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Co-sensitized quantum dot solar cell based on ZnO nanowire

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ABSTRACT

An efficient photoelectrode is fabricated by sequentially assembled CdS and CdSe quantum dots (QDs) onto a ZnO-nanowire film. As revealed by UV–vis absorption spectrum and scanning electron microscopy (SEM), CdS and CdSe QDs can be effectively adsorbed on ZnO-nanowire array. Electrochemical impedance spectroscopy (EIS) measured demonstrates that the electron lifetime for ZnO/CdS/CdSe (13.8 ms) is calculated longer than that of ZnO/CdS device (6.2 ms), which indicates that interface charge recombination rate is reduced by sensitizing CdSe QDs. With broader light absorption range and longer electron lifetime, a power conversion efficiency of 1.42% is achieved for ZnO based CdS/CdSe co-sensitized solar cell under the illumination of one Sun (AM 1.5G, 100 mW cm^{-2}).

1. Introduction

Zinc oxide (ZnO) is a multifunctional material with a wide direct band gap (3.37 eV) and large exciton binding energy (60 meV) [1], which has attracted tremendous attention as a potential candidate for applications in filed emissions [2], electrochromic display [3], dye-sensitized solar cells (DSSCs) [4], and quantum dot sensitized solar cells (QDSSCs) [5,6]. Compared with TiO_2, ZnO has better electron mobility (ZnO, 115–155 $cm^2\ V^{-1}\ s^{-1}$; TiO_2, $10^{-5}\ cm^2\ V^{-1}\ s^{-1}$) [7], and it has other unique advantages suitable for QDSSC photoanode. For example, ZnO can be easily fabricated in nanowire form; a morphology that helps to improve the electron transport by avoiding particle-to-particle hopping that occurs in the TiO_2 network [8]. ZnO-nanowire array also acts as an efficient antireflection coating layer to increase light coupling in solar cells [9].

However, few QDSSCs based on ZnO have been reported and the efficiency is rather low. Leschkies et al. performed plasma treatment on ZnO nanowire to effectively adsorb mercaptopropionic acid capped cadmium selenide (CdSe) and the power conversion efficiency obtained was 0.4% [8]. In our previous work, we employed thioglycolic acid capped CdSe QD loaded on ZnO nanorod and achieved an efficiency of 0.66% [5].

In this paper, we shall report a QDSSC with ZnO-nanowire photoanode fabricated by hydrothermal method. Cadmium sulfide (CdS) QDs grown by chemical bath deposition (CBD) method and pre-synthesized CdSe QDs were sequentially assembled on ZnO-nanowire film to form a co-sensitized structure solar cell. The co-sensitized structure has better performance than the single CdS or CdSe sensitized solar cell and PCE up to 1.42% was achieved in this work.

2. Experiment

ZnO nanowire was grown by a hydrothermal method at 95 °C [10]. The thickness of ZnO film was 9–10 μm. Then the as-grown nanowires were treated by oxygen plasma for 2 min. The CBD method was used to assemble CdS QDs onto ZnO film and the procedure described elsewhere [11]. ZnO film was dipped into an ethanol solution containing 0.5 M $Cd(NO_3)_2$ for 5 min, rinsed with ethanol and then dipped for another 5 min into 0.5 M Na_2S menthol solution and rinsed again with menthol. The two-step dipping procedure is termed as one CBD cycle and it repeated 10 times for ZnO film covered with CdS QDs. After that, ZnO film with CdS QDs immersed into pre-synthesized CdSe ethanol solution for 6 h. The procedure of pre-synthesized CdSe ethanol solution described elsewhere [12]. The ZnO/CdS and ZnO/CdS/CdSe photoelectrodes were

