REGULAR ARTICLE

Photocatalytic Activity of Graphene/ZnO Nanocomposite Fabricated by Two-step Electrochemical Route

A R NANAKKAL and L K ALEXANDER*

Department of Physics, University of Calicut, Kerala 673 635, India

Email: LKA@uoc.ac.in

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Abstract. Graphene-Zinc oxide nanocomposite was synthesised by a novel, facile and environment-friendly two-step electrochemical route aimed at water purification by photocatalysis. The X-ray diffraction, Raman spectroscopy and electron microscopy demonstrate successful implementation of electrolytic route for the synthesis of graphene-metal oxide nanocomposite. UV-Visible diffuse reflectance spectroscopy and photoluminescence measurements were also used to characterise the samples. Based on this work, it is found that for the UV incident radiation, Graphene-ZnO nanocomposite shows an enhanced photocatalytic activity over ZnO. The photocatalytic activity of annealed graphene-ZnO was compared to a standard catalyst Degussa P25 TiO₂. The electrochemical synthesis technique is envisioned to open a reliable, cost-effective and environment sensitive method to fabricate graphene-metal oxide nanocomposites which could lead to various applications especially for photocatalysis.

Keywords. Graphene-metal oxide; nanocomposites; electrochemistry; photocatalysis; water purification.

1. Introduction

Graphene (GN), an allotrope of carbon material, conquered the world of nanotechnology in the last decade because of its unique properties.¹ The properties of graphene, such as 2D structure, large surface area (~2600 m²/g), theoretical high mobility of charge carriers (~200000 cm²/Vs), *etc.*, made graphene more attractive for use as a phase matrix for developing nanocomposites using nanoparticles aiming at potential photocatalytic applications.^{2–8} Among the photocatalysts, TiO₂ and ZnO are two remarkable nanoparticles because of their non-toxicity, stability and low cost.^{9–12} It is reported that ZnO shows better efficiency than TiO₂ for the degradation of some organic dyes during photocatalytic process.¹⁰ Moreover, it is reported that the electron mobility of ZnO is higher than of TiO₂.^{11,13} The widely studied compound, ZnO is a semiconductor metal oxide material with a wide band gap energy of 3.37 eV.^{12,14} The quick recombination of photogenerated electron hole pairs is considered as a major problem for employing ZnO as a catalyst in photocatalytic applications.^{10,11} One of the ways adopted to address this issue is by hybridisation of ZnO with graphene to form graphene-ZnO nanocomposite.^{10,11,15}

Since the properties of graphene and its composites depend on the synthesis route, researchers employed

different methods - both for the synthesis of graphene and for the fabrication of graphene nanocomposites.¹⁶ Graphene can be synthesised using various techniques such as chemical vapour deposition (CVD),¹⁷ exfoliation of graphite,¹⁸ electrochemical method,¹⁹ *etc.* Among the techniques, electrochemical method was reported as a reliable and low cost method to produce highly pure graphene.^{19–21} For the fabrication of graphene based nanocomposites, different methods like reduction method, hydrothermal method, electrochemical method, various *ex situ* methods, *etc.*, are reported.^{16,22–25} Among them the electrochemical deposition method is regarded as a facile, speedy, cost effective and green technique. Moreover, it is a reliable method for controlling the material properties such as size, shape and percentage of functionalisation by changing the variables like molarities of electrolytes, pH of the electrolytic solution, power supply voltage and time of electrolysis.¹⁶ Majority of the composites reported to be synthesised by electrochemical method was focussed on graphene-noble metal composites such as GN-Pt,²⁶ GN-Au,¹⁶ *etc.* We could not find any report on successful anchoring of metal oxide nanoparticles like ZnO on graphene sheets by the electrochemical method.

In this paper, we report the successful synthesis of graphene-ZnO nanocomposite by the electrolysis method. A three-step process was followed for the synthesis. X-ray diffraction (XRD) and Raman spectroscopy were utilised for structural characterisation of samples.

