Performance enhancement in titania based quantum dot sensitized solar cells through incorporation of disc shaped ZnO nanoparticles into photoanode

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Abstract: Disc shaped ZnO particles are embedded into traditional titanium dioxide photoanodes and quantum dot sensitized solar cells are assembled using these electrodes. With the aid of ZnO discs cells display enhanced performances that peaks at 5% disc loadings with a short circuit current density of 15.34 mA/cm², open circuit voltage of 659 mV and power conversion efficiency of 5.36% respectively. Transmission electron microscopy, scanning electron microscopy, electrochemical impedance spectroscopy suggest that performance enhancement is as a result of improved conductivity of ZnO discs in the photoanodes.

Key words:

Semiconductors

Crystal structure

Electrical properties

Energy storage and conversion

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1. Introduction

Benefit from its high electron transport rate, efficient electron injection [1], zinc oxide attracts growing attention in photoanode applications either solely or with extra nanoparticle components [2-6]. When ZnO is decorated into photoanode, significant improvements are received, including dye adsorption, light scattering, and electron transfer rate [7]. However, QDSSCs based on zinc oxide photoanode generally receive lower power conversion efficiencies (PCEs) than those using traditional P25 photoanodes, which is attributed to the high surface charge recombination in ZnO or low surface area compared to its nanoparticle cousin [2,8]. Cao, *et al.* attributes the heavy surface charge recombination to the defects present on the surface of zinc oxide [9]. Delicate controlled synthesis of ultra-long ZnO nanowire arrays are reported for a large surface area and a PCE of 7% [2]. All of the present applications of ZnO as photoanode are based on the better conductivity of ZnO, thus the direct connection of ZnO with the substrate is expected in spite of the shape or orientation of ZnO particles, which varies the physical properties drastically. According to our previous research, several orientations may exist in the nanowire decorated P25 photoanodes, namely, dangling, laying, and standing on the substrate [10]. The connection of ZnO with the FTO substrate, which is an important factor affecting the conductivity.

The electron mobility varies along different directions in ZnO crystals. There are reports on the ZnO nanowires in photoanode for the enhanced electron collection [11,12]. Intrinsically, the mobility of electrons in *c*-axis-oriented ZnO thin films along the *ab*-plane is 15 times larger than that across the *ab*-plane [13,14]. The differential in electron mobility sheds a strong clue on the stacking of low surface defect discs as a better electron transport pathway for high efficiency sensitized solar cells. We have demonstrated the hydrothermal synthesis and surface enhanced photocatalytic activity of ZnO discs [15,16]. The morphology of the ZnO discs is controlled by sodium citrate, which is easy to be removed so as to leave a clean crystal surface for the photocatalytic reaction. Encouraged by the fact of higher electron mobility across *c*-axis in ZnO, we demonstrate in this report on a disc enhanced photoanode for a high performance quantum dot sensitized solar cell.

In this report, we embedded ZnO discs into traditional P25 photoanode. Photoanodes were co-sensitized with CdS and CdSe by successive ionic layer adsorption and reaction method, and then assembled in to solar cells. At 5 wt% ZnO decoration, cells receive the optimized power conversion efficiency of 5.36 % with a short-circuit current density of 15.34 mA/cm², open-circuit voltage of 659 mV, respectively. Scanning electron microscopy is used to investigate the orientation of ZnO disc in the photoanode film. Electrochemical impedance spectroscopy is subjected to discover the mechanism for the better cell performance.

2. Experimental

2.1 Materials

All reagents, including zinc acetate dihydrate ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$), sodium hydroxide (NaOH), sodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$), lead acetate ($\text{Pb}(\text{OAc})_2$), ethylenediaminetetraacetic acid disodium salt (Na_2EDTA), selenium powder (Se), sodium sulfite (Na_2SO_3), sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$), cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), sulfur sublimed (S), methanol (CH_3OH), and absolute ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) were analytical grade, purchased from Sinopharm Chemical Reagent Co., and used without further purification. P25 was purchased from Germany Degussa Co. Fluorine doped tin oxide (FTO) glass ($7 \Omega/\square$) and hot-melt gaskets were purchased from WuHan GEAO company.

