

Electrochemical Fabrication of Nanoporous ZnO/Q-CdSe Photovoltaic Device

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Use of nanoporous ZnO/CdSe as a photoelectrode has been successfully realized by applying low temperature electrochemical and chemical methods. A nanoporous n-type ZnO consisting of high crystalline structure with internal nanoporous sponge-like network (~5 nm) enabling high surface area was cathodically electrodeposited on F:SnO₂ coated glass substrate in one-step. A thin layer of CdSe with the thickness of 40-50 nm was chemically coated at room temperature on the nanoporous ZnO with the aim of use as a photoelectrode to form inorganic pigment sensitized solar cell. Structural, surface morphological and optical studies have been performed by X-ray diffraction, scanning electron microscopy and optical spectroscopy. Nanocrystalline nature of CdSe film has been confirmed by structural studies. ZnO/CdSe electrode displayed the characteristic of CdSe in the visible region with remarkable blue shift due to quantum size effect. Polysulfide and polyiodide have been tested as electrolytes in the photoelectrochemical device. The obtained current densities were 2.89 and 0.43 mA cm⁻² for polysulfide and polyiodide electrolytes, respectively under illumination with a simulated sun light (AM 1.5, 100 mW cm⁻²). This could give rise to interesting option for developing a new type of photovoltaic device.

Key words: Electrodeposition, Nanoporous, ZnO, CdSe, Solar cells.

1. INTRODUCTION

Grätzel et al. firstly prepared nanocrystalline semiconductor films with a high surface area, which permits adsorption of dyes in a high amount, enough to ensure efficient light harvesting [1]. These cells become a topic of general interest due to its remarkably high conversion efficiency [2]. Moreover a range of organic dyes have been synthesized which have excellent spectral overlap with solar spectrum and strong chemical adsorption at the surface of semiconductor nanoparticles and whose excited state energy level matching with the conduction band of the semiconductors. In addition to organic dyes, narrow band gap semiconductors nanocrystals, such as PbS and CdSe have attracted significant interest as light harvesters in TiO₂ solar cells [3-6]. One important aspect is to form sensitized solar cell by organizing a small gap material on another large gap material. The main advantage of this sensitized structure is that the region in which light excites electron is separated from that in which charge is transported, the recombination rate is then largely decreased and the photoelectric conversion efficiency is increased. Furthermore the band gap of the nanocrystals can be tuned by controlling their size so that the absorption spectrum can be tuned to match the full spectrum of solar energy. CdSe is a traditional semiconductor material with energy gap $E_g=1.7$ eV.

Previously our group has reported one-step fabrication of ZnO/eosin Y hybrid thin films by cathodic electrodeposition obtaining the high crystalline ZnO films. Extraction of the loaded dye

with the alkaline treatment resulted into nanoporous ZnO with high surface area [7]. This has enforced us to fill this nanoporous area (~5 nm) with narrow band gap semiconductor (e.g. CdSe) to use as a good sensitizer. Present work is focused on the electrochemical fabrication of wide band gap semiconductor ZnO porous films and photosensitization by Q-dots of chemically deposited CdSe with the aim to develop inorganic pigment sensitized solar cell. This could actually be a challenge to fill and to cover the nanopores of ZnO with CdSe nanoparticles. Hence efforts have been made to deposit very thin layer of nanoparticles of CdSe on nanoporous ZnO and further characterized by structural, surface morphological and optical absorption studies. Furthermore, photovoltaic effect has been studied with polysulfide and polyiodide as electrolytes and results are incorporated therein.

2. EXPERIMENTAL

2.1 Electrodeposition of porous ZnO

F:SnO₂ (FTO) coated glass substrates (10 Ω/□ Asahi glass) were cleaned ultrasonically in acetone, 2-propanol, soap solution, water, etched in 45 % HNO₃ for 2 min and finally rinsed with distilled water prior to the electrodeposition.

An aqueous solution was prepared containing 5 mM ZnCl₂ (Merck), 0.1 M KCl (Merck) and 45 μM Eosin Y (Kanto) using Milli-Q pure water (18.2 MΩ) for the deposition of ZnO/eosin Y hybrid film. A three-electrode single compartment cell was used. FTO glass working electrode (area 3.83 cm² using masking tape) was used as a rotating disc electrode

(500 rpm) by applying the electrode to a Radiometer Analytical (CTV101) rotating electrode system. A Zn wire (99.9%) was used as a counter electrode. The potential control was referred to a saturated calomel electrode (SCE). The cell was placed in a thermostat bath maintained at 70°C. Solution was saturated with oxygen by bubbling it at 100 ml min⁻¹ for 30 min prior to the actual deposition and the same gas flow was maintained during the deposition. Deposition was carried out for 20 min potentiostatically at -1.0 V (vs. SCE). A Hokuto Denko HSV-100 was used for the potential control and the measurement of charge counting. The deposited film was colorless since dye molecules were loaded in their reduced state. The film was rinsed, dried and sustained in air for 24 h at room temperature to reoxidize the dye molecules. Extraction of the dye molecules were performed by soaking the film in dilute alkaline solution (KOH, pH~10.5) for overnight. Completely desorbed state represents colorless film as previously reported [7] and was subjected to the further deposition.

