OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 3, No. 4, April 2009, p. 338 - 342

Nanostructures based photoelectrochemical cells for energy conversion

J. K. DONGRE*, V. NOGRIYA, R. ALONEY, M. RAMRAKHIANI
Dept. of Postgraduate Studies and Research in Physics & Electronics, Rani Durgavati University, Jabalpur (M.P.), 482001, India

In this paper, we present a comparative study of photoelectrochemical cells based on the films nanoparticles (NPs) and nanowires (NWs) of cadmium sulphide (CdS) thin films grown by chemical bath deposition (CBD) and wet chemical etching. The CdS samples are characterized by XRD, SEM and UV-vis absorption spectroscopy. The cell configuration n-CdS/1M (NaOH-Na_2S-S)/C(graphite) is used for studying the I-V characteristics under illumination, photovoltaic output characteristics and transient photoresponse. Performance of the PEC cell is found to be improved by converting NPs of CdS into NWs.

(Received March 10, 2009; accepted April 23, 2009)

Keywords: Chemical bath deposited CdS, Nanoparticles and nanowires, Surface morphology, Photoelectrochemical cells

1. Introduction

Nanoparticles (NPs), nanorods (NRs) and nanowires (NWs) have been used to improve charge collection efficiency in solar cells to demonstrate carrier multiplication and to enable low-temperature processing of photovoltaic devices [1]. Due to quantum confinement effect which appears in nanocrystal, electron and hole can perform reduction and oxidation reaction in PEC cells that cannot proceed on the bulk semiconductors [2]. Other advantages of using nanostructured layers in thin film solar cells are the optical path for photon absorption is increased than the actual thin film thickness due to multiple reflections and light generated electron and holes need to travel over a short path therefore, recombination losses are greatly reduced [3]. However, nanoparticle PEC cell rely on trap-limited diffusion for electron transport, a slow mechanism that can limit device efficiency [4]. Important differences in transport, internal electric field distribution and light scattering should make comparative studies of wire and particle devices fruitful. Here we introduce a version of the PEC cell in which the traditional nanoparticle film is replaced by dense randomly-oriented, crystalline CdS nanowires. CdS is an important II-VI semiconducting material used for different applications in optoelectronics such as nonlinear optics, flat panel displays, light emitting diodes, lasers and thin film transistors. Various methods have been developed to prepare one-dimensional (1D) CdS nanostructures in the past few years, including: electrochemical synthesis [5], chemical synthesis [6], solvothermal route [7], thermal evaporation [8], chemical vapor deposition [9], vapor-liquid-solid growth [10] etc.

One way to make a NW is etching (dry and wet) process, by which variety of materials such as GaAs, Si, and rhenium [11-14] has been fabricated. Recently, Zhang et al [15] have prepared CdS nanowire by chemical bath deposition (CBD) using porous anodic aluminum oxide (AAO) template. The nanoscale patterning and fabrication of nanostructured materials do not necessarily require sophisticated method and equipment [16]. In this paper, we report the synthesis of film of CdS nanowire by a simple chemical bath deposition process followed by chemical etching, which is an easier, low-cost and highly efficient technique. PEC cells based on films of CdS nanowires were fabricated and their performance was compared with cells made of nanoparticles of the same material.

2. Experimental details

In the present study analytical grade reagents were used without any further purification. Preparation method of CdS nanostructures consisted of two steps. In the first step films of CdS nanoparticle were prepared by CBD. The nanoparticle films were converted into fibril-like nanowire using chemical etching in second step.

