PREPARATION OF CdSe NANOROD BY SUCCESSIVE IONIC LAYER ADSORPTION AND REACTION METHOD FOR USING AS A LIGHT ABSORBER IN DYE-SENSITIZED SOLAR CELL DEVICES

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ABSTRACT

CdSe nanorods were prepared by the successive ionic layer adsorption and reaction (SILAR) methods used as a light absorber in dye-sensitized solar cell (DSSC) system. CdSe nanorods were coated on the nano-TiO_2/F-SnO_2 (FTO) substrate. The NiS_2 films were deposited on the FTO substrates by an electrodeposition technique, and were used as the counter electrode. The surface morphology and crystalline structure of the CdSe films were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) technique. The averaged diameter and averaged length of CdSe nanorod are about 97±38 nm and 404±189 nm, respectively. The sulfide/polysulfide (S^{2-}/S_x^{2-}) and iodide/tri-iodide (I^-/I_3^-) redox couple systems were used as the cell electrolyte. The short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and solar cell efficiency (η) of the sulfide/polysulfide DSSCs are 2.19 mA/cm^2, 0.344 V, 0.489 and 0.37%, respectively. Whereas, J_{sc}, V_{oc}, FF and η of the iodide/tri-iodide DSSCs are 2.36 mA/cm^2, 0.734 V, 0.439 and 0.76%, respectively. The cell performance of the iodide/tri-iodide DSSC cell is higher than that of the sulfide/polysulfide DSSC cell is due to the high electrolyte conductivity.

KEYWORDS: *Dye-sensitized solar cell; CdSe nanorod; Solar cell, Inorganic dye*

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INTRODUCTION

Dye-sensitized solar cell (DSSC) is the most interesting new generation solar cell. Because, it is cost effective solar cell due to the simple fabrication process, high efficiency and environmentally friendly solar cell [1]. Normally, DSSC device composes of three parts, working electrode, counter electrode and electrolyte. The working electrode composes of dye molecules (Ru-complex dye is mostly used as light absorber) coated on the porous-TiO_2/F-SnO_2 (FTO) substrate. The platinum (Pt) metal or carbon nanomaterials [2] are used as a catalyst. The iodide/tri-iodide and sulfide/polysulfide redox electrolyte are popular used as an electrolyte. Unfortunately, this solar cell is still facing a reliable issue because of its poor life time and Ru is the rare transition metal (expensive material). To solve these problems, Ru-complex dyes should be replaced by the inorganic compound materials; for example cadmium selenide (CdSe), cadmium sulfide (CdS), tin sulfide (SnS), zinc sulfide (ZnS), lead sulfide (PbS), lead telluride (PbTe) etc. Their optical and electrical properties of these semiconductors are strongly size dependent [3]. Among these colloidal semiconductor nanocrytals, cadmium selenide (CdSe) is one of the most interesting semiconductors because it has many special properties for optoelectronic devices [4], light emitting diodes [4], nanosensing [5] and high

efficiency solar cells [6], photocatalyst [7], respectively.

In this study, CdSe nanorod will be coated on the TiO_2/FTO and glass slide substrate by the successive ionic layer adsorption and reaction (SILAR) techniques. CdSe nanorod will be applied as the light absorber in DSSC devices.

MATERIALS AND METHODS

CdSe nanorod preparation

CdSe nanorod was coated on the TiO_2/FTO and glass slide substrates by SILAR method. The sodium selenosulphite (Na_2SeSO_3) solution was used as a source of the Se ions by mixing of 9.0 g Se powder and 15.0 g of sodium sulfite (Na_2SO_3) in 250 mL de-ionized water. The 0.50 M of cadmium acetate dihydrate ($Cd(CH_3COO)_2{\cdot}2H_2O$) with 0.5 M of citric acid monohydrate ($C_6H_8O_7{\cdot}H_2O$) in the de-ionized water was used as the source of the Cd^{2+} cations. A one SILAR deposition cycle consisted of two step process as following. Firstly, the substrate was dipped into 0.50 M cadmium acetate dihydrate solution for 60 s at room temperature, and cleaned with de-ionized water. In this step, Cd^{2+} ion will be adsorbed on the substrate surface. Second, the substrate from the first step was immersed into the sodium selenosulphite solution for 45 s, and then cleaned with de-ionized water. By repeating 5 deposition cycles, CdSe nanorods were obtained.

