Synthesis and characterization of Graphene oxide/Zinc oxide nanorods sandwich structure

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Abstract. Graphene-ZnO nanostructures composite materials have been used as very efficient candidates for various optoelectronic applications. Nowadays, the composite structure formation of ZnO nanostructures with graphene or graphene oxide is a novel, cost effective and efficient approach to control the morphology, surface defect states, band gap of ZnO nanocrystals. In this paper, we have prepared ZnO nanorods between two layers graphene oxide (GO/ZnO NRs/GO) via a simple hydrothermal method. Their morphology, structural and optical properties have been investigated. The obtained results of our composites GO/ZnO NRs/GO presented here showing an enhancement in the structural and optical properties. Thus may hold great promise to the development of the optoelectronic devices.

1. Introduction
Recently, Zinc oxide became one of the most promising materials for optoelectronic applications, gas sensing devices, transparent conductive oxide in solar cells, short wavelength electronic devices. For these applications, ZnO presents strong advantages: a wide direct band gap (3.4 eV), high electron mobility of 155 cm²V⁻¹s⁻¹, a high exciton binding energy (60 meV) at room temperature, low cost, and facility for synthesizing nanostructures with different morphologies [1]. One-dimensional ZnO nanostructures such as nanorods [2], nanowires [3], nanobelts [4], nanotube [5] and others have attracted attention owing to their interesting physical, chemical, optical, and electronic properties. A number of chemical and physical techniques have been used to easily synthesize ZnO nanostructures such as chemical bath deposition (CBD) [6], metal-organic chemical vapour deposition (MOCVD) [7], green synthesis method [8], solvothermal method [9], hydrothermal method [10] and microwave-assisted hydrothermal synthesis [11].

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Graphene is a single monolayer of graphite, which has recently attracted much attention due to its unique electrical and optical properties. Furthermore, graphene has a very high carrier mobility and remarkable electroconductivity, mechanical flexibility, high chemical stability and optical transparency [12–15]. On the other hand, graphene oxide is receiving an increasing attention because it possesses the similar properties of graphene, as well as the special surface structures with the introduced hydroxyl and carboxyl groups for synthesis of graphene oxide containing nanocomposite [16,17]. Also, Graphene oxide contains a range of reactive oxygen functional groups, is considered to be a good candidate for chemical functionalization [18]. Thus, graphene oxide additives are often semiconducting, metallic or even polymeric in nature [19-21].

Composites based on graphene oxide and semiconductor nanostructures have attracted more and more attention of scientist researches, because graphene based composite materials shows potential as a class of new exciting materials [22], and it has large variety of current and future technological applications. A great number of inorganic nanostructures have been compositied with graphene or graphene oxide, which include inorganic nanoparticles such as Fe3O4, TiO2, SnO2 and ZnO [23-26]. Currently, the composites formation of ZnO nanorods with graphene or graphene oxide is still novel and few studies discussing their elaboration have been reported in the literature. For example, Qin et al [27] developed a facile room temperature approach for graphene oxide-ZnO nanorods composites with enhanced photocatalytic activity. Alaver et al [28] reported the optical and structural properties of ZnO nanorods grown on graphene oxide and reduced graphene oxide by hydrothermal method. Vessali et al [29] synthesized ZnO NRs/graphene oxide sheets using a chemical bath deposition. Their result shown that GO sheets deposited below the ZnO nanorods should affect the sensor resistance, reducing its responses to volatile organic compounds detection when compared to ZnO NRs sample.

In this study, the preparation of graphene oxide/ ZnO nanorods composites with sandwich structure via a simple hydrothermal method is reported. The optical, structural and morphology of graphene oxide/ZnO nanorods/graphene oxide were studied by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and UV-Vis spectroscopy. The obtained results reveal the efficiency of our methodology to improve the structural and optical properties of GO/ZnO NRs/GO nanocomposites, which might have great potential applications especially in optoelectronic devices.

2. Experimental method

2.1. Synthesis of ZnO nanorods
ZnO precursors used in this work were purchased from Sigma-Aldrich. To synthesize ZnO nanorods, an equi-molar aqueous solution of 0.1 M zinc nitrate (Zn(NO3)2) and hexamethylenetetramine (C6H12N4, HMT) was prepared using deionized water. This mixture was heated at a constant temperature of 90°C in an oven for 24 h. The obtained materials were deposited on Si 〈1 0 0〉 substrates and dried at 50°C for 2 hours.

2.2. Synthesis of graphene oxide (GO)
GO was prepared from graphite powder using modified hammers method [30]. Initially, 2 g of graphite powder was added to 46 ml of concentrated H2SO4 and kept in an ice bath for 2 h. Then, 6 g KMnO4 was added gradually over a period of 30 min under stirring and cooling. Next, 46 ml deionized water was added slowly to this mixture and the temperature was maintained at ~100 °C for 15 min deionized water (280 ml) was then added, followed by 10 ml of 30% H2O2 solution, and the mixture was stirred for 30 min. The product was then filtered with 500 ml of 10% HCl solution to remove metal ions and then thoroughly washed with deionized water.
2.3. Synthesis of GO/ZnO NRs/GO composites
Firstly, a thin layers of GO was deposited on Silicon substrate and dried an oven at 60 °C vacuum for 1h. Secondly, ZnO nanorods were grown on the as-deposited GO surface. After 2h at 90 °C, another layer of GO covered the ZnO nanorods surface in order to prepare sandwich like structure composites.

