X-ray diffraction investigations of nanostructured ZnO coated with reduced graphene oxide.

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Abstract. Nowadays, nanocomposites containing ZnO with various morphologies and graphene, graphene oxide (GO) or reduced graphene oxide (rGO) have been attracting many researchers according to their properties and board application in optoelectronic devices. In this study, rGO/ZnO nanorods were synthesized using different procedures. In the first procedure, ZnO nanorods prepared by using the hydrothermal method. In the second procedure, the surface of ZnO nanorods was coated with rGO using the drop coating process. The pure ZnO, rGO and rGO/ZnO nanorods were characterized by X-ray diffraction (XRD) and the average crystallite size was calculated using Debye-Scherrer equation.

1. Introduction

In recent years, ZnO material has attracted an important research interest due to its outstanding physical and chemical properties. ZnO is a II–VI group semiconductor material with a direct band gap of 3.37 eV, and a large exciton binding energy (60 meV) at room temperature and the ease with which highly crystalline nanostructures can be grown [1,2]. It is a preferable material for many important applications in optoelectronic devices, such as solar cells, gas sensors and energy storage [3]. The ZnO nanorods can be fabricated by hydrothermal method, chemical vapor deposition, sol-gel method and electrodeposition technique, etc. Among these methods, the hydrothermal process is a simple and low-cost process compared to other techniques [4]. Another attractive feature of ZnO is the possibility of growing it in different structural forms such as nanorods, nanowires and nanosheets on a wide range of substrates [5–7]. In this study, the ZnO nanorods were fabricate by hydrothermal synthesis.

Graphene, a two-dimensional (2D) layer of sp²-bonded carbon material has attracted a lot of attention in the research community over the last few years due to its extraordinary unique physical
and chemical properties [8]. Its derivative, such as reduced graphene oxide (rGO) has attracted extensive attention because of its properties such as excellent mobility of charge carriers, superior electrical conductivity, high surface area [9-12]. rGO is an optional coating material and demonstrates great promise for the fabrication of solar cell devices [13]. Although, rGO has been verified as excellent additives with ZnO nanostructures to form nanocomposite structure for optoelectronic applications. Several researchers have studied the composite materials of rGO/ZnO. Jijun Ding et al have prepared rGO/ZnO nanorods by spin coating and studied its PL properties [14]. Lei Huang et al have synthesized rGO-ZnO nanorods by chemical vapor deposition (CVD) [3]. Kavitha et al synthesized rGO-ZnO nanocomposite with a complete coating layer by hydrothermal method [15].

In the present work, nanocomposites based on rGO and ZnO nanorods are synthesized by a simple hydrothermal approach. The rGO coating ZnO nanorods is performed. The structure of these composites is investigated in order to probe the effect of the interaction of the rGO with ZnO nanorods on their dispersion and structure.

2. Method of preparation

2.1. Synthesis of rGO

GO was first prepared by the modified Hummers method [16]. To synthesis rGO, 0.1 g graphene oxide was mixed in 400 ml deionized water and ultrasonicated for 30 min to form a homogeneous suspension. Then 10 ml of hydrazine hydrate was added as reducing agent and stirred for 6 h at 60 °C. The color of the solution was changed from brown to black confirmed the formation of rGO. Finally, rGO was recovered by centrifugation (4000 rpm for 30 min).

2.2. Synthesis of ZnO nanorods and rGO coated ZnO nanorods

In the synthesis process, an equi-molar aqueous solution of 0.1 M zinc nitrate (Zn(NO$_3$)$_2$) and hexamethylenetetramine (C$_6$H$_{12}$N$_4$, HMT) was prepared using deionized water, mixed well and stirred for about half an hour till a white colored precipitate appeared. The precipitate 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. Then the surface of ZnO nanorods was coated with rGO using the drop coating. A schematic representation of rGO coated ZnO nanorods is shown in Figure 1. The crystal structure of the product was analyzed using X-ray diffractometer (Rigaku Smart Lab system) with CuKα (λ=1.54178 Å) radiation.
Figure 1. Schematic of preparation process for ZnO nanorods and rGO coated ZnO nanorods