Counter electrode preparation

The NiS_2 films were deposited on the FTO substrate and it was used as the DSSC counter electrodes. The NiS_2 film was prepared as following details. First, Ni metal film was deposited on the FTO substrate by an electroplating method under a constant voltage of 5.0 V for 45 s using the 0.05 M $NiSO_4{\cdot}6H_2O$ in de-ionized water as an electroplating solution. The pH of an electroplating solution was adjusted to 2.76 by citric acid before using. Second, Ni film was reacted with the sulfur environment in the vacuum furnace at 300 °C for 1 h. After cooling down, the NiS_2/FTO electrode was obtained.

Working electrode preparation

FTO (sheet resistance 13 Ω/sq., Pilkington) was used as the conductive glass substrate. The 8.0 μm thick TiO_2 transparent films, with an active area of 0.30 cm^2, were coated on the FTO substrate using a screen printing method employing TiO_2 pastes, (PST-18NR, JGC Catalysts and Chemicals Ltd). TiO_2 films were annealed at 500 °C for 1 h, then were used as host for CdSe nanorods coating by the SILAR method for five rounds (as decribed in the CdSe nanorod preparation section).

DSSC assembly

The NiS_2 films were used as the counter electrodes in DSSC devices. The iodide/tri-iodide liquid electrolyte, which consisted of 0.10 M NaI, 0.05 M I_2, 0.50 M *tert*-butylpyridine (TBP) and 0.60 M 1-methyl-3-propylimidazolium iodine (PMII) in acetonitrile and the sulfide/polysulfide liquid electrolyte consisted of 0.5 M Na_2S, 0.1 M sulfur(S) in ethanol:water (8:2 v/v) were used as an redox electrolyte. A 200 μm thick polymer film (Parafilm^R) was used as a spacer and a sealant between the working and counter electrodes.

Characterization

The surface morphology of the CdSe nanorods were characterized by scanning electron microscopy (SEM, LEO, 1450VP, UK) at the 15.0 kV of the electron beam voltage acceleration. The phase of CdSe nanorod was identified using X-ray diffraction (XRD, PANalytical, Empyrean), with 2θ ranging from 20° to 80° and using Cu$K\alpha$ radiation (λ = 0.1542 nm). The optical properties of CdSe nanorod coated on the substrate was characterized by UV-visible spectroscope (SHIMADZU, UV-1800). The electrolyte conductivity was measured by the VersaLab^{TM} equipment with the AC conductivity mode at frequency of 97.6 Hz. The photocurrent density–photovoltage curve (J-V curve) was measured using a Keithley 2400 source meter under an illuminated condition with a solar simulator (Peccel, L11, Japan) at an air mass (A.M.) of 1.5 with an irradiation intensity of 100 mW/cm^2.

RESULTS AND DISCUSSION

Reaction mechanism of CdSe formation

The formation of CdSe involves the following steps. First, the hydrolysis of sodium selenosulphite releases selenide anions as presented by Eq. 1 and Eq. 2.

$$Na_2SeSO_3 + OH^- \leftrightarrow Na_2SO_4 + HSe^- \quad (1)$$

$$HSe^- + OH^- \leftrightarrow H_2O + Se^{2-} \quad (2)$$

The cationic precursor solution (cadmium acetate dihydrate complexed with citric acid) releases Cd^{2+} ions from complex $[Cd(\text{citric acid})]^{2+}$ media as described by Eq.3.

$$Cd[citric\ acid]^{2+} \rightarrow Cd^{2+} + citric\ acid \quad (3)$$

When the substrate is immersed in the Cd^{2+} cations containing solution, Cd^{2+} cations are adsorbed on the surface of the substrate (Cd^{2+}/TiO_2/FTO or Cd^{2+}/glass). After soaking of the substrate in the Se^{2-} anion containing solution, the reaction in an Eq. 4 takes place.

$$Cd^{2+} + Se^{2-} \rightarrow CdSe \quad (4)$$

Formation of CdSe nanorods

SEM micrographs in Fig. 1(a) and Fig. 1(b) show that there are CdSe nanorods formed on the TiO_2/FTO substrate. The averaged diameter and averaged length of CdSe nanorods, which are estimated from Fig. 1(b), are about 97±38 nm and 404±189 nm, respectively. The CdSe nanorods in Fig. 1(a) were not fully covered all the TiO_2 surface. The growth mechanisms of CdSe nanorod are proposed as a solution-liquid-solid mechanism [8]. In these mechanisms, the effects of nucleation and growth rate are the critical factor for fabricating different structures. CdSe nanorods are usually formed under the fast growth rate [9, 10]. It is also possible to synthesis nanorod with the complex agents [11].

