

## Synthesis and Characterization of Nanocomposite CdS/ZnO for Sensor Application

J P Panda<sup>1</sup>, G S Roy<sup>2\*</sup>

1. Saraswata Mahavidyalaya, Anantapur, Balasore, Odisha
2. Principal, Bhadrak Autonomous College Bhadrak, Odisha  
[gsroy2004@gmail.com](mailto:gsroy2004@gmail.com)

**Abstract:** A simple sonochemical route for the surface synthesis of CdS nanoparticles on ZnO is reported. Ultrasonic irradiation of a mixture of ZnO, cadmium chloride, and thiourea in an aqueous medium for 2 h yields ZnO and CdS nanoparticle (ZnO/CdS) composites with core/shell-type geometry. The powder X-ray diffraction of the ZnO/CdS composites shows additional diffraction peaks corresponding to the hexagonally structured CdS, apart from the signals from the ZnO cores. Transmission electron microscopy images of the ZnO/CdS composites reveal that the ZnO are coated with CdS nanoparticles with typical diameters of about 5-10 nm. The room temperature photoluminescence spectrum of the ZnO/CdS composites has two emission bands: an ultraviolet emission peak at 376 nm and a green emission around 523 nm. The conductance of the ZnO/CdS composites shows an enhancement compared with that of the uncoated ZnO. The appealing application of the ZnO/CdS composites as ethanol sensors is presented and a possible sensing mechanism is discussed.

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### Introduction

Over the past decades, nano materials have been the subject of enormous interest. These materials notable for their extremely small feature size have the potential for wide ranging industrial, biomedical and opto electronic applications. Fundamental physical, chemical, electronic, magnetic, and optical properties are also quite different at this nano level when compared to larger scale materials. Most of the recent research topics on developing Nanostructured materials fabrication for Opto-electronics application, with superior mechanical and optical properties are going on. Research is being done on nanosynthesis and nanostructural materials, which intends to explore new nanoscaled materials such as nano tube, nanowire, nano cones and nanosheets [1].

Surfaces and interfaces are also important in explaining nanomaterial behavior. In bulk material only a relatively small percentage of atoms will be at or near a surface or interface. In nano materials the small feature size ensures that many atoms perhaps half or more in some cases will be near interfaces. So that the surface properties such as energy level, binding energy, electronic structure and reactivity can be quite different from interior state and give rise to quite different material properties. The fast expected products with nanomaterials come in the areas of electronics, photonic, health and environment. Some of the products are already appeared in the above fields [1].

Ceramic oxide nanomaterials will be prepared by chemical route and these nanoscale materials are then self assembled into a larger

nanostructure system, by which new light sensor and solar cell is planned to be designed. ZnO have the special features over other metal oxides for sensor applications. ZnO with CdS in nanoscale enhanced efficiency about 15 times larger than that of original ZnO. The degree of improvements is dependent on impurity and defect concentration in original samples [2].

### Preparation of ZnO by Sol-Gel Method

ZnO is prepared by sol-gel method. 2-methoxyethanol and monoethanolamine were used as the solvent and stabilizing agent respectively. Monoethanolamine of 1.5gm and 55 ml of 2-methoxyethanol are mixed at room temp by magnetic stirrer. Zinc Acetate of 5.4gm was dissolved in a mixture of 2-methoxyethanol and monoethanolamine. The concentration of zinc acetate was 0.45 mol/liter and the molar ratio of monoethanolamine to zinc acetate was kept as 1:1. Then stirring the solution at 80° C temperature and reflux ion method is used for better homogeneity and avoids evaporation of mixture. After stirring the solution for one hour a homogeneous and transparent sol was obtained. [3], [4].

### Preparation of ZnO Thin films by dip coating method

ZnO thin film is formed on glass substrate by dip coating method. Glass substrate is immersed in the ZnO sol with pulling rate of 3cm/min. Then it dried at room temperature. This is followed by drying at 100° C for two hours.

### Sensitization with CdS

ZnO thin films on glass substrate which is already prepared by sol-gel process and dip coating is sensitized by CdS. CdS powder is dispersed in equal volume of chloroform and pyridine mixture.

