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**PAPER**

**In-situ** one pot synthesis of graphene-ZnO nanohybrid and its application to UV light detection

Sonal Rattan\textsuperscript{1,2}, Suresh Kumar\textsuperscript{1,2,3}, \(\text{E-mail: skphyscsnano@gmail.com}\) and J K Goswamy\textsuperscript{4,5}

\textsuperscript{1} Centre for Nanoscience and Nanotechnology, Panjab University, Chandigarh, India
\textsuperscript{2} Department of Applied Sciences, UIET, Panjab University, Chandigarh, India
\textsuperscript{3} Authors to whom any correspondence should be addressed.

**Abstract**

The development of molecular/nanoscale level assemblies allows the foundation of many potential novel applications. Chemical approach is one of the most favoured techniques to manipulate the nano-materials in a controllable manner. Herein, we report a simple and reliable one pot technique for preparing graphene-ZnO nanohybrid by coordinating zinc metal ions from precursor, which further led to the growth of ZnO nanoparticles on graphene sheets. The developed heterostructures were characterized through X-ray diffractometry, Fourier transformed infra-red (FTIR) spectroscopy, UV-visible spectroscopy and field emission scanning electron microscopy (FESEM). Morphological details revealed the dense loading of ZnO nanoparticles onto the surface of graphene. The nanohybrid was found to be electrically more responsive to the incident UV light compared to ZnO nanoparticles alone. The proposed method can lead to the fabrication of highly sensitive flexible light detector.

1. Introduction

Graphene for the first time was extracted by A Geim and Noveselov in 2004 from graphite flakes using adhesive tape. However, graphene/graphite oxide was already prepared by Hummers and Offeman, Staudenmaier and Brodie from natural graphite [1]. The shortcomings of these methods were removed by J. Tour and his co-workers [2]. Graphene (single graphitic sheet) has sp\(^2\) hybridized carbon-carbon bonding and exhibits excellent physiochemical properties [1]. Graphene has found applications in almost all scientific and engineering fields [3–7]. In particular, graphene has found many advanced applications in electronic devices such as sensors, field effect transistors and logic gates [8–10]. Intrinsic graphene does not possess any band gap and therefore many efforts have been made for its band gap opening using different approaches [11]. In order to use graphene in photovoltaic applications, large bias voltage is required to separate electron-hole pairs before their recombination [12]. Xia and co-workers studied the photosensitive electronic properties of graphene based sensing platform and found high dark current and very small optical On/Off ratio [13]. Hybridization of semiconductors with graphene can decrease the charge carrier recombination and hence improve the charge separation efficiency. Semiconductor nanoparticles have excellent optoelectronic properties and therefore their hybrids with graphene have been studied by many research groups [14–16]. Depending upon the material characteristics, semiconductor photodetectors convert the incident light of a particular wavelength range into measurable current.

ZnO at nanoscale has many interesting electronic properties, which are highly desirable for optoelectronic devices, transparent conducting electrodes and sensing devices [17, 18]. However, the mode of interactions between nanoparticles and graphene highly affect the electrical response of the nanohybrid. Therefore in this study, a facile method has been demonstrated to directly grow ZnO nanoparticles on the defects or functional sites on graphene oxide templates. Electrical response of the hybrid in dark and under UV light has been carefully recorded. Graphene-ZnO nanohybrids combine the unique properties of graphene and ZnO nanoparticles and hence the hybrid can act as improved material for the opto-electronic applications [19–25].

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2. Experimental

2.1. Preparation of graphene oxide

Graphene Oxide (GO) was produced by following the improved Hummers method [2, 3, 26]. Graphite powder (2.0 g), concentrated H$_2$SO$_4$ (84 mL) and H$_3$PO$_4$ (16 mL) were intermixed in a beaker using magnetic stirrer. KMnO$_4$ (9.0 g) was slowly added to the graphite–acid solution. The reaction mixture was magnetically stirred at room temperature for three days. After the completion of oxidation process, 5ml of H$_2$O$_2$ was added giving bright yellow colour. Afterwards, deionized water (400 mL) was added to the solution. 1M HCl was used for filtering and washing the mixture to wash out metal ions. Graphite oxide was washed with deionized water till the pH of filtrate reached the value ~6–7. The aqueous dispersion of graphite oxide was sonicated to exfoliate graphene oxide sheets. Graphene oxide solution was centrifuged at 8000 rpm. GO was dried at 40 °C and kept for further use.