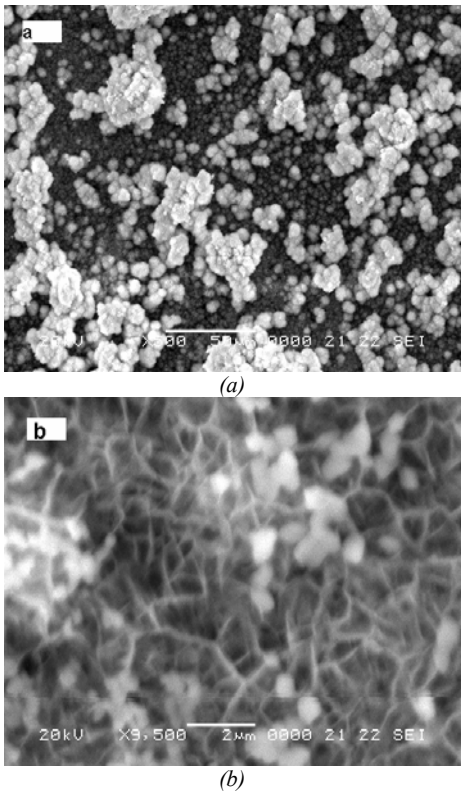
CdS films of nanoparticles were grown over transparent plastic sheet and titanium (Ti) substrates. The chemicals $CdSO_4$, thiourea and NH_4OH were used as staring compound. Detailed description of the sample preparation is given elsewhere [17]. Nanocrystalline sample was prepared from an aqueous alkaline bath (pH~12) with deposition time 5 hours, at room temperature 300K. To obtained nanowires from clusters of CdS nanoparticles, the freshly prepare nanoparticles coated substrate was immersed in dilute hydrochloric acid at low temperature.

The thickness of CdS film was measured with the help of weight difference method employing sensitive electronic microbalance. Thickness of film was 435 nm. The structural characterization of CdS nanowires film was performed by an X-ray diffractometer (Rigaku rotating anode H-3R) using Cu Kα radiation taken from 10^0 to 60^0. The surface morphology of the film was characterized by

scanning electron microscopy (SEM; JEOL-JSM 5600). The transmission data in the range 400–700 nm were obtained with Perkin Elimer, Lambda-35 spectrometer. PEC cell was fabricated using a two electrode configuration, comprising n-CdS thin film as photoelectrode and graphite as a counter electrode. The redox electrolyte was an aqueous solution of 1M NaOH + 1M Na_2S + 1M S. The distance between working electrode and counter electrode was fixed to 10 mm with plastic cello-tape spacer. Photocurrent–voltage (I–V) performances of as-deposited (NP) and etched (NW) CdS photoelectrodes were measured under 100 mW/cm^2 light illumination intensity.

3. Results and discussion

Depending on the preparative parameters to synthesizing the nanoparticles and nanowires of CdS, blue shift of 0.16 eV and 0.06 eV are observed in optical band gap of NPs and NWs of CdS sample respectively. The band gap values are estimated to be 2.58 eV for as-deposited film consisting of nanoparticle whereas it is 2.48 eV for etched sample consisting of nanowire. These band gap values are higher than that of bulk value of CdS (2.42 eV at 300K). For the nanowire of CdS sample, values of 1.62×10^{-2} and 5.8 nm are obtained for strain and average crystal size respectively. Crystal size and strain are calculated by Williamson-Hall method. A detailed description about X-ray diffraction and UV-vis absorption spectroscopy is given elsewhere [17].



(a)

(b)

Fig. 1. SEM image of CdS (a) nanoparticles film and (b) nanowires film.

3.1 Morphology of nanofilms and formation mechanism of nanowires

Fig. 1 (a) represents the SEM micrograph of as-prepared clusters of CdS nanoparticles, onto plastic substrate fabricated by CBD for deposition time of 5 hrs. The SEM image shows that surface is not smooth, spherical shaped large grains are clearly seen on the micrograph. To obtained nanowires from clusters of CdS nanoparticles, the freshly prepare nanoparticles coated substrate was immersed in dilute hydrochloric acid at low temperature. The morphology of etched semiconductor materials depends on the etching condition [18]. Therefore, we have tried-out various preparation conditions of CdS nanowire to study the influence of the chemical etching parameters on film quality. So, using optimizing preparative parameters such as concentration of hydrochloric acid, temperature and reaction time, clusters of CdS nanoparticles are successfully transferred into nanowires. Fig. 1 (b) shows the SEM micrograph of the CdS nanowires, fabricated by CBD for deposition time of 5 hrs followed by chemical etching. The micrograph shows interconnect fibril-like wires with incorporated clusters of CdS nanoparticle. The nanowires have widths in the range of 50-150 nm and have lengths of the order of a few micrometers. We believe that the formation of nanorods/nanowires from the CdS clusters is by dissolution-condensation (recrystallization) process [19]. We think that in our experiment, the CdS molecules first dissolved into the solvent (HCl acid) and then diffuse through the solvent and deposited onto the preferential surface (002) resulting in the growth of nanorods/nanowires. A detail of the formation mechanism of nanowire is reported earlier [17].