After mixing it properly, a cleaned glass substrate is dipped in the mixture at the pulling rate of 3cm/min. Then it dried at room temperature. This is followed by drying at 100° C for two hours. As a result thin film of ZnO/CdS is formed on the substrate.

### Results and Discussion

#### Structural Characteristics of ZnO/CdS Composites

Figure 1a shows the X-ray diffraction (XRD) patterns of the uncoated ZnO nanorods. All the diffraction peaks can be indexed to the hexagonally structured ZnO with cell constants of  $a = 0.324$  nm and  $c = 0.519$  nm, which are consistent with the standard values for bulk ZnO (JCPDS Card No. 36-1451), revealing that the ZnO nanorods are crystalline with a hexagonal structure. No diffraction peaks from the other crystalline forms were detected. After the ZnO nanorods were sonochemically treated in an aqueous solution of cadmium chloride and thiourea, some additional diffraction peaks corresponding to the hexagonally structured CdS phase (JCPDS Card No. 41-1049) appear, revealing that hexagonally structured CdS is produced in the reaction mixture during the ultrasound irradiation. The broad nature of the CdS XRD peaks shows that the sizes of the CdS nanoparticles are very small. The diameters of the sonochemically generated CdS powders are about 8 nm (estimated from the Scherrer formula). The coating level of CdS in the ZnO/ CdS composites is 6% (weight percent) calculated from the XRD spectrum (Figure 1b). In Figure 2a, we present TEM images of the uncoated ZnO nanorods. It can be seen that the needlelike ZnO nanorods are smooth on the surface, usually 20-40 nm in diameter, and several microns in length. It is also found that the ZnO nanorods are single crystalline with hexagonal structures as determined by the selected-area electron diffraction (SAED) pattern (inset of Figure 2a). The TEM micrograph of the sonochemically generated CdS (Figure 2b) shows the presence of nanosized particles. The diameter distribution of the CdS nanoparticles is obtained using the statistical results of 20 particle sizes obtained during the TEM observation. It shows that the diameters of the CdS nanoparticles varied from 5 to 12 nm, with an average of 8.5 nm, in good agreement with the XRD results (~ 8 nm).

However, due to a strong tendency of aggregation, 18 many of the individual CdS

nanoparticles seem to be attached to each other to form particles with bigger sizes (20-50 nm), as shown in Figure 2b. The inset of Figure 2b shows the corresponding SAED pattern of the CdS nanoparticles. All the diffraction rings can be indexed to a hexagonally structured CdS phase, which is in agreement with the XRD results. Figure 3 shows typical TEM images of the ZnO/CdS composites. In comparison with Figure 2a, it can be seen clearly that ZnO nanorods have been coated with CdS nanoparticles with the aid of the ultrasound irradiation. The CdS nanoparticles are nearly spherical in shapes and show some aggregation. From Figure 3a-c, one can see that the individual ZnO nanorods have been coated with different amounts of CdS nanoparticles, from several particles (Figure 3a) to a beplastered layer (Figure 3c). A high-resolution TEM image (Figure 3d) shows an individual CdS nanoparticle closely attached on the ZnO nanorod core. The measured spacing of the crystallographic plane is 0.316 nm, which corresponds to the {101} lattice plane of a hexagonal CdS crystal. This states that the sonochemical growth of CdS nanoparticles is along the  $\langle 101 \rangle$  direction. Moreover, it can also be observed that the ZnO-CdS heterostructure possesses a very clean interface, revealing that the CdS nanoparticles are grown directly from the ZnO nanorod surface. No buffer layers, crystalline or amorphous, are observed in the interface regions.

