

# Enhanced Photocurrent from CdS Sensitized ZnO Nanorods

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**Abstract** – Structure and optical properties of cadmium sulphide-zinc oxide composite nanorods have been evaluated by suitable characterization techniques. The X-ray diffraction spectrum contains a series of peaks corresponding to reflections from various sets of lattice planes of hexagonal ZnO as well as CdS. The above observation is supported by the Micro-Raman spectroscopy result. The optical reflectance spectra of CdS-ZnO is compared with that of ZnO where we observe an enhanced absorption and hence diminished reflection from CdS-ZnO compared to that from only ZnO. A very small intensity of the visible photoluminescence peak observed at 550 nm proves that the ZnO nanorods have very low concentrations of point defects such as oxygen vacancies and zinc interstitials. The photocurrent in the visible region has been significantly enhanced due to deposition of CdS on the surface of the ZnO nanorods. CdS acts as a visible sensitizer because of its lower band gap compared to ZnO.

**Keywords:** Nanorod, Composite nanostructures, Raman spectrum, Photocurrent

## 1. Introduction

Arrays of crystalline ZnO nanorods have been utilized as transparent electrodes in photovoltaic cells [1] and photo electrochemical cells [2] because their higher surface areas and vertically aligned electrical pathways are expected to increase the efficiency of those photoelectric devices. However, the efficiency of such a device as a solar cell is hindered because being a wide band gap semiconductor, ZnO itself cannot absorb and utilize the visible region of the solar spectrum (>420 nm) and less than 4 % of the solar radiation is in ultraviolet region. In order to absorb visible light and generate electron-hole pairs, ZnO nanorods should be coupled to a narrow band gap sensitizing material. Early researchers have used organic dye molecules and inorganic quantum dots for visible sensitization in ZnO nanorod array electrodes for solar cell applications [3]. CdS has the same crystal structure as that of ZnO, its band gap (2.4 eV) is in the visible region and it can be synthesized by a simple and inexpensive chemical bath technique. Several researchers have reported various types of CdS sensitized semiconductor nanostructures and most of those studies have focused on CdS/TiO<sub>2</sub> hetero-nanostructures for photo energy conversion applications, such as photocatalysts and solar cells [4]. However, to our knowledge, a few articles related to synthesis, characterization and application of CdS sensitized ZnO nanorods have so far been reported. One of the most recent

reports includes the interesting results reported by Han et. al. where the authors have successfully fabricated CdS quantum dot sensitized ZnO nanorod based solar cell with power conversion efficiency of 0.54 % [5]. In this way, the above system has been a topic of greater interest for today's researchers. In this article, we report a solution based two-step process for growth of CdS-ZnO composite nanorods followed by evaluation of their structure, optical and photoelectrical properties by suitable techniques.

## 2. Experimental

CdS-ZnO composite nanorods were deposited on Indium Tin Oxide (ITO) substrate by a two step growth method. Initially, a seed layer of ZnO was grown on ITO by electro-deposition. 10 ml of 0.01 M Zn(NO<sub>3</sub>)<sub>2</sub> was mixed with 10 ml of 0.01 M (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> and the solution was stirred for one hour at 62 °C. With above solution mixture as the electrolyte, the electro-deposition was carried out in a three-electrode cell with a platinum plate as the anode, a saturated calomel electrode as the reference electrode and an ITO/quartz as the cathode. After 1 minute of electro-deposition at -1.4 V, under potention-static condition, the sample was thoroughly rinsed in de-ionized water ( $\rho=18$  M $\Omega$ .cm) and dried in a regular laboratory oven at 50 °C for one hour. Subsequently, the sample was annealed at 500 °C for 20 minutes in N<sub>2</sub> atmosphere. For the deposition of ZnO nanorods, the seeded sample was immersed in a screw capped laboratory pyrex bottle containing an aqueous solution mixture of 10 ml of 5 mM Zn(NO<sub>3</sub>)<sub>2</sub> and 10 ml of 5 mM (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>, and the mixture was refluxed inside a laboratory oven for 12 hours at 95 °C. After 12 hours, the bottle was taken out, cooled to room temperature and opened. The sample was thoroughly rinsed in the de-