2.2 Preparation of ZnO discs

The round ZnO discs were prepared according to our previous reports [12-13]. Typically, 0.55 g of zinc acetate dihydrate and 0.74 g of sodium citrate were dissolved in 40.0 mL deionized water. After the salts were dissolved, 4.0 mL of 1-4 M sodium hydroxide solution was added to the solution under continuous stirring for 1 h. The final mixture was transferred to a 50 mL Teflon-lined stainless steel autoclave for hydrothermal reaction at 120°C in an oven for 8 h. When the reaction was completed, the autoclave was cooled to room temperature naturally. The resulting white precipitate was collected by centrifugation and purified by washing with deionized water and absolute ethanol several times, and finally dried at 60°C for 8 h.

2.3 Fabrication of ZnO discs/ TiO_2 mixed photoanodes

Four pastes containing mixed ZnO round discs and TiO_2 nanoparticles (Degussa P25) were prepared with ZnO discs concentration of 0, 2.5, 5.0, 7.5 wt%, respectively, which are dispersed in terpeneol with ethylcellulose as binder. The paste was then coated on fluorine doped tin oxide (FTO) glass substrate via the doctor-blade technique and annealed in air at 450°C for 30 min to get microporous film.

2.4 Fabrication of CdS/CdSe sensitized photoanodes

The as-prepared ZnO discs/ TiO_2 films were sensitized with CdS/CdSe QDs by the successive ionic layer adsorption and reaction (SILAR) method. Firstly, the microporous films were immersed in a solution containing 0.1 M $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in methanol for 1 min. Then, the films were immersed in a methanol-water mixture (1:1 by volume) which contains 0.1 M $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ for 1 min. The films were thoroughly rinsed with methanol to remove the excess precursor after each immersion. The same procedure was repeated 5 times to form CdS sensitized TiO_2 electrodes. For CdSe QDs deposition, 5 cycles of TiO_2/CdS electrodes were immersed in a solution containing 0.1 M $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in methanol for 10 min. Subsequently, the electrodes were immersed in 0.02 M Na_2SeSO_3 aqueous solution at 50°C for 20 min. The electrodes were thoroughly rinsed with pure solvent to remove the excess

precursor after each immersion. The same procedure was repeated 7 times to form CdSe sensitized electrodes. Finally, the CdS/CdSe cosensitized electrodes were coated with ZnS passivation layer by twice dipping alternately into $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.1 M) and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (0.1 M) aqueous solutions for 1 min.

2.5 Fabrication of PbSe counter electrode (CE)

PbSe CE was prepared by a simple one-step pulse voltage electrodeposition method according to our works [17]. Typically, the FTO glass was used as the working electrode and a graphite rod was used as the counter electrode. The electrolyte for the electrodeposition of PbSe was an aqueous solution composed of 0.02 M $\text{Pb}(\text{OAc})_2$, 0.04 M Na_2EDTA , and 0.02 M Na_2SeSO_3 (prepared by refluxing Se powder (0.3 M) and Na_2SO_3 (0.6 M) in distilled water at 70°C for 7 h). The pH was adjusted to 7.5-8.0 with NaOH solution before the addition of the Na_2SeSO_3 solution. The PbSe was electrodeposited at room temperature using a 3 V of pulse voltage with the 0.4 s on-time and 0.1 s off-time for 5 s. After deposition, the PbSe CE was rinsed successively with distilled water, ethanol, and then dried in the open air.

2.6 Fabrication and measurement of QDSSCs

The polysulfide electrolyte (1 M Na_2S , 1M S and 0.1 M NaOH aqueous solution) was sandwiched between the CdS/CdSe sensitized photoanode and the PbSe CE to give the cell, which was separated by using a silicone spacer (thickness: 50 μm). The area of the cell was 0.28 cm^2 . The current-voltage characteristics were monitored and recorded by a source meter (Keithly 2400) under an irradiation of simulated solar light (AM 1.5G, 100 mW/cm^2).

2.7 Characterization

The phase and purity of the ZnO structures were characterized by X-ray diffraction (XRD) with Cu $\text{K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The size and morphology were observed using Philips-FEI Quanta 200 scanning electron microscope (SEM). Transmission electron microscopy (TEM) images of the product were collected with a Hitachi H-600 TEM. High-resolution electron microscopy (HRTEM) images were taken on a JEOL JEM-2010 high resolution transmission electron microscopy. The IPCE was measured as a function of wavelength from 325 to 750 nm by using CROWNTECH Q-test station 500TI. Electrochemical impedance spectroscopy (EIS) analyses were performed on electrochemical workstations (CHI660D, ShangHai) under light illumination (100 mW/cm^2), the bias voltage was set at -0.7 V and the frequency was from 0.1 Hz to 100 kHz.

