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CdS quantum dot sensitized zinc oxide based solar cell with aluminum counter electrode

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High cost conducting metals such as Au or Pt are generally used as counter electrodes in quantum dot sensitized solar cells. In this article, we report working of a CdS quantum dot sensitized ZnO thin film solar cell, having FTO as working electrode and aluminium as counter electrode. The CdS quantum dots are prepared by simple low cost chemical technique and characterized by absorption spectroscopy, X-ray diffraction, atomic force microscopy and high resolution trans electron microscopy. These quantum dots are used as an active layer in a solar cell and current density–voltage characteristic of the solar cell is obtained under white light illumination and dark conditions.

Keywords: CdS quantum dots, solar cell, Al counter electrode.

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1. Introduction

The Shockley-Queisser limit predicts that due to thermodynamic limitations, the conversion efficiency in solar cells cannot exceed $\sim$ 32 % for single junction devices [1]. There are few methods for overcoming this upper limit, such as generating multiple electrons per photon, hot carrier extraction and the use of multiple layers, such as tandem devices [2]. Among various wide band gap semiconductors, TiO_2 and ZnO are widely used in photovoltaic cells because of their high carrier mobilities and energy levels [3]. In this context, ZnO is better suited as an active layer because the nanostructures can be easily formed and it has a large diffusion coefficient [4]. Quantum dots are used as sensitizing materials in solar cells because of their unique properties such as large absorption coefficient, size tunable band gap, quantum confinement, large extinction coefficient which are beneficial for photosensitization purposes [5]. Size-tuned QDs can be incorporated in the fabrication of tandem and multijunction cells for improved utilization of the full solar spectrum [6]. In particular, CdS QDs have been used in the fabrication of devices because of their direct band gap electronic structure and broad light harvesting capability, spanning the UV, visible, and NIR regions of the spectrum [7].

The counter electrode plays a crucial role in the efficient working of solar cells. But commonly used counter electrode materials in QDSSCs suffers from major disadvantages. For example, platinum suffers from oxidation, migration, loss of active surface area which can 'poison' the oxide, reducing its activity and efficiency [8]. On contrary, though gold plated electrodes improve efficiency to certain extent in comparison to platinum, but it also suffers from the surface poisoning problem [9, 10]. Also, the high cost and purity requirement of platinum or gold makes them a less practical material for photovoltaic applications. Furthermore, carbon electrodes are a popular choice as counter electrode in Perovskite solar cells only, and are not compatible with QDSSCs. The polysulfide electrolyte that is employed as a redox electrolyte in quantum dot sensitized solar cells provides stability to the photoanode but introduces significant redox limitations in carbon based counter electrode through undesirable surface reactions [11]. In the present work aluminum (Al) metal plates has been explored as counter electrode instead of the commonly used electrode materials for QDSSC. Al does not suffer from surface poisoning problems and is compatible with polysulfide electrolytes. Also as an added advantage, Al is a cheap and readily available metal and thus can be considered a more practical and economic alternative counter electrode material for low cost photovoltaics.

In this work, we fabricated a Quantum Dot Solar cell with ZnO oxide layer and CdS as the sensitizing QD layer and aluminum plates as the counter electrode. The general structure and working of a QDSSC is shown in Fig 1. The colloidal quantum dots were synthesized using polyvinyl alcohol (PVA) as capping layer as it restrains the QD size growth during synthesis. Quantum dots were studied using UV-VIS, XRD, AFM and TEM. The current density v/s voltage characteristics of the QDSC were obtained and solar cell parameters such as open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor (FF) and power conversion efficiency (PCE) values were calculated from it.