*For correspondence

The morphology of the samples was analysed using field emission scanning electron microscopy (FE-SEM) and high resolution transmission electron microscopy (HR-TEM). UV-Visible diffuse reflectance spectroscopy (UV-Vis DRS) was used to obtain the band gap energy. Photoluminescence (PL) measurements on the composites were made to obtain preliminary information on the photocatalytic capability of the nanocomposites. The photocatalytic activity studies were conducted in a photoreactor using UV light source. In order to analyse the rate of degradation of methylene blue (the dye impurity) solution with respect to the irradiation time, UV-Visible spectroscopy was used. We have compared and analysed photocatalytic reaction rates of ZnO and GN-ZnO nanocomposite.

2. Experimental

2.1 Synthesis of Graphene and Graphene nanocomposite by electrochemical process

The design of electrolytic cell set up consist of graphite rods (purity 99%, metals basis, Alfa Aeser), sodium chloride, zinc sulphate (Merck), and conc. sulphuric acid (purity 98% ACS Empesti, Merck). The synthesis process can be categorised into three steps (schematic representation is shown in the Figure 1): (i) Synthesis of graphene by electrolysis, (ii) Modification of as-synthesised graphene sheets by introducing defects, and (iii) Functionalisation of modified graphene sheets using ZnO nanoparticles by electrolysis. In the first step, an appropriate constant DC voltage was applied across two fresh graphite rod electrodes (duration 60 min) dipped in 0.01 M of sodium chloride electrolytic solution to obtain graphene sheets on anode graphite rod. The detailed description of the mechanism involved in this process was reported by Low *et al.*²⁷ Then, the graphene coated electrode was treated with sulphuric acid (0.002 M) so

as to introduce more defects on graphene sheets. In the third step (functionalisation), the graphene-deposited graphite rod was employed as cathode and zinc sulphate solution (0.01 M) was used as electrolyte. Then, the electrolysis led to deposition of ZnO nanoparticles on the graphene sheets resulting in GN-ZnO composite. The functionalisation time (Step 3) was 50 min. The resultant powder collected from the cathode was oxidised by drying in an oven. The freshly synthesised GN-ZnO sample (*via* electrolysis) was annealed at 500°C for 2 h in a furnace. The resultant powder was labelled as GN-ZnO(h). To obtain ZnO, appropriate potential was applied for one hour across two fresh graphite rod electrodes dipped in 0.01 M zinc sulphate electrolyte solution. The collected powder (from the cathode) was taken to a oven and dried at 60°C. The as-synthesised ZnO was heated in a furnace at 500°C for 2 h to get ZnO(h) sample. In all the electrolysis process a DC voltage of 14 ± 1 V was applied.

2.2 Material characterisation

The crystallographic characterisation of the samples was carried out using X-ray diffraction (XRD) technique (Rigaku 600) at Cu K α ($\lambda = 1.542$ Å). The Raman spectra of graphene samples were obtained using micro Raman spectrometer (Fischer Scientific DXR Raman 532 nm). The morphology of the samples was studied using SEM (Hitachi SU 6600-FESEM) and HRTEM (JEOL - JEM 2100, 200 kV). The reported UV-Vis spectra (including DRS) were done using UV-Vis spectrophotometer (JASCO V-55). Photoluminescence (PL) study was carried out using fluorescence spectrometer (Perkin Elmer LS 55).

2.3 Photocatalytic experiments

Photocatalytic studies on the samples were conducted by measuring the degradation of methylene blue solution (MB): 0.1 g of catalyst was added to 50 mL MB solution (10 ppm)

Figure 1. Schematic illustration of three-step synthesis.

taken in a beaker and the resultant mixture was stirred continuously for 30 min in dark room condition. In order to attain adsorption – desorption equilibrium between dye solution and the catalyst, the mixture was kept in a dark room for additional 1.5 h. The mixture in equilibrium was then exposed to UV light. The solution samples were collected at fixed time intervals during UV irradiation. UV-Visible spectra of the irradiated samples were taken. Photocatalytic experiments on ZnO(h), GN-ZnO and GN-ZnO(h) were done under UV light using Luzchem LZC-4X photo reactor.