3. Results and discussions

The as-prepared samples are indexed as pure hexagonal phase ZnO with wurtzite structure (JCPDS No. 36-1451) according to XRD characterization (Fig. 1a). Typical SEM image at low magnification illustrates the uniform disc shape and size of the samples (Fig. 1b). From the image, some standing discs display a thickness of 200~300 nm. TEM image at high

magnification shows discs with diameter around 1.0 μm (Fig. 1c). Further structural characterizations on the ZnO discs are performed using selected area electron diffraction (SAED) and high-resolution TEM (HRTEM). The SAED pattern (inset in Fig. 1c) and HRTEM image (Fig. 1d) viewed from [0001] zone axis. The SAED composed of bright spots in 6-fold symmetry without any additional diffraction spots and rings of second phases indicates that the disc-like ZnO microcrystal is a single crystal. From the HRTEM image, the lattice spacing is 0.28 nm, which corresponds to that of [1010] planes. This indicates that the disc grows mainly perpendicular to [0001] zone axis, and the growth along $\langle 0001 \rangle$ direction is suppressed [15,16]. The attained ZnO discs were facing c plane.

When ZnO discs are embedded into P25 film, SEM images with different ZnO content are taken (Fig. 2). From the top-down images, ZnO discs can be well detected embedded in the P25 film (Fig. 2b, c, and d). All the ZnO discs seem facing c plane in the up-down direction. In a typical cross-section SEM image (inset in Fig. 2b), there is no observable ZnO disc with c plane facing the cross section direction. Further stripping the 5.0 % ZnO embedded photoanode to around 6 μm thickness by using a tape (Fig. 3). ZnO discs are also located in the film with c plane facing up (inset in Fig. 3a). There is also no observable ZnO disc along other stacking directions (Fig. 3b). These are thus suggested that the ZnO discs are piled up in a layer by layer way, inserting into P25 films. The present ZnO orientation can be well ascribed to the large c -plane size versus the thickness of the disc and the doctor-blade technique for the preparation of the film. In this case, ZnO discs are stacking in a layer by layer way, which favors the electron transport, resulting in a better cell performance.

J - V curves of cells with different ZnO disc content are recorded (Fig. 4a). The variation of cell performances are largely attributed to the ZnO content since the photoanode film thickness of around 10 μm with different ZnO content can be deduced from SEM images inset in Fig. 2. All the cell parameters are summarized in Table 1. The reference with traditional P25 photoanode records a PCE of 4.12%, which is close to the CdS/CdSe co-sensitized solar cell efficiency reported [18] and paves a sound base efficiency for the later experiments. Open circuit voltages (V_{oc}) and fill factors (FF) of all ZnO disc embedded photoanode cells are higher than that of reference cell. There are several reasons for the increased V_{oc} , one of which is the higher Fermi level of the semiconductor in the photoanode. There are reports of the same Fermi levels of ZnO and TiO_2 [19]. However, Fermi level is sensitive to the environment. And there are also reports for higher ZnO Fermi level compared to that of TiO_2 [4-6,20], both Fermi level and the valance/conduction band of ZnO are higher than that of TiO_2 . Such a ZnO/ TiO_2 composite favors the separation of exciton via the electron and hole injection from ZnO to TiO_2 and vis-a-vis. So, we suppose Fermi level should be one possible reason for the higher voltage. Another possible reason for the higher

V_{oc} may be the better electron mobility and collection along with the retarded recombination in the ZnO disc decorated photoanode cells [6,21-24]. Short-circuit current density increases with increasing ZnO content until 5%, after which J_{sc} decreases to a value even lower than that for the reference cells with traditional P25 photoanode. Nevertheless, the PCE of 7.5 % ZnO embedded photoanode cells is still higher than that of the reference cell, benefiting from the higher fill factor. Further evidence for the higher FF and variation of J_{sc} is disclosed using electrochemical impedance spectroscopy (EIS) analysis.