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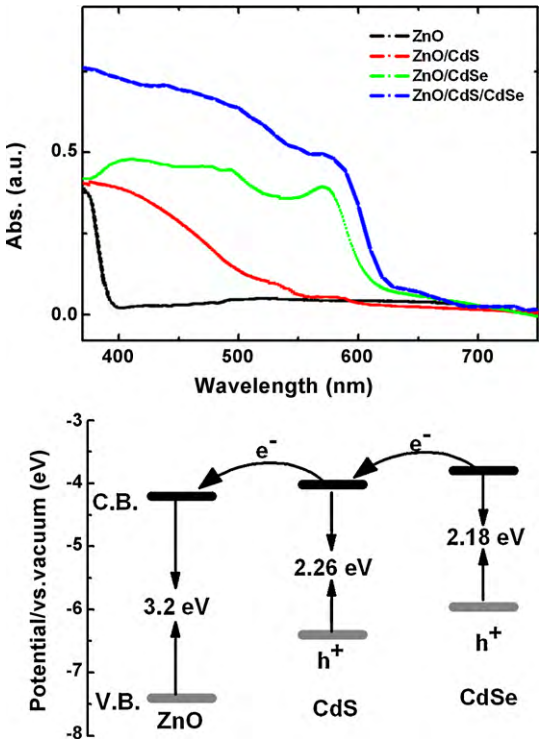

Fig. 1. (a) The UV–vis absorption of ZnO, ZnO/CdS, ZnO/CdSe, and ZnO/CdS/CdSe electrodes and (b) the band position of ZnO, CdS QD, and CdSe QD.

assembled with a 20 nm platinum-coated indium tin oxide (ITO) substrate as the counter electrode. The cell gap was maintained by a 60 μm thermal-plastic spacer. The polysulfide electrolyte consisting of 1 M Na_2S and 1 M S was injected into the cells by capillary effect.

The absorption spectra were recorded using a SHIMADZU MPC-2200 UV-VIS Spectrometer. The current density–voltage (*J–V*) characteristics were measured with a Keithley 2440 Sourcemeter and the cell was subjected to the irradiation of a solar simulator (Abet-technologies, USA) operating at 100 mW cm^{-2} (AM 1.5G). IPCE was measured with QE/IPCE Measurement Kit (Oriel, USA) in the wavelength range of 350–700 nm. Electrochemical impedance spectra (EIS) were measured under open circuit potential with oscillation potential amplitudes of 10 mV from 10^{-1} to 10^6 Hz.

3. Results and discussion

Fig. 1a shows the absorption curves of four photoelectrodes of ZnO, ZnO/CdS, ZnO/CdSe, and ZnO/CdS/CdSe. It can be seen that the optical range of ZnO/CdS/CdSe is broader than ZnO/CdS and ZnO/CdSe. As a result, the co-sensitization effect of CdS and CdSe QDs can be observed by the extending of absorption range and the increase of absorbance. Fig. 1b shows the band position of ZnO, CdS QD and CdSe QD. From the excitonic transition wavelength of 570 nm for ZnO/CdSe photoelectrode, the sizes of these QDs are estimated as 3.5 nm, and the band gap of 2.18 eV [13]. The absorption edges, obtained from the intersection of the sharply decreasing region of a spectrum with its baseline, are ca. 550 nm for ZnO/CdS, corresponding to the band gap of 2.26 eV. Therefore, both the conduction and valence bands positions of the three materials increase in the order: ZnO < CdS < CdSe, which is benefit for the electrons transfer from the conductive band of CdSe QD to ZnO. It was reported that the CdS layer between ZnO and CdSe can prompt the conduction band position of CdSe, leading to a higher driving force for the injection of excited electrons out of CdSe layer [13].