3. Results and Discussion

3.1 Characterisation of graphene and GN-ZnO

The XRD of the graphene shows three peaks: a main peak at an angle $2\theta = 26.2^\circ$ corresponding to the (002) reflection of graphene (Figure 2(a)) and the minor characteristic peaks of graphitic compound at $2\theta = 44.3^\circ$ and $2\theta = 54.4^\circ$ corresponding to (101) and (004), respectively. The XRD spectrum matches well with JCPDS file no. 75-1621. The presence of phase-pure ZnO in the graphene-based composite was confirmed by X-ray diffraction pattern of the samples. As shown in Figure 2(b), all the peaks of the graphene-ZnO nanocomposite could be indexed and was found in agreement with JCPDS file no. 75-1621 combined with file No. 36-1451.^{22,28,29} Figure 3(a) shows XRD pattern for ZnO nanoparticles prepared by electrochemical route. The XRD pattern of GN-ZnO is shown in Figure 3(c). It was reported that annealing to a higher temperature can increase the crystallinity of ZnO. Therefore, ZnO and GN-ZnO were heated to 500°C . The resultant XRD is shown in Figure 3 (b and d). As seen, the intensity of ZnO peak dominates over the peaks of

graphene in the spectrum (Figure 3(d)). This is expected for the reason that ZnO got better crystallinity on heating. This is attributed to the change in crystal size.³⁰ Particle size of the samples were estimated from the well-known Debye-Scherrer's formula: $d = K\lambda / \beta \cos\theta$; where, d is the crystal size, λ is the wavelength of irradiation used, K is the Scherrer constant (0.9), β is the full width at half maximum and θ is the Bragg angle. The particle size in all the samples was found to be in the range 20–30 nm.

Raman Spectroscopy was used for further confirmation of graphene formation by electrolytic method. In general, Raman spectroscopy is a powerful technique for the characterisation of all types of carbon nanostructures, especially graphene.³¹ The presence of G and

Figure 3. XRD patterns of (a) ZnO, (b) ZnO heated at 500°C , (c) GN-ZnO, and (d) GN-ZnO heated at 500°C . Starred peaks indicate the peaks of zinc.

Figure 2. XRD patterns of (a) graphene and (b) GN-ZnO. Peaks of graphene are left un-indexed in Figure (b).

Figure 4. Raman spectrum of graphene obtained in first step of the electrolytic process.

Figure 5. FE-SEM images of (a) graphene and (b) GN-ZnO nanocomposites.

D bands in the Raman spectrum describes the features of nanostructures.³¹ Here, Raman spectrum shows characteristic peaks at 1350 cm^{-1} and 1581.8 cm^{-1} for D band and G band, respectively (Figure 4). The G band arises due to first order scattering of the E_{2g} mode indicating the in-plane stretching motion of sp^2 C-C bond. The D band, considered as the disorder peak, originate from sp^3 defect-based breathing mode phonons of A_{1g} symmetry.^{23,24,32} The D band to G band intensity ratio (I_D/I_G) is commonly treated as a measure of defects or disorder.¹¹ The I_D/I_G ratio was found to be 0.88, which underlines the formation of graphene sheets.^{23,33–35} Based on XRD and Raman spectroscopy, it is clear that the graphitic nanomaterial formed in the first step of electrolysis process was few-layer graphene sheets.

Morphology of the samples was investigated using SEM analysis. Figure 5 (a and b) shows the FE-SEM images of GN and GN-ZnO, respectively. The HR-TEM images are shown in Figure 6. From the SEM and HR-TEM images, it is clear that ZnO nanoparticles are intensely decorated on graphene sheets.