The enhancement in cell efficiency is also reflected in the incident photon-to-current efficiency (IPCE) curves (Fig. 4b). The integrations of current increase with ZnO content until 5%, which peaks at around 64% at 460 nm. The integrated current of 7.5% ZnO content cell then decreases to a level even smaller than that of non-ZnO-content cells. However, the overall PCEs of ZnO content are higher than that of pure P25 photoanode cells, which is believed to be benefit from the higher open-circuit current of the former cells. The tide of IPCE is in good agreement with those of short-circuit current densities. The high electron mobility of ZnO compared to TiO_2 (ZnO: 200-300 $cm^2 V s^{-1}$ vs TiO_2 : 0.1-0.4 $cm^2 V s^{-1}$) [25] makes the overall PCEs of cells with ZnO content are higher than that of pure P25 photoanode cells. However, ZnO with the size in the micrometer range has much lower surface area than that of P25. Too many ZnO discs in the photoanode decreases surface area, resulting in a low QD loading. There are less photogenerated electrons eventually. As a consequence, there is an optimal ZnO decoration ratio [26-28]. In this paper, the optimal ZnO decoration ratio is 5%. Dark current curves (Fig. 5a) and EIS characterizations (Fig. 5b) are recorded to further disclosure the effect of ZnO in the enhancement of cell performances. Dark current reflects the charge recombination at the photoanode/electrolyte interfaces [29]. The on-set of pure P25 photoanode is the lowest among all the photoanodes, which suggests that less recombination occurs in the ZnO decorated photoanodes. 5% ZnO content photoanode also shows the highest on-set voltage among the samples, which fits the following EIS results. EIS analysis was performed to elucidate the characteristics of electron transport in the QDSCs fabricated with the pure P25 and the ZnO decorated photoanodes [21,30]. EIS analyses were performed under light illumination (100 mW/cm^2) with a bias of 700 mV. The Nyquist plots (Fig. 5b) were fitted by the Zview software. The equivalent circuit is illustrated in the inset of Fig. 5b. The charge transport resistance at photoelectrode/electrolyte interface, R_{ct} , can be determined from the Nyquist plots at the intermediated frequency (Fig. 5b) [21,30]. The values of the R_{ct} are listed in Table 1. For the photoanodes with different ZnO content of 2.5%, 5%, and 7.5%, the R_{ct} is 26.20, 17.51, and 20.92 Ω , respectively. The values are smaller than that for pure P25 photoanode of 27.08 Ω , as a result of the favorable and effective electron transport at the interface [30]. The results reflect the better conductivity of ZnO decorated photoanode, and is in good agreement with

the tendency of J - V and dark current traces.

4. Conclusions

Photoanode conductivity is one of the key factors that affect the efficiency of sensitized solar cells. Zinc oxide along c -axis possesses higher carrier mobility than in other directions. When ZnO discs are embedded into P25 photoanodes, the resistances are eventually decreased and cell efficiencies are enhanced. At 5% ZnO content, cells co-sensitized by CdS/CdSe receive a PCE of 5.36%.

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Figure Captions:

Fig. 1. XRD pattern (a), SEM image (b), TEM image (c), and HRTEM image of the sample (d). Inset in (c): SAED pattern image.

Fig. 2. SEM Top-down viewing images of P25 films embedded with different ZnO content. 0.0 % (a), 2.5 % (b), 5.0 % (c) and 7.5 % (d). Insets showing the cross-section SEM images of the corresponding film.

Fig. 3. SEM images on the 5.0 % ZnO embedded photoanode striped off with a tape: (a) surface SEM images. Inset showing the partial magnified images of (a); (b) cross-sectional SEM image.

Fig. 4. J - V curves (a) and IPCE curves (b) of quantum-dot sensitized solar cells using ZnO/P25 photoanodes with different ZnO content from 2.5 % to 7.5 %.

Fig. 5. Dark current traces (a) and Nyquist plots (b) of the cells with different ZnO content. Inset in (b) equivalent circuit fit from the Nyquist plots.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Table Captions:

Table 1

Cell Parameters for Different Working Electrodes

ZnO content (%)	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	PCE (%)	R_{ct} (Ω)
0	14.78	603	46.23	4.12	27.08
2.5	14.97	633	46.43	4.40	26.20
5.0	15.34	659	53.02	5.36	17.51
7.5	14.10	646	55.00	5.01	20.92

Table 1