2.2 Chemical Deposition of CdSe

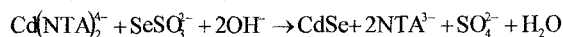
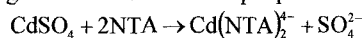
Nanocrystalline CdSe film was prepared on ZnO porous thin film by using the deposition conditions reported by Zhang et. al. [8]. In the standard volumetric flask, 17.5 ml solution of 0.23 M CdSO₄ was mixed with 10 ml solution of 0.7 M N(CH₂COONa)₃ (NTA) to form a complex. Then 20 ml of 0.2 M Na₂SeSO₃ solution was added in the above solution. Nanoporous ZnO coated FTO substrate was placed inclined in the deposition bath in such a way that ZnO surface face towards the bottom of the flask. This avoids the sticking of the bulk precipitate on ZnO surface. The deposition was performed at room temperature (25°C) for 3 h. After the deposition, film was taken out, rinsed with distilled water and dried. The obtained film was red in color.

2.3 Characterization

X-ray diffraction (XRD) patterns were measured on a Rigaku-RINT-Ultima II/PC using CuKα radiation whereas scanning electron microscopy (SEM) images were recorded using Hitachi, S-4300 (Type-G) to study the surface morphology of the films. UV-Vis absorption spectra of the films were measured in a HITACHI U-3000 spectrophotometer. Photo-electrochemical measurements were performed for CdSe coated ZnO electrode. A thin layer sandwich type solar cell was fabricated by using a 50 μm-thick Teflon sheet as a spacer to fill the electrolyte between the deposited film photoelectrode and platinum coated conducting glass counter electrode. The exposed device area was 0.2 cm². Two electrolytes as polysulfide (1 M NaOH, 1 M Na₂S and 1 M S), and polyiodide (acetonitrile / ethylene carbonate mixed solution with 0.5 M tetrabutylammonium iodide and 0.05 M I₂) have been tested. Photocurrent was measured under illumination of AM 1.5 simulated sunlight (100 mW cm⁻²). Photocurrent action spectra were measured under illumination of monochromatic light with constant photon number (0.05x 10¹⁶ s⁻¹ cm⁻²). A Bunko-Keiki CEP-2000 system was used for these measurements.

3. RESULTS AND DISCUSSION

Electrodeposition of ZnO under the conditions in the present study resulted in a formation of a ZnO film of 3 μm thickness and ca. 50% porosity as previously reported [7]. Coating of the porous ZnO surface with CdSe nanoparticles has been attempted. Cadmium sulfate forms a complex with sodium nitriloacetate. This reacts with the selenium ions gives rise to CdSe as proposed below:



In the present case, the growth favors cluster-by-cluster mechanism, namely, by surface agglomeration of CdSe nanoparticles formed in the solution phase, since there is a formation of bulky particles formed as aggregates of nanocrystalline CdSe that precipitate in the solution. Detail of the mechanism of CdSe formation was proposed and discussed by Groer and Hodes using potassium nitriloacetate [K₃(NTA)] [9].

X-ray diffraction patterns of nanoporous ZnO and ZnO/CdSe films on FTO coated glass substrates with FTO as reference are shown in Fig. 1. Sharp diffraction peak along (002) plane with hexagonal crystal structure is observed for ZnO film indicating preferential orientation of the crystallites along their c-axis perpendicular to the substrate. Three tiny peaks (101), (102) and (103) are also observed. The sharpness of the diffraction peak indicate the high crystallinity of ZnO as its growth occurs in a typical atom-by-atom fashion. On the other hand, CdSe coated film indicate additional small broad humps at 25.35 and 42.00 degree for (111) and (220) planes of

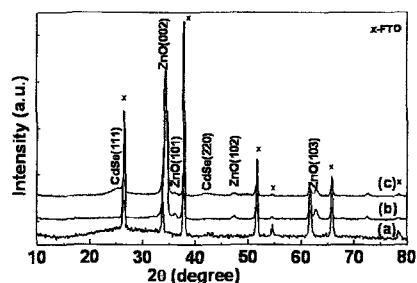


Fig. 1 X-ray diffraction patterns of (a) FTO-as reference, (b) nanoporous ZnO and (c) ZnO-CdSe thin film.