2.2. Preparation of RGO/ZnO nanohybrid

A definite weight % of GO was dissolved in ethanol and then mixed with 10 mL of (0.01 M) zinc acetate dihydrate (Zn(Ac)$_2$.2H$_2$O) under continuous magnetic stirring. This solution was then sonicated for 10 minutes at ambient temperature for achieving proper mixing of the reactants. Afterwards, 10 mL of LiOH. H$_2$O (0.002 M) in ethanol solution was added into the reaction mixture [27]. This solution was sonicated again for about 30 minutes and kept for 24 hrs to assure full reduction of the precursors. Different concentrations of RGO-ZnO were prepared with careful adjustment of the molar concentration of ZnO and GO. The GO/ZnO ratio was altered gradually and named as RGO/ZnO-A (GO: 0.15 wt%), RGO/ZnO-B (GO: 0.6 wt%) and RGO/ZnO-C (GO: 2 wt%). Figure 1 displays the schematic of the preparation of graphene-ZnO heterostructure.

2.3. Characterization

X-ray diffractometry (XRD) of ZnO and nanohybrids was accomplished via Bruker D8 Advance X-ray diffractometer (using Cu Kα with λ = 0.154 nm). Morphological investigation of the samples was done using FESEM (Hitachi SU8010). FTIR (Shimadzu IR affinity1S) spectrometer was used to identify the functional groups on graphene. The UV–Visible spectrum (200 to 800 nm) was recorded through Shimadzu UV2600 spectrometer. I-V measurements in dark as well as in the presence of UV light were recorded with Keithley source-meter (model 2461) in a linear sweep mode with voltage scan range of −1V to +1V.

3. Results and Discussion

During the process of GO formation, GO solution was first centrifuged at 1500 rpm to get rid of un-exfoliated graphite flakes. Graphene sheets with oxidative functionalities and defects can act as perfect templates for the growing ZnO nanoparticles. The formation of GO was ascertained via X-ray diffractometry. Figure 2(b) displays the XRD results of ZnO giving diffraction peaks corresponding to crystal planes (100), (010), (102), (211), (110), (103), (201) at 2 theta values of 31.86°, 34.48°, 36.33°, 47.58°, 56.65°, 62.88°, 64.41°, 68.01° and 69.13° respectively, with wurtzite structure (ICPDS no. 396–1451) [15]. XRD response of the RGO/ZnO nanohybrid is shown in figure 2(a). The addition of reducing agent (lithium hydroxide) reduced graphene oxide sheets and zinc ions simultaneously. The additional band at 2 theta ~27° is accounted for the reduction of graphene oxide. The XRD analysis indicated the formation of the RGO/ZnO hybrid. XRD analysis of the as synthesized samples, showed no alteration in peak shapes and positions compared to pure ZnO XRD pattern. It showed that adding RGO had negligible impact over the crystallographic orientations of pure ZnO [28]. Figure 3 displays energy dispersive X-ray spectrum (EDS) of RGO/ZnO nanohybrid. The spectrum displayed the strong peaks for zinc, oxygen and carbon elements, which clearly ascertained the formation of the nanohybrid. Field emission scanning electron microscopic analysis of graphene and graphene/ZnO nanohybrid is shown in figure 4. Morphological details of the electron micrographs ascertained the growth of ZnO nanoparticles on graphene.
sheets. GO prepared by wet chemical oxidation contains oxidative-functional groups and many defect sites [29]. The defects and functional groups attract the metal ions and serve as nucleation sites for growing ZnO nanoparticles. Figure 5(a) gives the UV–vis absorption spectra of RGO/ZnO sample.

UV–Visible spectrum of RGO/ZnO hybrids showed an absorption peak at ∼340 nm but usually ZnO nanoparticles display a peak around 375 nm [30]. The blue shift in absorption spectrum aroused due to the quantum size effect of ZnO as one side of the nanoparticle growth was hindered by the graphene template [31]. The additional absorption peak in RGO/ZnO UV–visible spectrum at 230 nm occurred due to π–π* electronic transitions of –C=C– bond electrons in graphene skeleton. The FTIR spectrum of RGO/ZnO nanohybrid scanned from 500 to 4000 cm⁻¹ wavenumbers is displayed in figure 5(b). The absorption peak at 1640 cm⁻¹ was due to C=C bond stretch in graphene sheet. A typical absorption peak at 460 cm⁻¹ appeared due to Zn–O

![Figure 2](image.png)

**Figure 2.** X-ray diffraction pattern of (a) RGO/ZnO nanoparticle hybrid and (b) ZnO nanoparticles.

![Figure 3](image.png)

**Figure 3.** Energy dispersive x-ray spectroscopic analysis for RGO/ZnO nanoparticle hybrid with atomic and wt% of elements present in the hybrid.

