A comparative study on the CDS sensitized and dye-sensitized ZnO photoelectrodes based on solar cell performance

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Abstract
Semiconductor sensitized solar cells (SSSCs) based on hetrostructure of CdS/ZnO electrode and dye sensitized solar cell (DSSC) based on ZnO-Eosin-Y was fabricated. The CdS thin film was deposited onto ZnO layer by chemical bath deposition method. The structure, morphology, optical study of CdS/ZnO film and the solar cell performance of CdS/ZnO and ZnO-Eosin-Y PEC cell were investigated. The CdS, ZnO and CdS/ZnO onto glass and titanium substrates were characterized by X-ray diffraction, atomic force microscopy, UV-vis spectroscopy. XRD shows that the films grown along the preferential directions. The crystallite size is calculated as 7 nm and 10 nm for ZnO and CdS films respectively using Scherrer’s formula. Photoelectrochemical (PEC) investigations were carried out using cell configuration as n-CdS/(1M NaOH + 1M Na2S + 1M S)/C. For dye-sensitized solar cell application, the dye-sensitized solar cell structure based on ZnO as a photo electrode was FTO/ZnO/Eosin-Y/electrolyte/Pt counter electrode. The photovoltaic output characteristics were used to calculate fill-factor (FF) and solar conversion efficiency ($\eta$). The CdS/ZnO hetrostructure film used for photoelectrochemical solar cells exhibited an energy conversion efficiency of about 1.08% at light intensity of 100 mW/cm².

Keywords: Thin films, CdS/ZnO, PEC cell

1. Introduction
Increasing petroleum price, huge energy demand and global warming has fueled the intensive search for alternative energy and technologies. Photovoltaic provide clean energy that can reduce world’s dependency on traditional energy resources. The major barrier for the large-scale use of solar energy is the high cost of existing solar cells. By utilizing oxide and inorganic materials, the cost of existing solar cell can be minimized at some extent. Several oxide materials including TiO₂, ZnO, SnO₂, CuO, NiO, In₂O₃ etc have been employed in dye sensitize solar cell. All these materials have band gap on the order of 3.0 eV. Calculations show that a band gap in the range of 1eV to 1.5 eV is highly desirable in optimized solar cells [1]. Wide band gap materials can absorb only few percent of solar spectrum in UV region result in low efficiency. One promising solution to this impasse is to anchor narrow bandgap sensitizers such as organic dyes or inorganic semiconductor onto the wide bandgap nanomaterials in order to enhance light harvesting in the visible 400–800 nm region, which encompasses much of the wavelength range of the incident solar flux. Compared to organic dyes, the use of inorganic semiconductor has several advantages such as higher light absorption and tailoring of optical absorption over a wider wavelength range [2]. Cost-effective photoelectric materials that could utilize visible-light irradiation efficiently are greatly desired. Narrow band-gap semiconductors such as CdSe [3] PbS [4], PbSe [5], InP [6] have been demonstrated as low-cost sensitizers for large band-gap semiconductors. The heterostructures of the two kinds of semiconductors can utilize visible light and own high surface-to-volume ratio. The heterostructures have been widely used for solar cells and as photocatalyst working under visible-light irradiation.

In comparison with the different techniques Chemical bath deposition (CBD) method is more suitable for preparing oxide and inorganic materials as it doesn’t require sophisticated instrument at a relatively lower temperature. In present work, we have tried out to prepare CdS thin film directly by
CBD instead of sequential chemical deposition, which not only help to reduce waste of materials but also save the time. Since ZnO has a tendency that it gets dissolve in water, therefore by optimizing the CBD parameters like pH of bath, temperature and time we have prepared CdS layer onto ZnO at low cost at some expense of ZnO and the results of their characterization by microstructural, optical and photoelectrochemical (PEC) studies.