cubic CdSe, respectively [10]. These broad humps confirmed the nanocrystalline nature of the CdSe film as expected for its cluster-by-cluster growth mechanism. From the full width at half maximum of the (111) diffraction peak, the average crystallite size of CdSe has been determined as 3.0 nm. For Cd(OH)₂, the peak with the highest intensity at 35.22 degree is masked by ZnO(002) peak, we checked the next intense peak at 18.16° but no evidence was observed for the formation of Cd(OH)₂ although it is supposed that the solution contains Cd(OH)₂ [9]. The electrodeposited porous ZnO prepared by our method has a sponge-like internal nanostructure with an average pore diameter of ca. 5 nm [7]. Hence, it is a challenge to introduce CdSe nanoparticles down to the bottom of the ZnO layer so that the surface of ZnO is uniformly covered with a thin layer of CdSe.

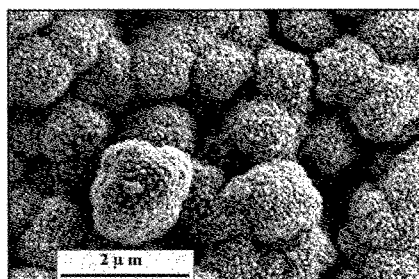


Fig. 2 Surface morphology of the CdSe film deposited on nanoporous ZnO.

Fig. 2 shows the surface morphology of the CdSe coated nanoporous ZnO film. The overall morphology of the film resembles that of porous ZnO before its coating with CdSe [7]. Attachment of large particles formed as aggregates of nanoparticulate CdSe was not observed on the surface. As the presence of CdSe is evident from the XRD, it is supposed that nanoparticulate CdSe is introduced into the pores of ZnO film and deposited on its surface. Further insights are obtained in the cross-sectional view of the layer (Fig. 3). The layer appears less porous than that of the porous ZnO before CdSe deposition. Even though the electrodeposited ZnO possess very fine porous structure, the CdSe particles seem to be small enough to swim through the nano channels of the ZnO layer. Nano size CdSe can otherwise be formed

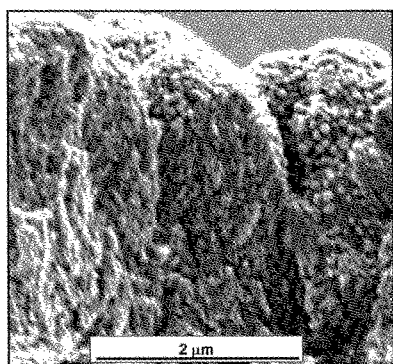


Fig. 3 SEM-cross sectional image of the CdSe film deposited on nanoporous ZnO.

in the pores by decomposition of the reactant present in the pores. In any case, the surface of ZnO is successfully coated with a very thin layer of CdSe down to the bottom of the porous ZnO film as long as we can judge from the SEM images.

Presence of CdSe was confirmed also by the EDX analyzer coupled with SEM technique (not shown here). Zn, O, Cd and Se elements were noticeably confirmed. Films were found to be slightly Se rich with inclusion of Si from the glass substrate. Although, filling of the nanoporous ZnO with CdSe will be studied in detail, this will be the future step. Optical properties of nanoporous ZnO and ZnO/CdSe has been studied by spectrophotometer in the wavelength range from 350 to 800 nm (Fig. 4). In the ultraviolet region, the bare ZnO electrode

exhibit abrupt increase of absorbance below 380 nm whose onset corresponds to the band gap of ZnO (ca. 3.2 eV). Coating of ZnO film with the CdSe particles

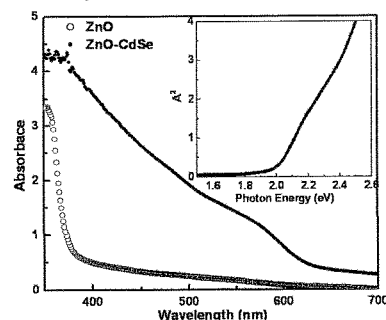


Fig. 4 Optical absorption spectra of ZnO and ZnO/CdSe thin films. The inset shows A^2 vs. photon energy plot generated from the spectrum of ZnO/CdSe thin film.

displays characteristic absorption of CdSe in the visible region gradually arising below ca. 630 nm and creating a shoulder at around 580 nm. The inset of Fig. 4 shows a plot of (absorbance)² against photon energy from which direct transition band gap energy of CdSe can be determined. By extrapolating the straight line portion of the plot to the energy axis curve represents an energy gap of $E_g = 1.98$ eV, significantly blue shifted compared with that of bulk crystalline CdSe ($E_g = 1.73$ eV). The enlarged the band gap energy clearly indicates quantum size effect [9] due to the smaller crystallite size. The observed energy gap, however, corresponds to a crystallite size of around 5 nm [11] which is slightly larger than that estimated from the XRD (3.0 nm). CdSe particles of 3 nm size is expected to possess an energy gap of around 2.3 eV. It is likely that a small number of somewhat larger particles are present so that the absorption onset appears at longer wavelength than that expected for 3 nm CdSe.