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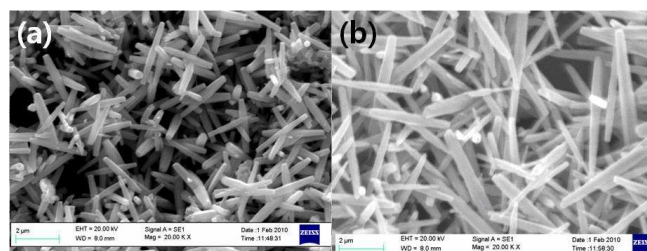
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ionized water to dissolve the surfactant and the residual salt and dried in a regular laboratory oven at 50 °C for 6 hours. In order to deposit CdS on the surface of the nanorods of the ZnO, we followed a chemical bath deposition method. The ZnO nanorod assembled thin film was dipped in an aqueous solution mixture of 0.1 mM Cd(CH<sub>3</sub>COO)<sub>2</sub> and 0.2 mM (NH<sub>2</sub>)<sub>2</sub>CS, maintained at 60 °C, under continuous stirring. Three sets of samples were prepared with deposition time of 20, 45 and 60 minutes. The last sample (time of deposition 60 minutes) was chosen for SEM, XRD, absorption, photoluminescence and Raman scattering study. After deposition, the samples were dried at 50 °C for 10 minutes. In order to improve the crystal quality of the CdS-ZnO composite structure, the sample was annealed at 250 °C in N<sub>2</sub> atmosphere for 30 minutes. The annealing temperature was restricted to 250 °C in order to avoid agglomeration of the nanorods. The SEM micrographs were recorded with a JEOL JSM 3010 field emission SEM with resolution 40 nm. The X-ray diffraction was carried out with a Philips X'pert diffractometer in the low angle configuration. The UV-VIS absorption of the samples was recorded with an Optizen 3220 spectrophotometer. The photoluminescence (PL) was carried out at room temperature (300 K) with a He-Cd laser ( $\lambda = 325$  nm) as the source of excitation. A PMT detector with a lock-in amplifier and a chopper was used for detection of the PL signal. The micro-Raman spectrum was recorded with a JY Raman spectrometer equipped with an argon laser, a Ramnour double monochromator (resolution, 1 cm<sup>-1</sup>) and an LN<sub>2</sub> cooled CCD detector. The laser power was maintained at 5mW in order to avoid any thermal degradation of the sample. In order to measure the photo current, a photo-electrochemical cell was designed with CdS-ZnO/ITO as the cathode, platinum anode, a saturated calomel electrode as the reference electrode and a mixture of aqueous solutions of 1 M KCl and 0.1 M Na<sub>2</sub>S as the electrolyte. The light source was a 300 W halogen lamp with spectral range from 420 nm to 800 nm.

### 3. Results and Discussion

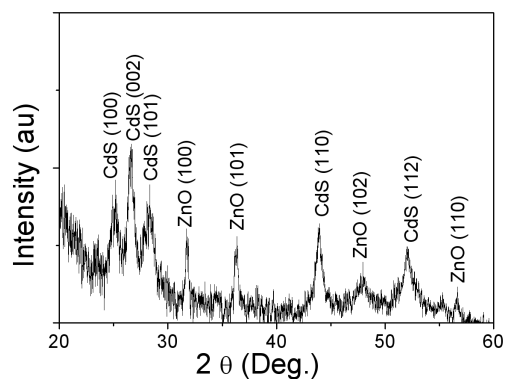
Fig. 1(a) shows the SEM micrograph of ZnO nanorods, randomly oriented but densely packed on conducting ITO substrate. The diameter of the nanorod is at least 100 nm and length is at least 5 microns. The orientations of the nanorods could not be controlled because of structural mismatch between polycrystalline ITO and hexagonal ZnO. The interfacial seed layer of electrodeposited ZnO was not effective enough to provide well isolated nucleation centers required for successful growth of aligned nanorods [6]. The shape of the tip of the nanorod depends on the rate of growth along different crystallographic directions. The above is determined by the temperature of the reaction medium. Usually, hexagonal tips are formed at higher temperature [7], however, we got a mixture of hexagonal

and sharp tipped nanorods. Fig. 1(b) shows the SEM image of the same sample after CdS deposition followed by annealing. The time of deposition of CdS was 60 minutes for this sample. Small increases in the diameters of the nanorods have been observed and the contrast of the image has remarkably changed because of CdS layers deposited on the surface of the nanorods.