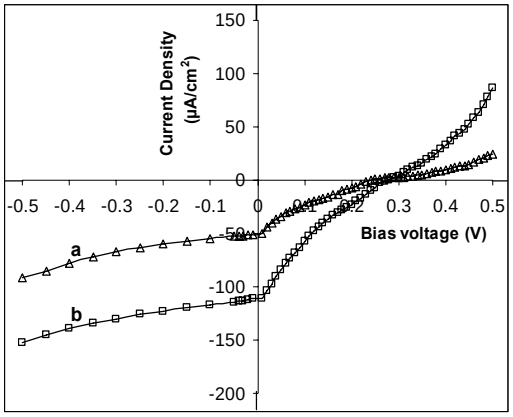


Fig. 2. I-V characteristics under illumination for n-CdS/1M (NaOH-Na_2S-S)/C PEC cell (a) nanoparticles photoelectrode (b) nanowires photoelectrode.

3.2 Photoelectrochemical studies

3.2.1 Type of conductivity

The PEC cell with the configuration n-CdS/(1MNaOH + 1M Na_2S + 1M S)/C was formed to

check the conductivity type exhibited by CdS thin film. It was found that in dark, PEC cell gives some dark voltage, V_d and dark current, I_d with CdS photoelectrode as negative and graphite counter electrode as positive polarities. The origin of the voltage, V_d is attributed to the difference between two half cell potentials in the PEC cell. After illumination, the magnitude of the open circuit voltage increases by retaining negative polarity towards CdS photoelectrode. Therefore, in the present case cathodic behavior of photovoltage of semiconductor is observed which indicates that the CdS thin film has n-type electrical conductivity [20].

3.2.2 Current-voltage (I-V) characteristics

Fig. 2 shows the I–V characteristics of CdS NPs and NWs films photoelectrodes under light illumination of 100 mW/cm^2 intensity. The non-symmetric nature of I-V curve in forward and reverse bias shows the rectification property of semiconductor electrolyte junction. Under illumination, shifting of the I–V curve in the fourth quadrant of the graph suggests that the electrons are the majority carriers, confirming the n-type conductivity of CdS. Information about junction quality is obtained using following diode equation as

$$\ln(\mathrm{I}) = \ln(\mathrm{I}_o) + \frac{qV}{n_d \kappa \mathrm{T}} \tag{1}$$

The plot of ln(I) versus V [Fig. 3 (derived from Fig. 2)] shows linear behaviour with junction ideality factor n_d determined to be 3.94 and 3.79 for nanoparticle and nanowire semiconductor-electrolyte junction respectively. The higher value of n_d is indicative of the series resistance effect, surface states and the charge carrier recombination at the semiconductor- electrolyte interface [21].

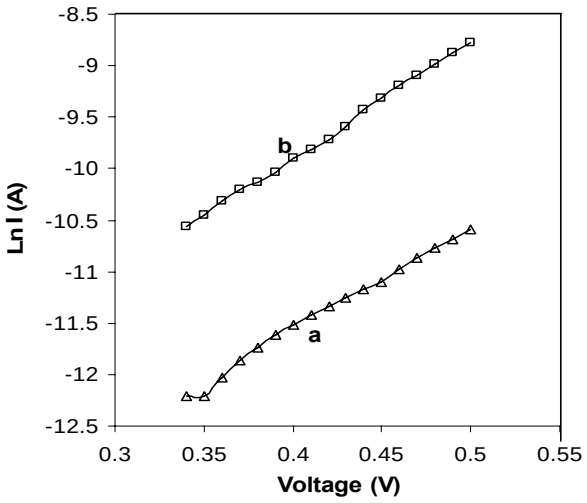


Fig. 3. Ln I versus voltage plot for n-CdS/1M (NaOH-Na_2S-S)/C PEC cells under illumination (derived from Fig. 2.) with same notation.

Flat-band potential is an important parameter to characterize the PEC cell, which can be obtained from I-V characteristics of PEC cell. The flat-band potential V_{fb} has been determined by using the relation [22]

$$J_{ph}^2 = Const.\alpha^2 W^2 (V - V_{fb}) \tag{2}$$

where J_{ph} is the photocurrent, α is the optical absorption coefficient and W is the depletion layer width for applied voltage V across it. As shown in figure 4 (derived from figure 2) the flat-band potential has been calculated by extrapolating the linear region of the plots I^2_{ph} vs. V on the potential axis. The flat-band potential is found to shift from -550 to -530 mV i.e. become less negative by modifying the films of CdS nanoparticles into nanowires. Obviously, the energy level for electron injection is decreased after modifying the films of CdS nanoparticles into nanowires which increases the driving force for electron injection and hence reduces recombination in space charge region. This implies that the, number of deep trap states existing in the surface of CdS is decreased, and thus electrons transport faster [23,24].

