interesting two-dimensional sheet which consists of single layer of sp^2 hybridized carbon atoms. Graphene has been attracting extensive scientific interest due to its extraordinary electronic, mechanical and thermal properties. The extraordinary properties include high carrier mobility exceeding 10^4 cm^2/Vs [1], high thermal conductivity of 10^3 W/mK [2], extremely high surface area of 2630 m^2/g [3], and large value of Young's modulus ~1 TPa [4].A great deal of scientific attention has been generated towards the optical properties of graphene because of the insight they provide into the excited states of this remarkable material, and potential that they offer for novel applications [5,6]. Perfectly exfoliated single layer graphene sheet is a zero band gap semiconductor, and is therefore not likely to show any photoluminescence. In such a material, carriers can fully relax through rapid electron-electron and electron-phonon interactions which are much faster processes compared to light emission. However, if ultrafast pump-probe processes are applied, some light emission can be observed in graphene [7]. Therefore designing photoluminescent graphene based nanocomposite material is a major challenge of optoelectronics.

Recently, glucose-derived water-soluble crystalline graphene quantum dots (GQDs) with an average diameter as small as 1.65 nm (5 layers) were prepared by a facile microwave-assisted hydrothermal method, which exhibited deep ultraviolet (DUV) emission of 4.1 eV, the shortest emission wavelength among all the solution-based quantum dots. The emission wavelength is independent of the size of the GQDs. The unique optical properties of the GQDs are attributed to the self-passivated layer on the surface of the GQDs [8]. Green luminescent graphene quantum dots (GQDs) with a uniform size of 3, 5, and 8.2(±0.3) nm in diameter were prepared electrochemically from MWCNTs in propylene carbonate by using $LiClO_4$ at 90 °C, whereas similar particles of 23(±2) nm were obtained at 30 °C under identical conditions [9].

In fact, the combination of such an extraordinary material with functional nanomaterials may lead to interesting nanocomposites for a variety of applications. For this reason, composites comprising of graphene (G) decorated with metal [10,11], metal oxides [12–14] and sulphides [15,16]have also attracted a great deal of attention recently. Yang et al synthesized Co-graphene nanocomposites (Co-G) by pyrolysis of organometallic-graphene composite precursor at 800 °C in Ar atmosphere [17]. Ji et al synthesized Co-G through in situ reduction in ethylene glycol medium at 110 °C in N_2 atmosphere [18]. Chen et al synthesized porous Co-G nanocomposite by annealing graphene/Co_3O_4 nanocomposite at 350 °C under Ar/H_2 gas flow [19]. Nevertheless, there is no single report of preparation of Co-G nanocomposite at room temperature in ordinary atmosphere.

In this paper, we report the synthesis of Co-G nanocomposite by co-reduction of graphite oxide (GO) and salt of Co^{2+} in solution, at room temperature and in ordinary atmosphere. We have observed strong violet-blue emission in the composite, which is not observed till date in metal-G nanocomposites. A Co-CoO-graphene nanocomposite is recently reported to have very high catalytic activity for electrochemical reduction of oxygen [20]. Synthesis of this composite is quite different from our procedure and the shape and size as well as the Co-CoO nanoparticle decoration of G sheets is different. However, this readily shows the importance of these classes of materials.

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2. Experimental details

2.1. Materials

Natural flake graphite was purchased from Loba Chemie. All the other reagents used in the experimental process were analytical grade, purchased from Merck and used without further purification.

2.2. Methods

GO was prepared from natural graphite using modified Hummers method [21]. In the typical synthesis of Co-G, 0.04 g GO was dispersed in 30 ml water using ultrasonication to form stable dispersion. 30 ml aqueous solution of hydrated cobalt nitrate ($Co(NO_3)_2\cdot 6H_2O$) (a maximum of 5 mM) was formed separately. Two solutions were mixed under constant stirring condition to form homogeneous solution and kept in an ultrasonicator. Subsequently, sodium hydroxide (NaOH) solution and 0.14 g sodium borohydride ($NaBH_4$) was added. After 30 min, a black precipitate was formed which was collected by centrifugation and washed several times with water and ethanol. The precipitate was left to dry in vacuum and the dried powder was used for further characterization. The flowchart of synthesis procedure is presented in Fig. 1. For comparison, graphene was also synthesized by reducing GO with $NaBH_4$under similar conditions.

2.3. Characterization

The synthesized samples were characterized using different techniques. Fourier transform infra-red (FTIR) and UV–Vis spectra of the samples were recorded using Shimadzu FTIR 8400S and Varian Cary 5000 UV–Vis–NIR spectrophotometers respectively. The morphology was visualized using JEOL 2010 Transmission Electron Microscope (TEM) operated at 200 kV and equipped with a detector for energy dispersive X-ray spectroscopy study. X-Ray diffraction (XRD) patterns of the powder samples were obtained using Rigaku Mini Flex Benchtop X-Ray diffractometer. Magnetic properties were investigated using a superconducting quantum interference device (SQUID) magnetometer (supplied by Quantum Design, USA) over the temperature range 2–300 K. Photoluminescence spectrum of Co-G nanocomposite at room temperature was recorded on F-2500 FL spectrometer, Hitachi.