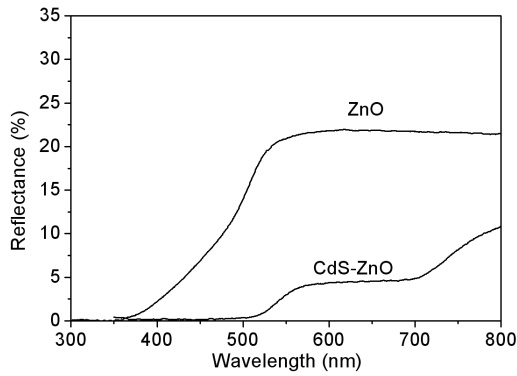


**Fig. 1.** Scanning Electron Microscopic image of (a) ZnO nanorods and (b) CdS-ZnO composite nanorods (CdS deposition time 60 min.) grown on ITO coated quartz substrate by an aqueous chemical growth technique.

Fig. 2 shows the low angle X-ray diffraction (XRD) spectrum of CdS-ZnO composite nanorods where one can observe a series of peaks corresponding to hexagonal CdS and ZnO. The time of deposition of CdS was 60 minute for the above sample. XRD peaks corresponding to the reflections from (100), (101), (102) and (110) planes of hexagonal ZnO and that corresponding to the reflections from (100), (002), (101), (110), (102) and (112) planes of hexagonal CdS are clearly observed in the spectrum. The peaks from CdS have higher FWHMs compared to that from ZnO which could be attributed to presence of ultra small CdS particles. The intensity of CdS peak is expected to be higher than that from ZnO because CdS forms the top layer of the sample. The intensity of the XRD peak with respect to the background is observed to be weak because of higher surface roughness of the sample. The surface roughness of our sample is believed to be high because the CBD grown CdS could not form a continuous layer on



**Fig. 2.** Low angle X-rays diffraction spectrum of CdS-ZnO composite nanorods deposited on ITO substrate.



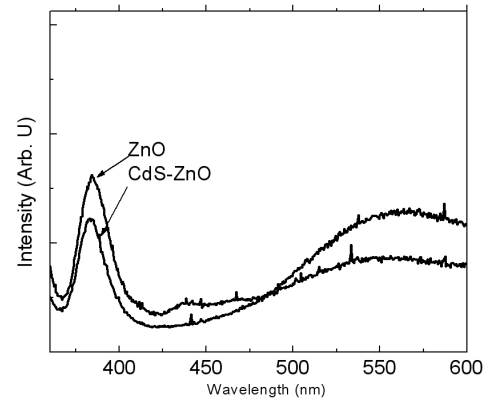
**Fig. 3.** UV-VIS reflectance spectra of ZnO nanorod and CdS-ZnO composite nanorods.

ZnO nanorods [8]. We did not observe any structural transformation of either ZnO or CdS. The XRD peak corresponding to any compound (alloy) formation because of diffusion of Cd or S component from the surface into the ZnO lattice was not observed either.

The UV-VIS reflectance of ZnO and CdS-ZnO composite samples are shown in Fig. 3. Here, one can clearly observe a red shift of optical absorption onset of CdS-ZnO composite with respect to that of only ZnO.

The magnitude of reflectance for ZnO is significantly higher than that of CdS-ZnO because the absorption in the visible range has been enhanced due to the CdS (band gap in visible region) coating on the surface of the ZnO nanorod.