3.2.3 Photovoltaic output characteristics

Photovoltaic output characteristics of as-grown nanoparticles film and film of nanowires, under the illumination intensity of 100 mW/cm^2, are shown in Fig. 5. The efficiency η (in %) of PEC cell was calculated from the relation

$$\eta = \frac{V_{oc}\,\mathrm{I}_{sc}\,FF}{\mathrm{P}_{input}} \times 100 \tag{3}$$

where P_{input} is the input light energy. The fill factor (FF) was calculated from the relation

$$FF = \frac{\mathrm{I}_m V_m}{\mathrm{I}_{sc} V_{sc}} \tag{4}$$

where the I_m and V_m are values of maximum current and voltage that can be extracted from PEC solar cell. Series resistance R_s and shunt resistance R_{sh} were estimated from slope of power output characteristics by using the relation [25]

$$\left(dI/dV\right)_{\mathrm{I}=o} = \left(\frac{1}{R_s}\right) \tag{5}$$

$$\left(dI/dV\right)_{V=o} = \left(\frac{1}{R_{sh}}\right) . \tag{6}$$

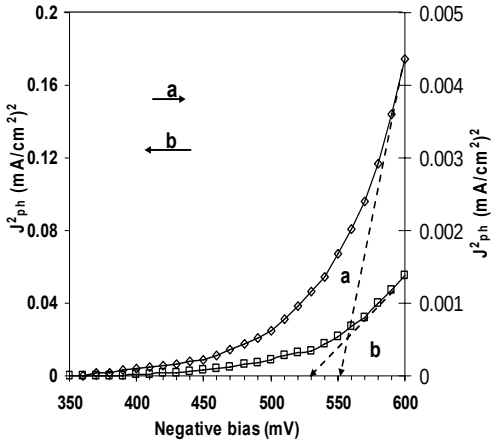


Fig. 4. Photocurrent square versus negative applied bias plot for n-CdS/1M (NaOH-Na_2S-S)/C PEC cells under illumination (derived from fig.2.with same notation).

The performances of both CdS-NP and CdS-NW PEC cells are summarized in Table 1. J_{sc} of the CdS-NW PEC cell is larger than that of the CdS-NP PEC cell one. On the other hand, the fill factor of the CdS-NP PEC cell is significantly lower than that of the CdS-NW PEC cells one. The lower FF in the CdS-NP PEC cell implies that the photoelectrons in the CdS-NP PEC cell are easier to back react with the polysulfide electrolyte in comparison with the CdS-NW PEC cell one [26]. The increase in the surface area of the NWs films is expected to enhance the cell performance. The NWs provide the direct path for the electron transport that decreases the probability of recombination (electron–hole), as the photogenerated electrons are transported quickly to the back contact. The low value of efficiency in present investigation may be due to the high series and low shunt resistance of the cells, and interfacial states responsible for recombination mechanism. Apart from this, the efficiency in CdS-polysulfide PEC cells is limited because of the wide band gap of CdS and strong absorption by the electrolyte, which absorb all radiation below 0.46 μm [27].

3.2.4 Transient photoresponse

Open circuit voltage decay (OCVD) method [28] was employed to investigate the electronic processes of the recombination in PEC cell. By measuring the subsequent decay of the V_{oc} after turning off the illumination, response time is obtained by the reciprocal of the derivative of the decay curve normalized by the thermal voltage

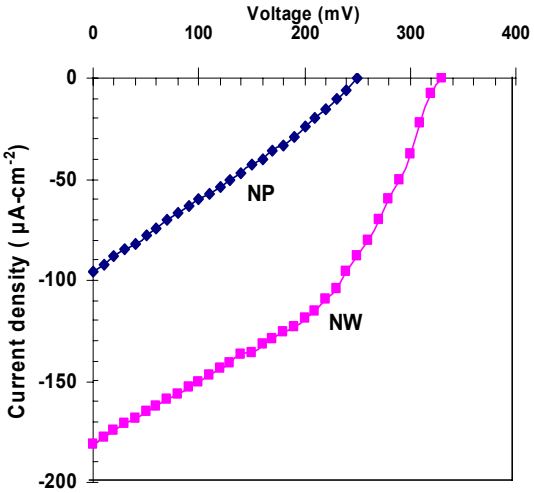


Fig. 5. Photovoltaic output characteristics for n-CdS/1M (NaOH-Na_2S-S)/C PEC cells of (a) Nanoparticle (NP) (b) Nanowire (NW).