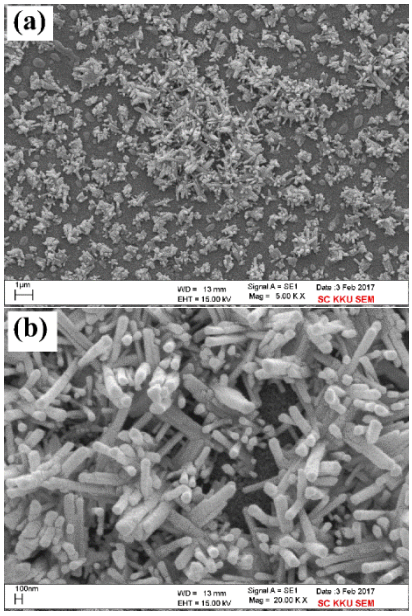

Fig. 1 SEM micrographs of the CdSe nanorods coated on the TiO_2/FTO substrate (a) with the magnification of 5,000x and (b) with the magnification of 20,000x.

Crystalline structure

Fig. 2 shows XRD patterns of CdSe nanorods coated on the glass slide substrate. The result shows that the diffraction peaks at 25.41°, 42.34° and 49.07°, are corresponded to the (111), (220) and (311) planes of the CdSe zinc-blende (cubic) structure (JCPDS 88-2346), respectively. We would like to noted that all observed XRD peaks are broad, which should be attributed to the imperfection of the CdSe nanorod cystalline struture.

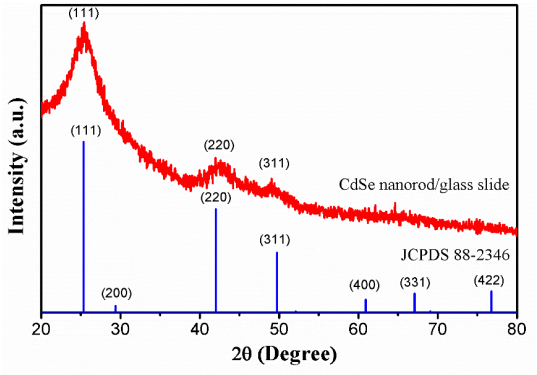

Fig. 2 XRD diffraction pattern of the CdSe nanorods coated on the glass slide substrate and the CdSe zinc-blende structure (JCPDS 88-2346).

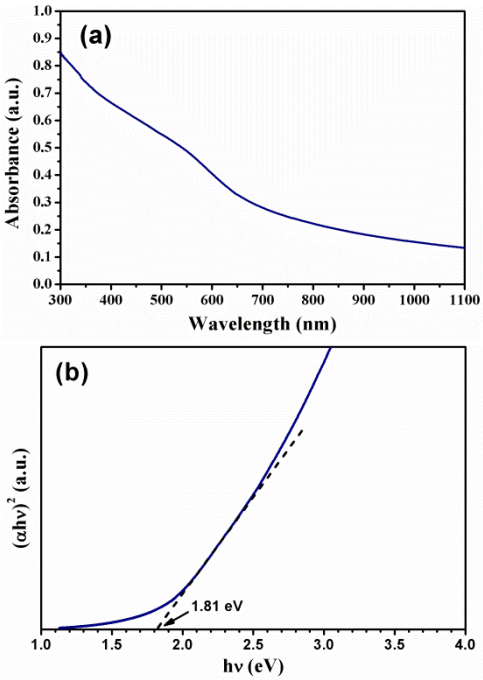

Fig. 3 (a) Absorption spectrum of the CdSe nanorods coated on the glass slide substrate, and (b) the Tauc plot method for determination of the energy bandgap (E_g) of the CdSe nanorod.