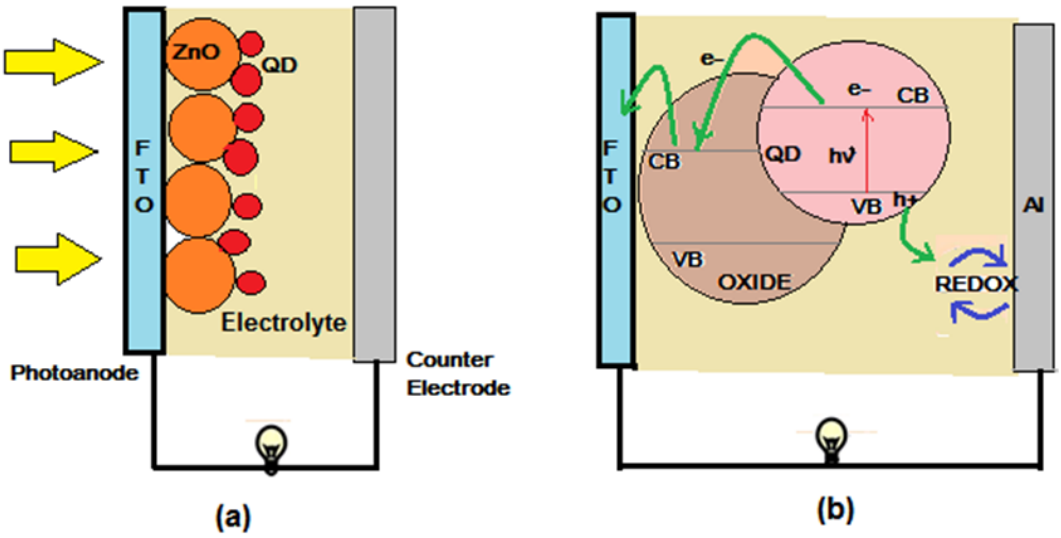


FIG. 1. (a) General structure and (b) working of a typical QDSSC

2. Experimental

2.1. CdS quantum dot synthesis

To synthesize CdS quantum dots by chemical route via one pot synthesis, 8 g of PVA were dissolved into 120 ml double distilled water. This mixture is taken in a three necked flask fitted with thermometer pocket and N_2 inlet. The solution was stirred in a magnetic stirrer at a rate of 200 rpm at a constant temperature of 70 °C for 5 hours. Thus, a transparent water solution of PVA was prepared. Similarly, a $CdCl_2$ solution was prepared by dissolving 7 g of $CdCl_2$ in 100 ml double distilled water. The solutions were degassed by N_2 bubbling for 3 – 4 h. Next, the PVA and $CdCl_2$ solutions were mixed and few drops of HNO_3 is added to the mixture followed by moderate stirring while an aqueous solution of Na2S was added slowly by means of a dropper until the whole solution turned yellow. The precipitate was filtered out and washed with de-ionized water multiple times to remove the traces of PVA. This solution is kept in darkness at room temperature for 14 hours for its stabilization.

2.2. QDSSC fabrication

Zinc Accetate and Sodium Sulfide (Na_2S) were mixed in ethanol to obtain ZnO, which was then deposited on conductive FTO coated glass (resistivity $<$ 10 Ohm/sq.) by using tape template method and doctor's blade technique. Then it was heated at 80 °C and annealed at 450 °C. Next, the ZnO coated glass plates were coated by immersion in the previously prepared CdS quantum dot solution to form CdS QD layer on the oxide by chemical bath deposition (CBD).

A polysulfide electrolyte solution was prepared by mixing 2M Na_2S and 3M S solutions [12]. A few drops of polysulfide solution were then added to the ZnO–CdS deposited FTO plate and then it was sandwiched with a thin aluminum plate, with thin glass cover slip spacers in between. The aluminum plate acted as a counter electrode and it was held together with the glass plate with adhesive tape and clips. Two metal crocodile clips were connected, with one to the FTO plate and the other to the aluminum plate.

3. Characterization

X-ray diffraction (XRD) patterns were obtained with a Philip X'pert X-ray diffractometer equipped with Cu Kα irradiation ($\lambda = 1.5406$ Å). The high resolution microstructure images were obtained by a JEM-2100 electron microscope. UV-vis light absorption spectra were obtained using Perkin Elmer Perkin Elmer Lambda 35 ultraviolet visible (UV-vis) spectrophotometer. Current voltage values were obtained using a multimeter (Keithley 2001) and photocurrent values were obtained using 500 W xenon lamp illumination.