3. Results and discussion

3.1. Structural properties
Figure 2. X-ray diffraction spectrum of (a) rGO, (b) pure ZnO and (c) rGO/ZnO nanorods.

The XRD patterns of the rGO, pure ZnO and rGO coated ZnO nanorods have been shown in Figure (2(a), 2(b) and 2(c)). The XRD pattern of rGO has two principal peaks: the first at $2\theta = 23.5^\circ$ confirming that GO was completely reduced by hydrazine solution [17] and the second peak situated at about $2\theta = 43^\circ$ is related to the (100) plane of the hexagonal carbon structure [18]. The diffraction peaks of ZnO nanorods/rGO composite are similar to those pure ZnO. All the diffraction peaks in the XRD pattern of ZnO nanorods can be indexed to the hexagonal phase wurtzite ZnO [19]. Furthermore,
the diffraction peaks at Bragg angles 31.8°, 34.5°, 36.5°, 47.8°, 62.8°, 66.5°, 67.9°, 69.3°, 72.6° and 76.9° are assigned to the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) planes, which can be indexed to the hexagonal crystalline phase of ZnO with the lattice constants a = b = 3.2357 Å and c = 5.1813 Å (α = β = 90, γ = 120); this is in good agreement with the standard JCPDS card no. 36-1451. In addition, the peak intensities for rGO coated ZnO nanorods is lower compared to the ZnO intensities due the interaction of rGO with ZnO [20]. Moreover, the diffraction peaks corresponding to the rGO did not appear in the nano composite. Similar result has already been reported by Jijun et al [16]; they found that GO and rGO diffraction peaks disappeared in the composite materials. It is due to the destroyed regular stacks and limited amounts of rGO in the rGO-ZnO films. Chen et al [21] found that two reflection peaks of rGO disappeared in the XRD pattern of ZnO/ rGO composites.

3.2. Crystallite size

In particular, the ZnO (100) diffraction peak is much stronger than the ZnO (101) peak. This indicates that the formed ZnO nanocrystals have a preferential crystallographic (100) orientation. The average crystallite size of the pure and composite was calculated from the XRD pattern according to the line width of the (100) plane refraction peak using Debye-Scherrer Equation [22]:

\[ D = \frac{k \lambda}{\beta \cos \theta} \]  

(1)

Where, D is the crystallite size, \( \lambda \) is x-ray wavelength (1.54178 Å), \( \beta \) is full width at half maximum (FWHM) of the observed peak and \( \theta \) is the diffraction angle. The average crystallite size was calculated by resolving the highest intensity peak. As listed in Table 1

The dislocation density (\( \delta \)), that indicate the amount of defects is defined as the length of dislocation line per unit volume of crystal, is calculated using the Equation [23]:

\[ \delta = \frac{1}{D^2} \]  

(2)

Where D is the crystallite size. The dislocation density (\( \delta \)) calculations is summarized in table (1)

The broadening of diffraction line is as a result of both crystallite size and strain according to the literature presented by Williamson and Hall. The broadening induced by strain in powders arising from crystal defect and distortion were calculated by using the formula:

\[ \varepsilon = \frac{\beta}{4 \tan \theta} \]  

(3)

The peak width from crystallite size varies as \( 1/\cos \theta \) and strain varies as \( \tan \theta \) confirmed from Equation (1) and (3).

Table 1: Shows the 2θ, (h k l), FWHM and crystalline size for the major indexing peak for as prepared ZnO and rGO coated ZnO nanorods

| Samples          | 2θ (hkl) | FWHM (radian) | Crystalline size (nm) | Lattice strain | dislocation density (nm\(^2\)) |
|------------------|----------|----------------|-----------------------|----------------|-------------------------------|
| Pure ZnO         | 36.48 (101) | 0.00314        | 73.2                  | 0.08           | 0.0218                        |
| rGO/ZnO nanorods | 36.58 (101) | 0.00366        | 74.2                  | 0.088          | 0.0254                        |
Figure 3. ZnO crystallite size variation as function of the concentration rGO for the different ZnO orientations.

Figure 4. Size estimation in pure ZnO (a) and (b) of rGO coated ZnO nanorods

In our previous work, we have prepared ZnO nanorods coated with GO nanosheets, we found that the crystallite size have decreased after interaction between the components. In this work, we have calculate the crystallite size which is increased after coating with rGO. This results confirm the functional groups roles in the growth of these nanorods. Thus, the absence of this groups and the vacancy produced after chemical reduction serves as nucleon site to improve the formation of ZnO nanorods. In addition, the plot in figure 4 presents an estimation of these pure and rGO caoted ZnO nanorods size calculated using Hall method where the obtained size average was found to be 778 (96) and 779 (88) respectively.
4. Conclusion

The purpose of this study was to investigate the structural properties of nanocomposites prepared by a hydrothermal method. The XRD measurement revealed that both pure and rGO coated ZnO nanorods have the hexagonal wurtzite structure with (100) plane as a preferred orientation for the growth of all samples. This study was focused to reveal information about the structural properties of rGO coated ZnO nanorods, which may improve their performance of some optoelectronic applications.

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