The UV-Visible absorbance spectra of the samples ZnO, ZnO(h), GN-ZnO and GN-ZnO(h) are shown in Figure 7. All the samples show an absorption maximum

in the UV region. A slight red shift is noticed in the absorption maximum of the samples calcined at 500°C . The band gap energy of the samples were obtained from the graph plotted by taking photon energy $h\nu$ (eV) on X-axis and the modified Kubelka-Munk function $[F(R)/h\nu]^2$ on Y-axis. The $F(R)$ was calculated using the equation, $F(R) = (1-R)^2/(2R)$, where R is the reflectance. The plot is shown in Figure 8(a–d). From the plot, it is found that the band gap energy of ZnO is $3.15 \pm 0.03\text{ eV}$ and $3.18 \pm 0.02\text{ eV}$ for ZnO(h). Similarly, the band gap energy of GN-ZnO and GN-ZnO(h) was found to be $3.16 \pm 0.02\text{ eV}$ and $3.20 \pm 0.02\text{ eV}$, respectively. The red shift observed in the absorption maximum and in the energy band gap of annealed samples with respect to the parent compounds (for example, GN-ZnO(h) vs. GN-ZnO) can be attributed to the increased agglomeration/change in crystallinity on annealing.^{36,37} In any case, all the samples have considerably lower band gap than that previously reported for bulk ZnO (3.37 eV).³⁸ The absorption edge of GN-ZnO and GN-ZnO(h) shows a minute shift towards higher energy side than the edge of ZnO and ZnO(h), respectively. This shift can be assigned to the interaction of ZnO particles with graphene sheets; for example, see ref. 37.

Figure 6. The HR-TEM images of GN-ZnO nanocomposite.

Figure 7. UV-Visible absorbance spectra of the samples: ZnO, GN-ZnO, ZnO(h) and GN-ZnO(h).

Photoluminescence (PL) experiments were conducted to study nature of defects in the composites. The PL of the samples ZnO(h) and GN-ZnO(h) were taken to examine the defects in ZnO before and after the composite formation. As per reports, ZnO may show green, yellow, and orange PL emissions in visible region.^{40,41} The origin of these spectra are reportedly controversial and different defects centres are assumed to be responsible for the colours of emission.³⁹ Based on literature, it can be concluded that green and orange-red emissions are attributed to deficiency and over-sufficiency of oxygen, respectively. The red emission is attributed to the interstitial zinc transitions.^{40–42} As seen in the Figure 9, PL spectra (exciting wavelength $\lambda = 325$ nm) of both ZnO(h) and GN-ZnO(h) shows a red emission at 662.5 nm; hence it can be assigned to the over-sufficiency of oxygen and also to the interstitial zinc transition.

Figure 9. Room temperature PL spectra of ZnO and GN-ZnO, both annealed at 500°C.

The intensity of the PL spectra peak at 662.5 nm was found to be nearly doubled in GN-ZnO(h) compared to ZnO(h). Curiously any type of quenching due to the presence of GN is not indicated in the PL spectra. The similar behaviour of enhanced intensity is reported for TiO₂-RGO.⁴³ The intensity increase indicates that GN-ZnO(h) can reach more excited state and hence produce more photogenerated electron-hole pairs.⁴³ So an enhanced activity can be predicted for GN-ZnO(h) over ZnO(h) from PL spectra. It is reported that in ZnO, with an increase in annealing temperature, the content of surface oxygen vacancy increases up to 500°C.⁴⁴ Beyond the annealing temperature 500°C, the oxygen vacancy content in the surface of ZnO falls down. So the selection of annealing temperature as 500°C plays an important role in the PL peak intensity.

3.2 Photocatalytic activity

Photocatalytic activity of the samples was studied by employing the degradation of methylene blue (MB) solution. The photoreactor used in the experiment produces UV radiation at wavelength (λ) above 270 nm (illuminance 150 lx). From the experiment almost complete degradation of MB solution was noticed within 80–85 min for GN-ZnO. GN-ZnO(h) took only 30–35 min for the dye degradation. The variation of normalised concentration with UV irradiation time is shown in Figure 10. The degradation rate constant of the catalytic reactions can be obtained using pseudo-first order kinetic equation:

$$\ln(C/C_0) = -kt \quad (1)$$

Here, C_0 is the initial concentration, C is the concentration at time t , and k is the degradation rate constant.