4. Results and discussion

Figure 2 shows the optical absorption spectra of CdS quantum dots. A strong absorbance edge is observed at 350 nm and from the absorbance edge, particle size has been estimated using hyperbolic band model [13]:

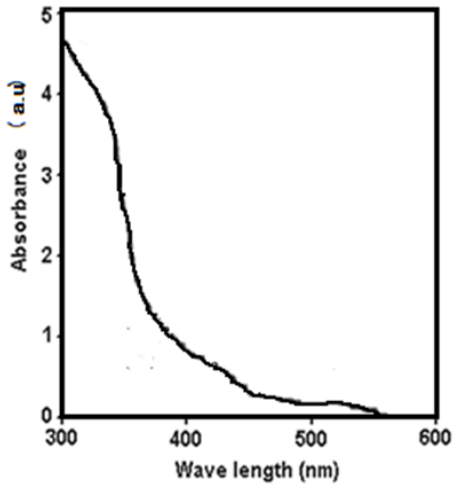


FIG. 2. UV-Visible absorption spectra of CdS quantum dots

$$R = \sqrt{\frac{2\pi^2 h^2 E_{gb}}{m^* \left(E_{gn}^2 - E_{gb}^2\right)}}, \tag{1}$$

where R is the quantum dot radius, E_{gb} is the bulk band gap, E_{gn} is the quantum dot band gap, h is Planck's constant, m^* is the effective mass of electron of the specimen. Here, the bulk band gap (E_{gb}) for CdS is 2.84 eV and electron effective mass at room temperature is $0.211m_0$ [10]; where m_0 is the electron rest mass. The quantum dot band gap (E_{gn}) of the prepared sample, as determined from the absorption edge wavelength is 3.54 eV for CdS. Thus, the radius (R) of the pure CdS quantum dots is determined to be around 4 nm i.e size is around 8 nm.

The XRD pattern for CdS quantum dots is shown in Fig. 3, the different peaks correspond to different crystalline planes of CdS. The average particle size (crystallite size) was obtained from X-ray diffraction data using the Scherrer formula [14, 15]:

$$D = \frac{0.9\lambda}{W\cos\theta}, \tag{2}$$

where, λ is the wavelength of the X-ray (0.1541 nm), W is FWHM (full width at half maxima), θ (theta) is the glancing angle and D is particle diameter (crystallite size). XRD investigation shows that pure CdS shows peaks at 24.8 (100), 29 (111) and 30 (200). Considering all the peaks (2θ in degree) in the X-ray diffractogram, the average crystallite (quantum dot) size was obtained using JCPDS to be 8.1 nm for CdS quantum dots.

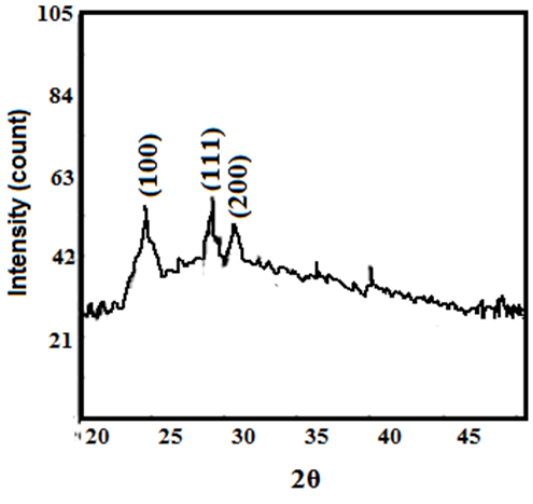
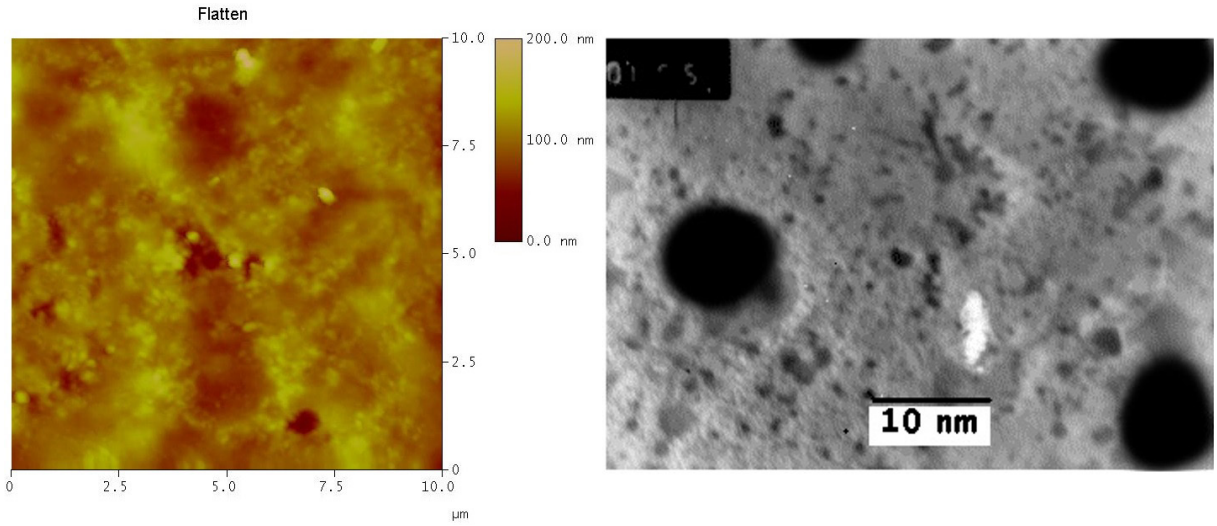