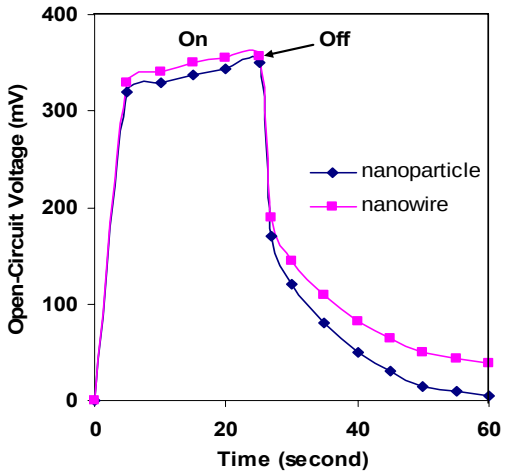


Fig. 6. Open-circuit voltage decay curves for n-CdS/1M (NaOH-Na_2S-S)/C PEC cells of nanoparticles and nanowires.

Table 2. Performance of PEC cells based on films of CdS nanoparticles and nanowires photoelectrode.

PEC Cells	Ideality Factor n_d	Shor-Circuit current I_{sc} (μA)	Open Circuit voltage V_{oc} (mV)	Series resistance R_s (Ω)	Shunt resistance R_s (Ω)	Fill factor ff (%)	efficiency (%)	Flat-band Potential V_{fb} (mV
NP	3.94	96	250	1666	2.5	28	0.006	550
NW	3.79	181	330	909	2.86	40	0.024	530

$$\tau_n = -\frac{k_B T}{e}\left(dV_{oc}/dt\right)^{-1} \quad (7)$$

The thermal energy is given by k_BT, e is the positive elementary charge, and dV_{oc}/dt is the derivative of the open circuit voltage transient. Fig. 6 shows the OCVD characteristics for the PEC cells formed with CdS-NP and CdS-NW photoelectrodes. Fig. 7 shows the lifetime values/response time obtained from Fig. 6 using equation (7) as a function of V_{oc}. It reveals that the response times in the CdS-NW PEC cell are higher than those in the CdS-NP PEC cell one in the low V_{oc} region, indicating that the CdS NPs possess a higher surface trap density in comparison with CdS-NWs one[26].

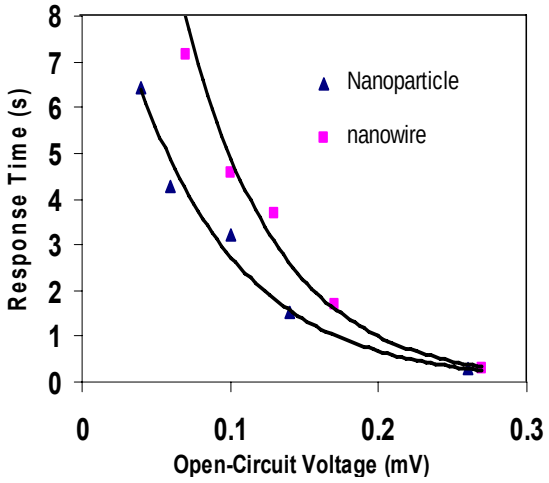


Fig. 7. Response time determined by OCVD for n-CdS/1M (NaOH-Na_2S-S)/C PEC cells (derived from Fig. 6 with same notation).

4. Conclusions

The PEC cells of films of CdS NPs and NWs having thickness about 435 nm have been fabricated using CBD method followed by wet chemical etching process. It is found that the CdS NPs possess a higher surface trap density in comparison with CdS-NWs one. The PEC performance of CdS photoelectrode is improved by converting NPs of CdS into NWs.

Acknowledgements

One of the authors (JKD) is indebted to UGC, central regional office, Bhopal for sanction of Teacher Fellowship. The authors are thankful to the UGC-DAE Consortium for Scientific Research, Indore Centre for Characterization of CdS samples.

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*Corresponding author: jk_dongre@yahoo.com