3. Results and discussion

3.1. X-ray diffraction
The XRD pattern of Pure ZnO and GO/ZnO NRs/GO nanocomposites is shown in figure 1. The major diffraction peaks in GO/ZnO/GO composite were observed at 2θ value 31.8°, 34.5°, 36.5°, 47.8°, 56.6°, 62.8°, 66.5°, 67.9°, 69.3° and 76.9° which correspond to (100), (002), (101), (102), (110), (103), (200), (112), (201) and (202) crystalline plane of ZnO respectively. These crystalline planes are indexed to the hexagonal phase wurtzite structure of ZnO matched with the JCPDS No. 36-1451. The peaks at 2θ = 9.5° and 2θ = 23°corresponding to (002) plane of GO and reduced GO respectively [31-32]. The appearance of these two peaks is a consequence of the partial reduction of the GO which due to the presence of ZnO NRs between the layers of GO. Therefore, it can be clearly observed that the interaction between the components is remarkable as well as the intensity of (100) plane found to be higher than of the pure ZnO, which lead to a change in the orientation direction of ZnO NRs.

![Figure 1. XRD pattern of GO/ZnO NRs/GO nanocomposites and Pure ZnO (Inset picture).](image-url)
3.2. Scanning electron microscopy
The surface morphology of the ZnO nanorods and GO/ZnO NRs/GO composites were studied by SEM as illustrated in Figure 1. The as-prepared ZnO nanorods in figure 2(a) it can be seen that ZnO-NRs were grown vertically with high density and showed hexagonal shape. The average diameter of the nanorods was about 400 nm and the surface of ZnO nanorods was very smooth. For GO/ZnO NRs /GO sample shown in figure 2(b), it is clearly seen that ZnO NRs are covered by semi-transparent few layered GO sheets thus confirming the formation of sandwich-like nanocomposites structure by the insertion of the ZnO nanorods between the inter-layer of GO sheets which can prevent the agglomeration of ZnO nanorods as well as avoid the stacking of GO sheets and thus lead to preserve their high surface area.

![SEM Images of (a) ZnO nanorods and (b) GO/ZnO NRs/GO](image)

3.3. Fourier transform infrared spectroscopy
The identification of molecular absorption surface of GO/ZnO NRs /GO nanocomposites was analyzed by FTIR spectroscopy technique and it is shown in Figure 3. The absorption band located at ~ 3340 cm\(^{-1}\) which can be assigned to the stretching vibrations of O–H groups from absorbed H\(_2\)O molecules, is almost disappeared due to the deoxygenation/reduction. The reduction makes the hydroxyl and epoxy edges of GO to interacts with ZnO fabrication [26]. Moreover, the peak at ~ 2347 cm\(^{-1}\) is assigned to CO\(_2\) molecules on the surface of the samples [33] and the peak located at 2922 cm\(^{-1}\) is associated with the C-H stretching vibration [34]. The strong absorption band of the C-C skeletal vibrations around 1580 cm\(^{-1}\) which indicates the presence of GO sheets [35]. The characteristic peak at 1435 cm\(^{-1}\) corresponds to stretching vibration of aromatic C-OH and the peak at 957 cm\(^{-1}\) which corresponds to the stretching vibration of C-O becomes stronger [36]. Finally, the absorption peaks at 497 cm\(^{-1}\)and 565 cm\(^{-1}\) can be attributed to the stretching vibration of Zn-O. The region between 400-700 cm\(^{-1}\) usually corresponding to the vibration mode of metal-oxygen [37].
3.4. UV-Vis spectroscopy

The ultraviolet-visible absorption spectrum of GO/ZnO NRs/GO nanocomposites was recorded to determine the effect of GO on the optical properties of ZnO nanorods and it is shown in Figure 4. The strong absorption band was observed at 370 nm corresponds to ZnO nanostructures. This indicates that the observed absorption peak is blue shifted from that of bulk ZnO due to nano size effect or may be attributed to the close conjugation of the ZnO nanorods and the graphene oxide that lead to high electron transfer which increased transition energy [31,38,39]. On the other hand the absorption peaks located at 370 and 412 nm can be attributed to $\pi \rightarrow \pi^*$ transition of aromatic C=C bands; from the valence to the conduction band ($O_{2p} \rightarrow Zn_{3d}$) as shown in the schematic diagram (figure 5) and the n→ $\pi^*$ transition of C=O bond respectively [40-41]. Moreover, we can mention also that the introduction of ZnO nanorods between two layers of GO has shown an enhancement in the light absorption by nanocomposites, which can be linked to the broad band absorption in the visible light region. However, our results show that the sandwich GO/ZnO NRs/GO structure is causing remarkable modifications on the optical character of ZnO NRs. Different transitions and absorption mechanisms indicated in the UV-Vis spectra were presented in the schematic diagram shown in the figure 5.
Figure 4. UV-Vis absorption spectrum of as-prepared GO/ZnO NRs/GO nanocomposites.

Figure 5. Schematic transitions diagram of ZnO and GO.
4. Conclusion
To summarize, GO/ZnO NRs/GO nanocomposites were synthesized via a simple hydrothermal synthesis method. The analysis of X-ray diffraction showed that the samples had hexagonal wurtzite structure, with (100) as a preferred orientation for the growth of the ZnO nanorods. SEM images also showed the formation of sandwich-like nanocomposites structure by the insertion of the ZnO nanorods between the inter-layer of GO while the vibrational properties are confirming the formation of these composites which assisted to the understanding of the growth mechanism. Furthermore, the GO/ZnO NRs/GO nanocomposites reveals a broad absorption in the whole region of (300-600 nm) where the strongest absorption was observed around 370 nm. The insertion of ZnO NRs between two layers of G0 showed an enhancement of the optical properties, which can be linked to the broad absorption band in the visible light region. Therefore, these results can be used to enhance the efficiency of some optoelectronic applications.

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