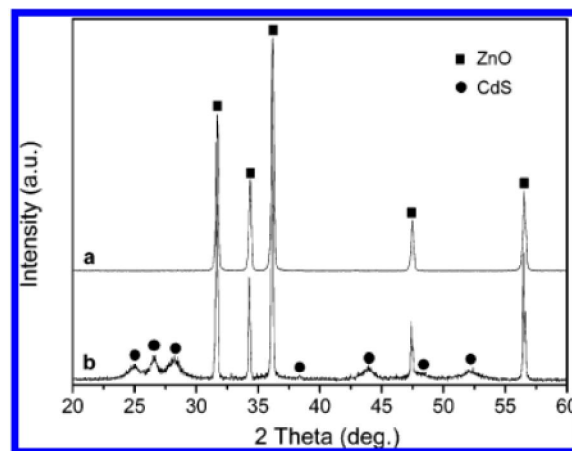


Figure 1. XRD patterns of (a) uncoated ZnO nanorods and (b) ZnO/CdS composites.

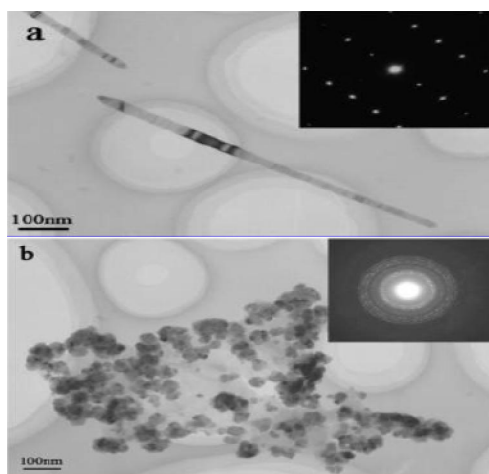


Figure 2. TEM images of (a) uncoated ZnO nanorods (inset, corresponding SAED pattern) and (b) sonochemically generated CdS powders (inset, corresponding SAED pattern).

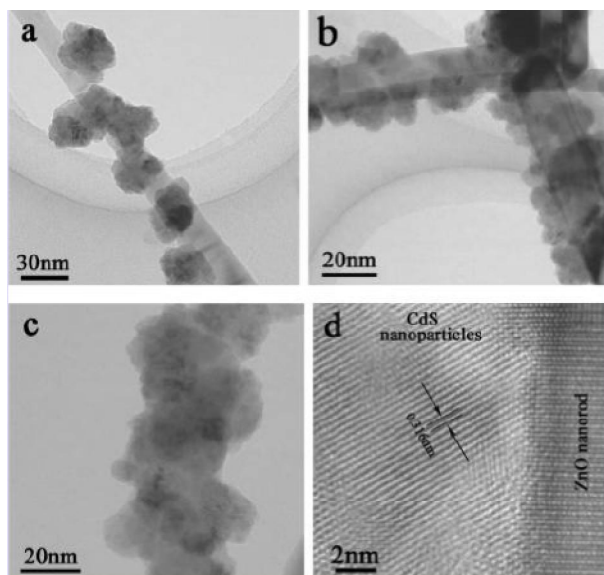


Figure 3. Typical TEM images of ZnO/CdS composites. (d) ZnO-CdS heterojunction interface.

#### Photoluminescence of ZnO/CdS Composites.

Figure 4 shows the room temperature photoluminescence (PL) spectra of sonochemically generated CdS nanoparticles, ZnO nanorods, and ZnO/CdS composites for comparison. The PL spectrum of the CdS nanoparticles (Figure 4a) show a broad emission band centered at 550 nm, which can be attributed to the emission from the defect states, such as cadmium interstitials or sulfur vacancies in CdS nanoparticles.<sup>18</sup> The PL spectrum of ZnO nanorods (Figure 4b) presents two emission bands. One is an UV emission peak at 382 nm, which corresponds to the near band edge emission of ZnO. The other is a broad visible emission band from