2. Experimental
All the chemicals used in this work were of analytic grade and used without further purification. ZnO film of nanocrystallites was prepared by CBD technique [7], on transparent plastic sheet, FTO (fluorine-doped SnO2) glasses and titanium (Ti) substrates. To prepare ZnO thin films NH3 solution (25%) was added in an aqueous solution of 0.1 M Zn(NO3)2 under constant stirring. To this solution the H2O2 (30 vol.%) was added. The pH of total solution was maintained at ~12 by addition of excess NH3 solution. Before deposition of the substrates were cleaned with ethanol, glassware detergent and diluted hydrochloric acid, and then rinsed with water. The precleaned substrates were kept vertically in the bath and rotated continuously by motor with speed of 72 rpm. The films were prepared onto different substrates such as plastic, titanium (Ti) and glass substrates at 333K. Thereafter thin films of CdS were prepared by using reagents Cd(NO3)2, NH3 solution (25%) and thiourea onto ZnO Films as reported earlier [8]. The structural characterization of films was performed by an X-ray diffractometer (Rigaku rotating anode H-3R) using Cu Kα radiation taken from 10° to 60°. The surface morphology of the film was characterized by atomic force microscopy (AFM; DIAFM-4). The absorption data in the range 300–700 nm were obtained with Shimadzu (1800) spectrophotometer. Photoelectrochemical (PEC) cell was fabricated using a two electrode configuration, comprising CdS/ZnO thin film as photoelectrode and graphite as a counter electrode. The redox electrolyte was an aqueous solution mixed of 1M NaOH + 1M Na2S + 1M S. Adsorption of the dye on the ZnO surface was performed by refluxing the ZnO electrode in 0.58 mM dry acetone solution of Eosin-Y (C20H6O5Br4Na2) at 30°C for 24 h, resulting in a photoelectrode. The apparent surface area of the dye-adsorbed ZnO electrode was 1.0 cm X 1.0 cm. A pure platinum plate was used as a counter electrode. The dye-sensitized ZnO electrode was incorporated into a thin-layer sandwich-type solar cell with a 50 mm-thick plastic sheet as a spacer. The electrolyte solution, a mixture of 0.03 M I2 + 0.3M LiI in an ethylene carbonate, was introduced between the ZnO and counter electrodes. The photovoltaic output power characteristics of photoelectrodes were measured under 100 mW/cm2 light illumination intensity. Intensity of light was measured by solar power meter (Tenmars Brand Model TM-207). Photovoltage and photocurrent of PEC solar cell was measured by Digital Multimeters (Tektronix DMM 4020).

3. Results and discussion
3.1 Structural properties
Fig. 1 shows the XRD patterns of the ZnO films deposited at 333K by CBD method. Diffraction pattern was obtained with 2h from 10 to 60°. The films deposited at 333K show (002) preferred orientation. The most prominent (002) peak for the film is observed at around 34.02°. The film prepared under these conditions show strong c-axis (002) orientation growth. The peak intensity of the films deposited 333K is broad and strong, which indicates the good crystal quality. It is due to the fact that the crystallite size for the film is small. It is also confirmed the nanocrystalline nature of the film. The XRD pattern of the deposited film shows that the film is crystallized in the hexagonal phase with a preferential orientation along the c-axis. Fig. 2 shows the X-ray diffraction (XRD) pattern of CdS thin film prepared onto glass substrate at 60°C for 15 min. It is evident from the figure that film is perfect crystalline with broad hump, which is due to the amorphous glass substrate. The spectrum showed various diffraction peaks at 2θ values of 26.72, 44.34 and 52.2. The peaks were identified to originate from (111), (220) and (311) planes of cubic phase of CdS respectively with a preferential orientation along the (111) plane.
The grain size, D, was estimated from the full width at half maximum (β) of the dominant (002) peak using Scherrer’s equation [9]:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where β, λ, and θ are the full-width at half maximum (FWHM) of the diffraction peaks, wavelength of the X-ray source and Bragg’s angle respectively. The calculated values of grain size are 7 nm and 10 nm for ZnO and CdS films respectively.