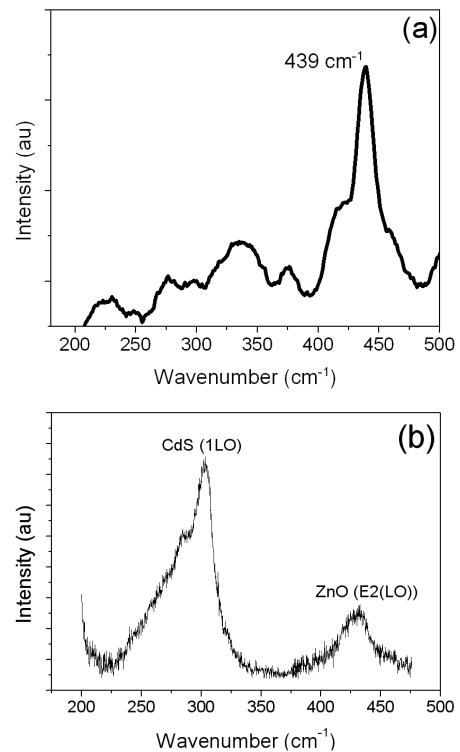
Room temperature (300 K) photoluminescence spectra of ZnO and CdS-ZnO have been displayed in Fig. 4. The time of deposition of CdS was 60 minute for the above CdS-ZnO sample. The well known ultraviolet (UV) peak occurring at about 380 nm corresponds to decay of free excitons in ZnO whereas the broad visible luminescence observed at about 550 nm corresponds to the point defects in ZnO such as oxygen vacancies. Two peaks with extremely small intensities are observed at 440 nm and 470 nm. The above blue luminescence could be attributed to zinc interstitials as observed by early researchers [9]. The intensity ratios between the UV peaks to the visible peaks, roughly estimated by gaussian fittings, were observed to be 2.15 and 0.64 for ZnO and CdS-ZnO respectively. In case of ZnO nanorods, the defect luminescence in the green-yellow region has been significantly suppressed indicating a small volume density of point defects. However, in case of CdS-ZnO nanorods, the visible luminescence is observed to be more intense than the UV luminescence. The enhancement in the visible luminescence is attributed to the well known yellow emission from surface CdS originating from its point defects such as cadmium interstitial and sulfur vacancies [10, 11]. Although the luminescence due to free exciton decay in CdS occurs at 515 nm, for microcrystals and nanocrystals of CdS, the room temperature luminescence is always dominated by a broad emission attributed to surface defects [12]. In case of



**Fig. 4.** Photoluminescence spectra of ZnO nanorod and CdS-ZnO composite nanorod

our samples, since CdS has a free surface and there is a strong probability of sparse deposition of fine CdS particles on the surface of ZnO nanorod, therefore we expect the defect luminescence to be broad enough to engulf the free exciton emission.

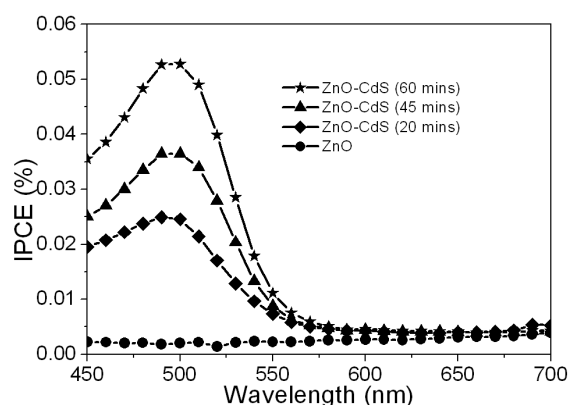
In order to confirm the co-existence of crystalline CdS and ZnO, we carried out micro-Raman spectroscopic study. Fig. 5 shows the Raman spectra of the samples before and after CdS deposition. For the above CdS-ZnO sample, the CdS was deposited for 60 minutes. For all Raman spectra, the background correction was performed with the LABSPEC3 software supplied with the system. Before CdS deposition, one sharp peak corresponding to E2 (LO)