An attempt has been made for the construction of a photoelectrochemical (PEC) solar cell with ZnO and ZnO/CdSe as photoelectrodes with polysulfide and polyiodide as electrolytes and the cell characteristics were measured under illumination with AM 1.5 simulated sun light. For ZnO/CdSe, even though rather high photocurrent (2.89 mA cm^{-2}) was observed with polysulfide, the energy conversion efficiency remained low (0.15 %) because of its small open circuit voltage (300 mV) and poor fill factor (0.17). A higher open circuit voltage (620 mV) was observed with polyiodide due to its more positive redox potential than the polysulfide [12]. A short circuit photocurrent of 0.43 mA cm^{-2} was measured with polyiodide. However, CdSe undergoes rapid photo corrosion so that the photocurrent quickly dropped even during the I-V scan making it impossible to measure a reasonable value of conversion efficiency.

The incident photon to current conversion efficiency (IPCE) is plotted as a function of excitation wavelength (Fig. 5). Bare ZnO electrode exhibits IPCE value below 400 nm due to the band gap of ZnO. For ZnO/CdSe, both the spectra cover

visible range of the solar spectrum. Rather high value of IPCE around 57 % is reached with polysulfide electrolyte indicating an efficient photosensitization of ZnO by Q-CdSe. This is another indication of good coverage of ZnO surface with CdSe particles so that most of photons absorbed by CdSe can contribute to generation of photocurrent. It should also be noticed that IPCE of around 14 % is observed at 700 nm with polysulfide, whereas that above this wavelength is almost zero with polyiodide. Current generation in such a long wavelength region indicates presence of rather large crystals of CdSe probably as attached to the outer surface of the porous ZnO layer. Such large particles with smaller energy gap may still be able to transfer hole to polysulfide, but not to iodide having more positive redox potential.

From the overlap integral of the curves in Fig. 5 with the AM 1.5 solar emission one can predict the photocurrents of 8.45 and 2.15 mA cm⁻² for polysulfide and polyiodide electrolytes, respectively. The measured values are much lower probably due to non-linear response of the cells. It is possible that the level of pore filling with CdSe was rather high for this example so that the remaining pore size became too narrow for hole transport by the electrolyte. Optimization of pore filling is necessary for improved efficiency of the system.

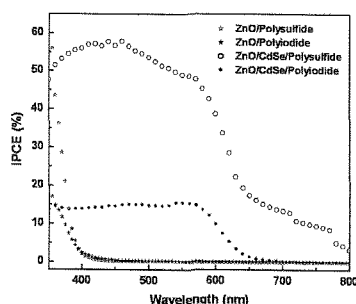


Fig. 5 Photocurrent action spectra obtained for ZnO and ZnO/CdSe photoelectrodes in polysulfide and polyiodide electrolytes, respectively.

Even though the system requires further optimization for the level of pore filling and more precise control of the crystal size of CdSe, what encouraging is the fact that the low temperature electrochemical and chemical methods of synthesis were successfully applied to yield a complex ZnO/Q-CdSe nanostructure. The observed IPCE was rather high for such a system indicating a firm attachment of CdSe particles onto the inner surface of porous ZnO. The high crystallinity of electrodeposited ZnO should also contribute to fast transport of injected electron to attain high IPCE. Photo corrosion of CdSe in liquid electrolyte is a severe problem to make the stability of the system very poor. The stability problem can be overcome by replacing electrolyte with solid-hole conductor. Recently, Tena-Zaera et al. have fabricated ZnO nanowire/CdSe/CuSCN solar cell [13] and reported remarkably high conversion efficiency (1.5-2.3%). Because the quantum efficiency of the present

system was found to be rather high, similar approach may lead us to an efficient and stable solid state sensitized solar cell that can be processed at low temperature and relatively low cost.

4. CONCLUSIONS

We have succeeded in fabricating ZnO/CdSe photovoltaic device based on low temperature chemical and electrochemical methods. Both the methods are inexpensive and suitable for large area production. ZnO surface has been well covered with nanocrystallites of CdSe which showed remarkable quantum size effect. Satisfactory IPCE performance was observed for PEC cell. Although the system is found to have poor stability but realised the real sense of working PEC device. Use of solid hole conductor in place of liquid electrolyte can overcome the stability problem although filling of the ZnO/CdSe pores will be a challenge. This will be the next task to achieve efficient and stable photovoltaic device.

5. ACKNOWLEDGEMENTS

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