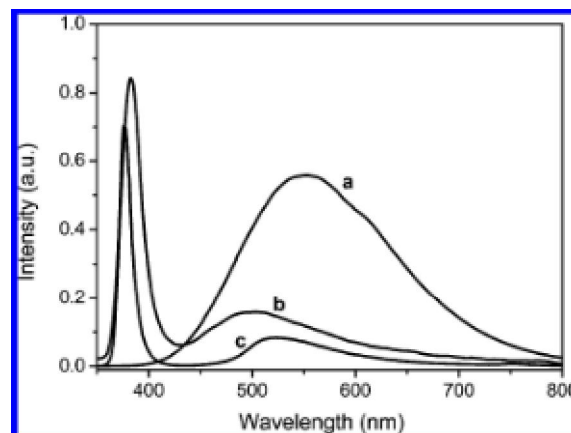


Figure 4. Room temperature PL spectra of (a) sonochemically generated CdS nanoparticles, (b) uncoated ZnO nanorods, and (c) ZnO/CdS composites.

450 to 600 nm with a peak at 500 nm, which has commonly been attributed to the oxygen vacancies of ZnO. [5,6] The PL spectrum of the ZnO/CdS composites (Figure 4c) is similar to that of the uncoated ZnO nanorods: a UV emission centered at 376 nm and a broad green emission peaked around 523 nm. In comparison with the uncoated ZnO nanorods, the ZnO/CdS composites show a small (~ 6 nm) blue shift in the UV region and a large (~ 23 nm) red shift in the visible emission. According to the structural characteristics of the ZnO/CdS composites, both the blue shift and the red shift in the PL spectrum could be attributed to the interaction between the two semiconductors of ZnO and CdS. In defect chemistry, ZnO is a well-known n-type ionic semiconductor originating from the intrinsic defects of oxygen vacancies. It is generally accepted that the chemical properties of oxygen and sulfur are similar to each other; consequently, the sulfur anions generated in the solution would have a tendency to be captured by the oxygen vacancies located mainly on the surface of ZnO nanorods.[5,6] Absorption of sulfur anions on the ZnO nanorods provides the initial nucleation sites for the surface growth of CdS nanoparticles, which is consistent with the TEM observation (see Figure 3d). The sulfur atoms can diffuse in further from the surface to the inner part of the ZnO nanorods, resulting a sulfur-doping effect in ZnO. An impurity atom in a semiconductor makes the choice of either a shallow donor in a substitutional site or a deep level via a lattice distortion. In the present case, it is reasonable that the sulfur dopants can act as singly charged donors in ZnO.[7,8,9] Due to the small density of states of ZnO near the conduction band minimum, the conduction band edge is filled by excessive carriers donated by

the impurities, leading to a blue shift of optical band-to-band transitions known as the Burstein-Moss (BM) effect. We suggest that a similar mechanism would be applicable to the blue shift in the UV region of ZnO/CdS composites in comparison with that of the uncoated ZnO. Moreover, it is understandable that the capturing sulfur atoms or CdS nanoparticles can greatly change the surface structures of the ZnO nanorods. For example, the oxygen vacancies in the surface area of ZnO nanorods will be annihilated with the absorption of sulfur atoms or CdS nanoparticles, which decreases significantly the 500 nm emission of the ZnO, as shown in Figure 4c. With the absorption of sulfur atoms or CdS nanoparticles, formation of new defect or surface states such as Zn-Cd-S, or Cd-Zn-O in the interface region of the ZnO-CdS heterojunction, [10] is expected to play an important role in the red shift in the visible region of the ZnO/CdS composites. However, details of these newly formed defect or surface states in the ZnO/CdS composites are not very clear at this stage.