Optical properties

The absorption spectrum of the CdSe nanorods coated on the glass slide substrate in Fig. 3 shows that the CdSe nanorods can absorb the broad range of the photon spectrum (300–700 nm). To determine of the optical band gap (E_g), the Tauc plot method based on Eq. 5 has been used

Table 1 The dye-sensitized solar cell parameters fabricated with two different redox electrolytes.

Redox electrolyte	Electrolyte conductivity (mS/cm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	Efficiency, η (%)
Sulfide/polysulfide	17.3	2.19	0.344	0.489	0.37
Iodide/tri-iodide	114.9	2.36	0.734	0.439	0.76

[12], where n is a number that relates to the nature of the transition. In this work, n is equal to 1/2, which is the direct band behavior. The factor β can be assumed to be constant. α, h and ν are the absorption coefficient and the Planck's constant, and the photon frequency, respectively. Thus, the optical gaps of the CdSe nanorods could be determined from extrapolating of the linear regions to zero as shown in Fig. 3(b). The optical band gap of the CdSe nanorods was found to be 1.81 eV.

$$\alpha h\nu = \beta\left(h\nu - E_g\right)^n \quad (5)$$

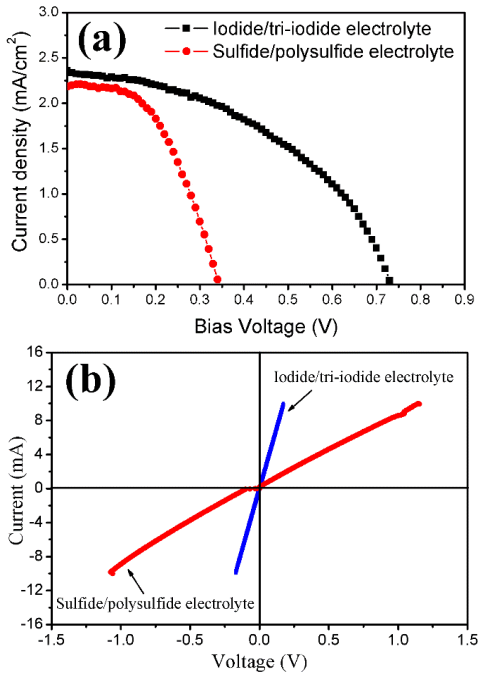

Fig. 4 (a) J-V curves of the dye-sensitized solar cells with two different redox electrolytes, and (b) I-V curves of two different redox electrolytes for estimating electrolyte conductivity.

Solar cell performance

The performance of the CdSe nanorod based DSSCs with two difference redox electrolytes are listed in Table 1. DSSC parameters are extracted from the J-V curves in Fig. 4(a). The short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and solar cell efficiency (η) of DSSCs using the sulfide/polysulfide electrolyte are 2.19 mA/cm^2, 0.344 V, 0.489 and 0.37%, respectively. Whereas, J_{sc}, V_{oc}, FF and η of DSSCs using the iodide/tri-iodide electrolyte are 2.36 mA/cm^2, 0.734 V, 0.439 and 0.76%, respectively. The resistance (R) of the electrolytes was estimated from the 1/slope of the current and voltage curves as shown in Fig. 4(b). An electrolyte conductivity (σ) was calculated by using this relation $\sigma = L/(RA)$, where A and L are the crossection area and distance between Pt electrodes, respectively. It seems that the electrolyte conductivity of the iodide/tri-iodide electrolyte is higher than that of the sulfide/polysulfide electrolyte. These results are consistent with the higher cell performance of the iodide/tri-iodide DSSCs compared to sulfide/polysulfide DSSCs.

CONCLUSION

CdSe nanorod was successfully prepared on the TiO_2/FTO or glass slide substrates by the SILAR method. The XRD measurement revealed that the crystals structure of CdSe nanorod is a zinc-blende (cubic) structure. The optical energy bandgap of CdSe nanorod, estimated from the Tauc plot method, is about 1.81 eV. The solar cell performance of the iodide/tri-iodide DSSCs is higher than that of the sulfide/polysulfide DSSCs due to the high iodide/tri-iodide electrolyte conductivity.

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