Fig. 2a and b shows the scanning electron microscopy (SEM) images of the ZnO nanowires before adsorbing CdS and CdSe QDs. It can be seen that this ZnO nanostructure consists of nanorod array on the bottom and the finer wires with 50 nm in diameter and 9–10 μm in length on the top. Therefore, this ZnO nanostructure can provide larger surface area, which increases the adsorption amount of QDs and facilitate electron transportation. Fig. 2c shows the SEM image of ZnO/CdS/CdSe photoelectrode. After sensitization by QDs, the surface of ZnO nanowire becomes rougher. The inset of Fig. 2d shows the TEM image of the bare ZnO nanorod with smooth surface. Fig. 2d shows a TEM image of CdS and CdSe QDs adsorbed on ZnO surface. It can be seen that each ZnO nanowire is fully covered by QDs.

Fig. 3a and b show *I–V* characteristics and the IPCE spectra of ZnO/CdS and ZnO/CdS/CdSe samples at 100 mW cm^{-2} (AM 1.5G). The inset of Fig. 3(a) shows the photo image for ZnO/CdS and ZnO/CdS/CdSe electrodes. After sensitizing CdSe QDs, the color of electrode changed from yellow to orange (for interpretation of the references to color in this sentence, the reader is referred to the web version of the article). From Fig. 3(a), it can be seen that the current density (J_{sc}) and open circuit voltages (V_{oc}) of ZnO/CdS and ZnO/CdS/CdSe samples are 3.36 and 5.19 mA cm^{-2}, and 0.543 and 0.661 V, respectively. The fill factor (FF) and power conversion efficiency (PCE) of ZnO/CdS/CdSe (41.5 and 1.42%, respectively) are higher than those of ZnO/CdS (34.2 and 0.63%, respectively). The higher performance of ZnO/CdS/CdSe is attributed to its broader light absorption range which leads to a higher photocurrent. In additional, the FF of ZnO/CdS/CdSe is larger than that of ZnO/CdS, probably due to the better coverage of QDs on ZnO. The increase in V_{oc} value is attributed to favorable intermediate conduction band levels of CdS QDs which provide an effective coupling and therefore facilitate fast charge injection kinetics [7].

The IPCE spectra (Fig. 3b) are consistent with the corresponding UV–vis spectra shown in Fig. 1a. It can be seen that, the maximum IPCE as high as 44% was obtained at 410 nm for ZnO/CdS/CdSe, while the maximum value is only 28% for the ZnO/CdS. In the shorter wavelength region (<550 nm), both CdS and CdSe QDs are photoactive, the increment of IPCE for ZnO/CdS/CdSe device is primarily due to the contribution of CdSe QDs in the light harvest. In the long-wavelength region (>550 nm), where only CdSe QD is photoexcited, the IPCE increment of the ZnO/CdS/CdSe device, compared to ZnO/CdS, indicates that the presence of CdS QDs does not prohibit the transport of excited electrons from CdSe QD to ZnO. That is, CdS QDs are benefit to facilitate excited electron transport from CdSe to ZnO film.

Lastly, to reveal the interfacial reactions of photoexcited electrons in QDSSCs, we measured EIS spectra of as-prepared QDSSCs. Fig. 3c shows the photovoltage response to on–off cycles of visible irradiation. The V_{oc} values were 0.54 and 0.66 V for ZnO/CdS and ZnO/CdS/CdSe devices, respectively. The V_{oc} showed very reproducible response, and the photovoltage generation was steady during on–off cycles of the irradiation. Fig. 3d shows Nyquist plots of QDSSCs using ZnO/CdS and ZnO/CdS/CdSe at an applied bias of V_{oc} and a frequency range from 10^{-1} to 10^6 Hz, with AC amplitude of 10 mV under the illumination of one Sun (AM 1.5G, 100 mW cm^{-2}). It can be seen that two semicircles were observed in the high-frequency region (>1 kHz) and middle-frequency region (10–100 Hz), respectively. It was reported that the middle-frequency peak reflects the properties of the photoinjected electrons with the oxide semiconductor [14]. Under V_{oc} condition, the electrons injected into the oxide semiconductor should be recombined by S_x^{2-} ions at the oxide/dye/electrolyte interface because there was no current passing through the external circuit