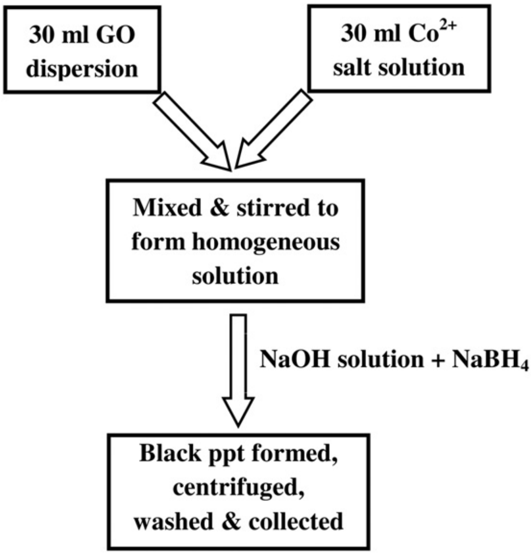

Fig. 1. Flowchart of synthesis procedure.

3. Results and discussion

3.1. Morphological study

The morphology of Co-G nanocomposite was examined using transmission electron micrographs (TEM). A typical micrograph is presented in Fig. 2(a). The figure shows a thin graphene sheet embedded with Co nanoparticles (higher electron density portions on the G sheet). It is clearly visible that the G sheet is very thin with folded edges. The weak contrast between the background and G sheet confirms the thinness of the sheet. Interestingly, the shape of the Co nanoparticles are not spherical but are in form of one-dimensional rod-like structure of average diameter ~3 nm and average length ~30 nm (Fig. 2(b)).

The high resolution transmission electron micrograph (HR-TEM) of Co-G sheet confirms the rod-like structure of Co nanoparticles (Fig. 3(a), (b)) and shows the lattice fringe with d-spacing 0.21 nm corresponding to (111) plane of Co. The HR-TEM also depicts that the non-agglomerated nature of nanorods.

3.2. X-ray diffraction study

To confirm the purity of the cobalt phase in the nanocomposite, XRD patterns of the samples were recorded. Fig. 4 presents the XRD patterns of GO, G and Co-G. The peaks in the sample Co-G can be indexed to cubic phase of Co (JCPDS No-15-0806) and graphene. This further strengthens our argument that the Co is present in metallic form as peaks corresponding to oxide are absent. The intensity of peaks of Co phase is relatively less compared to that of graphene, as the fraction of Co is relatively low compared to graphene. The elemental composition of Co-G nanocomposite was determined from energy dispersive spectrum (EDS) and is presented in Fig. 4(b). The spectrum confirms the presence of elements C, Cu and Co. The element Cu is attributed to the carbon coated copper grid on which the sample for TEM was cast. The weight fraction of Co compared to C was found to be within 10%. The result of XRD study corroborates well with the result of EDS.

3.3. FT-IR spectroscopy

The FT-IR spectra of GO, G and Co-G are presented in Fig. 5. The FT-IR spectrum of GO shows the presence of C—O (alkoxy) stretching bond (~1065 cm^{-1}), the C—O (epoxy) stretching peak at (~1227 cm^{-1}), C=C stretching bond (~1634 cm^{-1}) and stretching mode of C=O (~1725 cm^{-1}) [22]. The peak at 1390 cm^{-1} corresponds to deformation of O—H group of adsorbed water molecules respectively. It can be clearly seen that the characteristic absorption bands of oxide groups in GO (~1725 cm^{-1}) is almost absent in G and Co-G, confirming the complete reduction of GO. The peaks corresponding to C=C and C—C aromatic bonds (~1629 cm^{-1} and ~1500 cm^{-1}) remain the most prominent signatures in G and Co-G. The presence of peak in the range 650–570 cm^{-1} in all the three samples corresponds to C—H out-of-plane bending for substituted benzene ring, which further confirms the presence of aromatic rings in the samples.

3.4. UV–Visible absorbance spectroscopy

Fig. 6 shows the UV–Visible optical absorption spectra of GO, G and Co-G nanocomposite dispersed in ethanol. The peak within the range 255–270 nm is present in all the three samples and corresponds to $\pi \rightarrow \pi^*$ transitions of aromatic C=C rings [23].

The peak at 256.4 nm in GO shifted towards red on reduction, as is observed in G and Co-G nanocomposite. The presence of this particular peak in Co-G confirms that carbon network is not interrupted in presence of Co nanoparticles. The Co-G nanocomposite shows an additional broad peak at around 398.2 nm which is attributed to surface plasmon resonance (SPR) of Co nanoparticles [24], arises from oscillation of conduction band electrons in presence of interacting electromagnetic