#### Ethanol-Sensing Properties of the ZnO/CdS Composites.

Figure 5a shows the response curve of ZnO/CdS composites to 10 ppm ethanol vapors in air at an operating temperature of 300 °C. For comparison, the response curve of uncoated ZnO nanorods measured at the same conditions is also presented. The sensitivity ( $S$ )  $G_{\text{gas}}/G_{\text{air}}$  of these devices is defined as the conductance variation in air ( $G_{\text{air}}$ ) and in target gases ( $G_{\text{gas}}$ ). It is found that, at any concentration of ethanol vapors, the ZnO/CdS composites have a higher sensitivity than the uncoated ZnO nanorods, as shown in Figure 5b. Clearly, the ZnO/CdS composites feature an improved ethanol-sensing performance such as high sensitivity compared to the uncoated ZnO nanorods. The sensing mechanism of the ZnO-based gas sensors has been discussed in much literature.<sup>27,36</sup> The most widely accepted model is based on the modulation of the depletion layer by oxygen absorption. Oxygen from the ambient adsorbs on the exposed surface of ZnO and, extracting an electron from the ZnO conduction band, ionizes to  $\text{O}^-$  or  $\text{O}^{2-}$ ;  $\text{O}^-$  is believed to be dominant.[11] Consequently, depletion layers are formed in the surface area of ZnO, causing the carrier concentration and electron mobility (due to scattering) to decrease. When exposed to such reducing gases as ethanol, the ethanol molecules will react with the adsorbed  $\text{O}^-$ , releasing the trapped electron back to the conduction band, and then both the carrier concentration and carrier mobility of ZnO increase. Such a variation in the conductance of ZnO can be used to detect target gases, for both reducing and oxidizing.[12] One can

see that the gas sensitivity of a ZnO sensor is dominated by its conductance variations; therefore, the factors that can improve such variations can enhance its gas sensitivity. It should be pointed out that the absorption-desorption process of oxygen occurs also on the surfaces of CdS nanoparticles.<sup>37,38</sup> When the electrons in the conduction band of CdS are mostly trapped in its depletion layer, the amount of electrons injected from CdS into ZnO is small. In a reducing atmosphere, the amount of free electrons in the conduction band of CdS will increase greatly due to the oxygen desorption; consequently, the amount of injection electrons from CdS into ZnO increases simultaneously to achieve new thermal equilibrium at the interface of the ZnO – CdS heterojunction. This reveals that electron injection from CdS nanoparticle shells into ZnO nanorod cores at a reducing atmosphere is more efficient than that in air.

These additional electrons can enhance further the conductance of ZnO, resulting in an improvement of the gas sensitivity of ZnO/CdS composites in comparison with that of the uncoated ZnO.

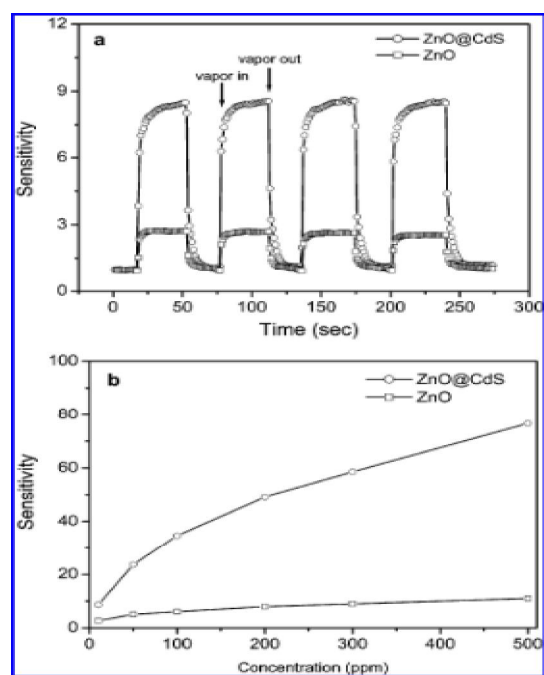


Figure 5. (a) Response curves of uncoated ZnO nanorods and ZnO/CdS composites to 10 ppm ethanol vapor in air. (b) Ethanol-sensing properties of uncoated ZnO nanorods and ZnO/CdS composites at various concentrations of ethanol vapors in air. Working temperature 300 °C.

## Conclusions

We have prepared (ZnO/ CdS) composites with core/shell-type geometry by ultrasonically irradiating a mixture of single crystalline ZnO, cadmium chloride, and thiourea in an aqueous medium for 2 h. It is found that the interaction between the ZnO and the CdS nanoparticle greatly influences the optical and electrical properties of the obtained ZnO/CdS composites. The method used in this paper can be exploited to other materials systems, which will offer promising opportunities for the design and fabrication of new optoelectronic devices such as highly sensitive gas sensors.

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