FIG. 3. XRD spectroscopy of CdS quantum dots

The surface topography and roughness of CdS quantum dots have been studied by atomic force microscope (AFM) as shown in Fig. 4(a) and the HRTEM image shows the formation of quantum dots in Fig. 4(b).



(a) (b)

FIG. 4. (a) AFM topography of CdS quantum dots on PVA host; (b) HRTEM image of CdS quantum dots on PVA

The current density and voltage characteristics of the device were obtained under both dark and illuminated conditions. In order to study the photo-current characteristics, the fabricated device was illuminated by a white light 500 W xenon lamp with an illumination area of about 0.3 cm^{-2} and the current density (J) v/s voltage (V) was measured. In practice, the measurements were taken in 5 cycles, each at an interval of three days. As similar J–V characteristics were obtained each time, the single characteristics for the fabricated device are presented in Fig. 5. The short circuit current density (J_{sc}) and open circuit voltage (V_{oc}) were obtained from J–V curve. The fill factor (FF) and efficiency (η) were calculated using equations (3) and (4). The efficiency was found to be around 0.99 % and other solar cell parameters for the CdS QDSSCs are shown in Table 1. Previously, an efficiency of 0.69 % was obtained for a single layer CdS–QD/ZnO-based solar cell as reported by Chen et al. [14]. Thus, the fabricated QDSSC displayed higher efficiency.

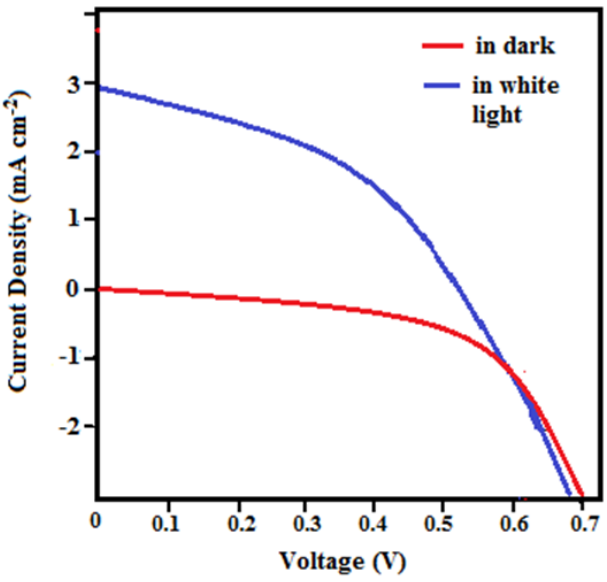


FIG. 5. Current density-voltage (J–V) characteristic in dark and white light illumination

TABLE 1. Solar cell parameters of the fabricated device

Solar cell parameters	Values obtained from J–V characteristics
J_{sc}	3 mA·cm^{-2}
V_{oc}	0.6 V
FF	0.55
η	0.99

$$FF = \frac{J_{\max} V_{\max}}{J_{sc} V_{oc}}, \tag{3}$$

$$\eta = \frac{V_{oc} \times I_{sc} \times FF}{P_{in}}. \tag{4}$$

5. Conclusion

CdS quantum dots were synthesized using a chemical method and were then characterized by using various techniques to determine their size, structural and optical properties. These quantum dots were introduced into a ZnO oxide based solar cell as sensitizing layer via simple dip coating technique. FTO glass was used as operating electrode and a low cost aluminum plate was used as counter electrode instead of commonly used platinum, gold or carbon based materials. The dark current and photocurrent response of the device clearly indicated that aluminum can be used as an alternate counter electrode material in low cost photovoltaic cells. An efficiency of as high as 0.99 % was obtained for the reported QDSSC device.

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