### 3.2 Morphological studies
The 3D view of the ZnO film over a scanning area of 10X10 µm and that of CdS film over scanning areas of 5X5 µm are shown in Fig. 3 (a) and (b). The image of films reveals the aggregation of the crystallites to form large clusters, which covers entire surface of the glass substrate, as can be seen from the figures. The smoothness of surface of the film was found to decrease in case of CdS film.

### 3.3 Optical study
Optical studies were performed by measuring the absorbance of the films prepared on substrates in the wavelength range 300-700 nm by subtracting the absorbance of the substrate, which was taken as a reference. Fig. 4 shows the absorbance spectra of the films of CdS and ZnO. A good PEC performance of semiconductor sensitized solar cells (SSSC) depends on better light harvesting by the semiconductors. The CdS/ZnO system can absorb visible light in the range of 300–600 nm wavelengths with a broader absorption range in the visible and ultra violet region of the spectrum as compared to CdS and ZnO film.

### 3.4 Solar cell performance
Fig. 5 shows the photovoltaic output characteristics of the CdS/ZnO heterostructure and dye loaded ZnO photoelectrode grown with CBD under the illumination at 100 mW/cm². The conversion efficiency η (in %) was calculated from the relation
\[ \eta = \frac{V_{\text{max}} I_{\text{max}} FF}{P_{\text{input}}} \times 100 \]

where \( P_{\text{input}} \) is the input light energy (in mWcm\(^{-2}\)). The FF was calculated from the relation--

\[ FF = \frac{V_{\text{max}} I_{\text{max}}}{V_{\text{oc}} I_{\text{sc}}} \]

where \( I_{m} \) and \( V_{m} \) are values of maximum current and voltage that can be extracted from photovoltaic output curve. The photoelectrochemical (PEC) parameters such as short-circuit current density \( (I_{\text{sc}}) \), open circuit voltage \( (V_{\text{oc}}) \), fill factor \( (FF) \) and the overall power conversion efficiency \( (\eta) \) which determined from the measured J–V curves are 6.013 mA, 350 mV, 0.51 and 1.08% respectively for CdS-ZnO system. Besides, for ZnO-Eosin-Y based system the PEC parameters short-circuit current density \( (I_{\text{sc}}) \), open circuit voltage \( (V_{\text{oc}}) \), fill factor \( (FF) \) and the overall power conversion efficiency \( (\eta) \) are 3.79 mA, 410 mV, 0.49 and 0.82% respectively. In both systems the charge separation processes have different mechanism. In CdS-ZnO based system the charge separation occurs through photovoltaic phenomenon. When light incident on to such a cell electrons are generated and electric field exist at the junction separates electron-hole pairs [10]. But in case of ZnO-Eosin-Y system, dye gets exited upon illumination the cell which injects an electron into the conduction band of semiconductor. The detail phenomenon of charge separation can be seen in the literature as described by Huang et al. [11]. The superior performance of CdS-ZnO based system could be due to larger fraction of light absorb in the visible region. Apart from this, CdS not only excite the ZnO but it also a super candidate as window material in hetrostructure solar cells.

4. Conclusions

Hetrostructure of CdS/ZnO and ZnO thin films was synthesized by a low cost chemical bath deposition (CBD) approach to improve the photovoltaic performance of (SSSC). The structure, morphology and optical study of CdS/ZnO, ZnO electrode and the solar cells performance of CdS/ZnO and ZnO-Eosin-Y cell were investigated. XRD of the film exhibits good crystallinity with the preferential orientation. AFM images show the cluster of small particles which covers the substrate well. UV-vis spectroscopy shows that CdS/ZnO system can harvest more light from the visible spectrum which enhance the efficiency of solar cell. The chemically synthesized CdS/ZnO photoelectrode yields 1.08% power conversion efficiency in the polysulfide electrolyte which is larger than the ZnO-Eosin-Y photoelectrode.

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References