**Fig. 5.** Micro-Raman spectra of (a) ZnO nanorod and (b) CdS-ZnO composite nanorods.

mode of hexagonal ZnO is observed at  $439\text{ cm}^{-1}$  [13], whereas after CdS deposition, one can observe a couple of peaks at  $301\text{ cm}^{-1}$  and  $438\text{ cm}^{-1}$ . The peak at  $301\text{ cm}^{-1}$  corresponds to 1LO from hexagonal CdS [14]. The peak exhibits an inhomogeneous broadening towards the lower wave number region which evidences the presence of ultra small CdS nanoparticles. The Raman spectrum from CdS-ZnO composite sample has lower signal to noise ratio compared to that from ZnO because of increased surface roughness after CdS deposition. The broad peak at  $438\text{ cm}^{-1}$  corresponds to E2 (LO) mode of hexagonal ZnO. Due to deposition of CdS, the Raman intensity from ZnO decreases with increase in the FWHM. The reduction of intensity is expected because of scattering in the CdS nanocrystals attached to the ZnO nanorod. However, the red shift and the inhomogeneity are not yet well understood. Since the diameter of the nanorod is at least 100 nm, there can be no phonon confinement effect. The only reason for the inhomogeneity in the peak could be a lattice strain at CdS/ZnO interface.

Fig. 6 compares the photo current action spectra of nanorod assembled thin film of CdS-ZnO with that of only ZnO. The spectrum of ZnO is completely flat in the visible region because ZnO cannot absorb visible light due to its wide band gap ( $E_g = 3.37\text{ eV}$  corresponding to 367 nm). The incident photon to current conversion efficiency (IPCE) is almost constant and its magnitude is less than 0.005 when the wavelength of the exciting radiation varies through the visible range (450 nm-700 nm). However, for the CdS-ZnO samples there is a drastic change in the nature of the spectra. Due to visible sensitization by the surface CdS layer, the IPCE has been significantly enhanced. As shown in the Fig. 6, the IPCEs for three sets of CdS-ZnO nanorod assembled thin film samples vary from 0.022 to 0.055 which are about 10 to 30 times that of the ZnO nanorod assembled thin film at an exciting wavelength of 500 nm. For a typical CdS-ZnO nanorod assembled thin film sample one can observe a wide band covering almost 50 % of the visible region. The IPCE starts shooting up at about 550 nm, peaks at 500 nm and then decreases slowly towards the lower wavelength region. The wavelength at which the IPCE starts increasing corresponds to the band gap of CdS. In the lower wavelength side ( $<500\text{ nm}$ ) the decrease in IPCE could be attributed to two possible reasons. (1) Saturation of absorption due to the large absorption cross-section for most of the materials in the UV region compared to that in visible region leads to lower effective IPCE. (2) The penetration of the UV radiation suffers due to scattering at lower wavelength and significant absorption of UV by ITO substrate [15]. Fig. 6 shows the spectra for three sets of samples synthesized at three different experimental conditions. With increase in the time of deposition of the surface CdS layer, the IPCE increases which suggests a strong sensitization effect attributed to CdS.



**Fig. 6.** Incident photon-to-current conversion efficiency curves of ZnO nanorods and CdS-ZnO composite nanorods.

Since the source of excitation is a halogen lamp (visible radiation), the carrier generation is possible in the CdS only. Once the carriers (electron-hole pairs) are generated in CdS, the electrons are instantaneously transferred from the conduction band of CdS to the conduction band of ZnO with a characteristic lifetime of  $10^{-15}\text{ sec}$ . [16]. Since there is no hole in the valance band of ZnO available for recombination, an efficient charge separation is achieved in CdS-ZnO composite. The separation lengthens the carrier lifetime. The concentration gradient is responsible for a diffusion type photo current in the external circuit in absence of any external bias. With increase in the time of deposition of CdS, the photocurrent increases. Thicker is the CdS layer, higher is the concentration of the photo generated carriers and hence higher is the IPCE. The band gap of the bulk CdS is 2.24 eV which corresponds to the wavelength of 500 nm. The observed band gap is lower than that of bulk CdS because of the surface states responsible for tunneling of conduction band electrons. The above observation demonstrates a successful generation of the electron-hole pairs in the CdS and consequent transfer of the electrons from the conduction band of the CdS to the conduction band of the ZnO. We are hopeful, in near future, to study the photovoltaic efficiency of the above composite.

#### 4. Conclusion

CdS-ZnO composite nanostructures have been synthesized by a two step aqueous chemical bath deposition technique. In the composite, both the components co-exist in their hexagonal phases without any phase mixing or alloying. The visible sensitization by a low band gap semiconductor such as CdS gives rise to an enhanced absorption and improved photocurrent which promises an efficient photovoltaic and catalytic application of the CdS-ZnO composite nanostructures.

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