![Figure 4](image.png)

**Figure 4.** Field emission scanning electron micrographs of RGO/ZnO nanohybrids at low and high magnifications.
metal-Oxide bond stretch \[31\]. The absorption peaks at 1732, 1184, and 1040 cm\(^{-1}\) disappeared from the spectrum, indicating the reduction of GO \[32, 33\]. Figure 6 shows the Raman spectra of GO and RGO/ZnO hybrid. The D and G bands for GO were observed at 1357 cm\(^{-1}\) and 1600 cm\(^{-1}\) respectively, whereas RGO/ZnO hybrid displayed the D and G bands of RGO at 1350 cm\(^{-1}\) and 1590 cm\(^{-1}\) respectively, alongwith a peak at 438 cm\(^{-1}\) indicating the E\(_2\) high frequency mode of wurtzite structure of ZnO \[34\]. The structural defects in ZnO correspond to 580 cm\(^{-1}\) peak is due to E\(_1\) mode. I\(_D\)/I\(_G\) value reduced from 0.96 (GO) to 0.94 (RGO/ZnO) hybrid due to the decrease in the number of defects.

Ultraviolet region is the energy region of the electromagnetic spectrum, lying in between the X-ray and the visible range. Figure 7(a) displays the schematics for carrying out the electrical measurement of the samples and figure 7(b) shows the band diagram of the RGO/ZnO hybrid.

The work function value for RGO is \(-4.41\) eV, the conduction band (CB) and valence band (VB) of ZnO corresponds to \(-4.05\) and \(-7.25\) eV, respectively \[19\]. The Fermi level of RGO lies below the CB of ZnO and it assists the transfer of photo-generated electrons from ZnO to graphene. This process effectively separates the photo-generated electrons and decreases the charge recombination rate and hence increases the electron conduction. The concentration of graphene in the hybrid structures affects the photo-current generation \[35\]. Some electrons interact with the atmospheric oxygen and form O\(_2\) and hydroxyl (OH) radicals \[35, 36\]. Figures 8(a)–(c) shows the current-voltage characteristics of the RGO/ZnO-A, RGO/ZnO-B and RGO/ZnO-C samples. Figures 8(d)–(f) shows the ln(I) versus V graphs for the reduced GO/ZnO hybrids. Figure 9(a) shows current-voltage characteristics of the ZnO nanoparticles and figure 9(b) shows the ln(I) versus V graph for ZnO nanoparticles. The response of the samples was recorded in dark as well as under the ultraviolet lamp. The changes in the electrical conduction response are clearly visible upon UV light exposure. It is observed that RGO/ZnO-A has the highest sensitivity and responsivity as compared to RGO/ZnO-B and RGO/ZnO-C. This is due to the fact that the decrement in the amount of ZnO nanoparticles compared to the GO causes reduction in the photo-generated charge carriers. Hence, optimal output is achieved in RGO/ZnO-A. The hybrids,
however, display a better response towards UV light as compared to bare ZnO nanoparticles because of the combined effects of ZnO and GO. Figure 10 shows the sensitivity vs time graph for the RGO/ZnO hybrid. The sensitivity ($S$) and responsivity ($R$) of the samples is calculated by the following equations:

$$S = \frac{I_{ph}}{I_d}$$

(1)
where: $I_{ph}$ represents the photocurrent; $I_d$ represents dark current; and $P_{op}$ represents the optical power of UV lamp.

The sensitivity for bare ZnO nanoparticles was found to be 1.10, whereas the sensitivity value was calculated to be 1.91, 1.31 and 1.22 for RGO/ZnO-A, RGO/ZnO-B and RGO/ZnO-C respectively. The responsivity value for ZnO nanoparticles was calculated as 0.011 $\mu$A W$^{-1}$ whereas for the hybrids RGO/ZnO-A, RGO/ZnO-B and RGO/ZnO-C it comes out to be 0.213 $\mu$A W$^{-1}$, 0.067 $\mu$A W$^{-1}$ and 0.018 $\mu$A W$^{-1}$ respectively.

4. Conclusions

The RGO/ZnO nano-hybrids were prepared by a simple one pot method. The hybrids were carefully examined via x-ray diffractometry, UV-Visible spectroscopy, FTIR and FESEM techniques. ZnO nanoparticles were directly grown onto the surface of graphene template. The reducing agent assisted the growth of ZnO nanoparticles as well as simultaneously reduced graphene oxide. The XRD patterns ascertained the formation of ZnO nanoparticles and RGO/ZnO hybrids. In addition, FESEM images show that RGO is a good platform for the high density ZnO nanoparticles growth. The major objective of this work is to combine the photosensitive properties of ZnO nanoparticles with superior electronic properties of graphene. The hybrid displayed good response to the incident UV rays.

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ORCID iDs

Suresh Kumar ⊗ https://orcid.org/0000-0002-6941-3925

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