Figure 8. Plots on $(F(R) h\nu)^2$ vs. photon energy ($h\nu$) of (a) ZnO, (b) GN-ZnO, (c) ZnO(h) and (d) GN-ZnO(h).

Figure 10. Comparison of photocatalytic degradation of MB in the presence of catalysts GN-ZnO, ZnO annealed at 500°C, GN-ZnO annealed at 500°C and P-25 (see text) under UV light. The solid line shows fit to determine photocatalytic reaction rate (k). The k value for P-25 is found to be $9.91 \times 10^{-2} \text{ min}^{-1}$.

Table 1 summarises the photocatalytic reaction rate constants obtained from the plots (Figure 10). As expected based on the PL spectra, highest activity is shown by GN-ZnO(h): $(5.39 \pm 0.23) \times 10^{-2} \text{ min}^{-1}$. The photocatalytic activity of Degussa P-25 TiO_2 (Nanoshel, 99.9%) was also studied under the same experimental conditions as a standard photocatalyst for comparison (Figure 10). There are previous reports on the general mechanism of photocatalytic degradation of dyes.⁴⁵ A schematic diagram of dye degradation mechanism for GN-ZnO is shown in Figure 11. The UV light excites electrons from the valance band of ZnO to the conduction band and hence photogenerated electron – hole pairs are formed. The photogenerated electrons get transferred to the graphene sheets. The graphene acts as a trap so that it prevents quick recombination of photogenerated electron hole pairs.¹⁶ The graphene-trapped electrons will react with oxygen dissolved in water forming oxygen radicals. Furthermore, the dissolved oxygen directly reacts with excited electrons on the ZnO surface and creates more oxygen radicals.^{16,46}

Table 1. Photocatalytic activity rate constant (k) of catalysts.

Compound	Photocatalytic activity Rate constant, $k(10^{-2} \text{ min}^{-1})$
ZnO(h)	4.06 (± 0.30)
GN-ZnO	2.81 (± 0.40)
GN-ZnO(h)	5.39 (± 0.23)
P-25 TiO_2	9.91 (± 0.20)

Figure 11. Schematic representation of the proposed photocatalytic degradation mechanism in MB solution under UV light irradiation in the presence of GN-ZnO catalyst.

These oxygen radicals react with water to form reactive hydroxyl species which will degrade MB dye. In the mean time, photogenerated holes also create hydroxyl radicals, which in turn degrades the dye molecules. The reactions included in the mechanism can be summarised as follows:

4. Conclusions

In this work, graphene and functionalised graphene with ZnO nanoparticles were successfully synthesised by electrochemical method. The samples are specially noted for its purity and maximum yield. Excepting the usage of 0.002 M sulphuric acid, the graphene synthesis and graphene functionalisation can be considered as an environment friendly technique. As demonstrated for ZnO in this paper, the reported three step route could be adapted to other metal oxides also. On the hybridisation of ZnO with graphene, the band gap energy of ZnO got slightly shifted to higher energies. An enhanced photocatalytic activity of GN-ZnO over ZnO was observed under UV light. The GN-ZnO annealed at 500°C shows an efficient photocatalytic activity with a degradation rate constant of $5.39 \times 10^{-2} \text{ min}^{-1}$. The methodology discussed in this report suggests a facile and efficient method for synthesis of metal oxide functionalised graphene usable for different applications such as sensing, lithium ion batteries and photocatalysis.

Supplementary Information (SI)

Additional information (Figure S1) comparing dependence of external UV irradiation on photocatalytic activity of blank methylene blue dye without catalyst and with catalyst is available at www.ias.ac.in/chemsci.

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