Research Article

Doped Heterojunction Used in Quantum Dot Sensitized Solar Cell

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Incorporated foreign atoms into the quantum dots (QDs) used in heterojunction have always been a challenge for solar energy conversion. A foreign atom indium atom was incorporated into PbS/CdS QDs to prepare In-PbS/In-CdS heterojunction by successive ionic layer adsorption and reaction method which is a chemical method. Experimental results indicate that PbS or CdS has been doped with In by SILAR method; the concentration of PbS and CdS which was doped In atoms has no significantly increase or decrease. In addition, incorporating of Indium atoms has resulted in the lattice distortions or changes of PbS or CdS and improved the light harvest of heterojunction. Using this heterojunction, Pt counter electrode and polysulfide electrolyte, to fabricate quantum dot sensitized solar cells, the short circuit current density ballooned to 27.01 mA/cm^2 from 13.61 mA/cm^2 and the open circuit voltage was improved to 0.43 V from 0.37 V at the same time.

1. Introduction

Doped quantum dot (QDs, semiconductor nanocrystal) which was fabricated by chemical method has been recently drawing great attention as a material for solar energy conversion. Incorporating foreign atoms can affect intrinsic property of semiconductor nanocrystals [1, 2]. By doping foreign atom, it is possible to modify the electronic and photophysical properties of QDs [3]. In addition, it is also possible to tune the optical and electronic properties of semiconductor nanocrystals by controlling the type and concentration of dopants [4]. The versatile properties of doped QDs such as red-shift of light harvest [5], create of electronic states in the mid-gap region of the QD [6], and long time of an electron [7] make them attractive candidates for quantum dot sensitized solar cell (QDSC).

The doped single QDs have been researched. But incorporating foreign atoms into the quantum dot used in heterojunction has always been a challenge for solar energy conversion. In addition, one of the current challenges for high performance QDSC is the limited light absorption range from the visible to the near-infrared (NIR) region for the solar spectrum, so wider light absorption range has

ability to generate extremely high J_{sc} [8]. Recently, the light absorption range red shifts to 1100 nm from 900 nm when PbS quantum dot was doped as Hg-PbS quantum dot, resulting in the short circuit current density (J_{sc}) remarkable increase. Although the J_{sc} have a remarkable increase, the open circuit voltage (V_{oc}) has no significant change [9]. While the V_{oc} was increased when CdS/CdSe were doped as Mn-CdS/CdSe, the J_{sc} has no significant change [10]. How to improve the J_{sc} and the V_{oc} of QDSC is always a goal that many investigators pursue.

We introduced foreign atoms—indium atoms into PbS/CdS heterojunction [11–13] on the TiO_2 film by successive ionic layer adsorption and reaction (SILAR) method [14]; SILAR method is a chemical method. The indium was doped in both the PbS and CdS, characterization of the sample display that incorporating of Indium atoms would enhance absorption in the near-infrared portion. Using Pt counter electrode and polysulfide electrolyte to fabricate QDSC, the J_{sc} ballooned to 27.01 mA/cm^2 from 13.61 mA/cm^2 and the V_{oc} was improved to 0.43 V from 0.37 V at the same time. Relative to other heterojunction cells [15, 16], we used the easier way to prepare doped heterojunction.

FIGURE 1: SEM image of (a) a bare TiO_2 mesoporous film and (b) In-PbS/In-CdS sensitized TiO_2 mesoporous film; (c) a cross-section SEM image of a bare TiO_2 film; (d) the EDX spectra of In-PbS/In-CdS QD sensitized TiO_2 film.

2. Experimental Procedure

The photoanode structure was FTO/ TiO_2 /QDs; mesoporous TiO_2 films were prepared by screen-printing of TiO_2 paste (the size of TiO_2 particle is about 20 nm) on clear fluorine-doped tin oxide (FTO) substrates, followed by sintering at 450°C for 30 min.

Quantum dots were deposited by successive ionic layer adsorption and reaction (SILAR) method. In brief, 0.1 M lead nitrate or cadmium nitrate in methanol was used as cation source and 0.1 M sodium sulfide in methanol as anion source. To incorporate doping of In^{3+} , indium chloride (0.01 M) was mixed with lead nitrate or cadmium nitrate. This allowed coadsorption of In^{3+} and Pb^{2+} (or Cd^{2+}) ions, which in turn facilitated incorporation of In^{3+} in the PbS (or CdS). The dipping time in the Pb^{2+} and S^{2-} solution was 60 s for each, and the SILAR cycle was repeated 2 times; the dipping time in the Cd^{2+} and S^{2-} solution was 5 min for each, and the SILAR cycle was repeated 6 times.

The counter electrode was Pt coated FTO, which was prepared by doctor blading chloroplatinic acid on FTO glass, then sintering at 450°C for 30 min. A solution of 0.5 M sodium sulfide, 2 M sulfur, and 0.2 M potassium chloride dissolved in 1:1 methanol and water was used as the liquid electrolyte. The cells were assembled in sandwich fashion using a parafilm spacer. Solar cell performance was evaluated under simulated AM1.5 irradiation conditions.

3. Results and Discussion

We prepared four different heterojunction types on TiO_2 film: (a) 2 SILAR cycles of PbS followed by 6 cycles of CdS ($\text{TiO}_2/\text{PbS}/\text{CdS}$), (b) 2 SILAR cycles of In-PbS followed by 6 cycles of CdS ($\text{TiO}_2/\text{In-PbS}/\text{CdS}$), (c) 2 SILAR cycles of PbS followed by 6 cycles of In-CdS ($\text{TiO}_2/\text{PbS}/\text{In-CdS}$), and (d) 2 SILAR cycles of In-PbS followed by 6 cycles of In-CdS ($\text{TiO}_2/\text{In-PbS}/\text{In-CdS}$). Figure 1(a) shows scanning electron micrograph (SEM) of a bare TiO_2 mesoporous film. It is clear that the particle size of TiO_2 ranges from 20 nm to 40 nm. When In-PbS and In-CdS were assembled in the TiO_2 film, a cluster of quantum dots in the surface was observed from the SEM images. This result indicates that a tiny amount of In-PbS and In-CdS was assembled in the SILAR process. A cross section SEM image of a bare TiO_2 mesoporous film is shown in Figure 1(c), in which the TiO_2 film thickness was clearly evident. Figure 1(d) presents energy dispersive X-ray spectroscopy (EDX) results obtained from $\text{TiO}_2/\text{In-PbS}/\text{In-CdS}$; EDX demonstrates the existence of In element in PbS or CdS. The actual Pb, Cd, and In concentration as measured from the inductively coupled plasma optical emission spectroscopy, ICP-OES, analysis was found to be 7.383%, 45.5%, and 0.97% in In-PbS/CdS QDs; 8.8143%, 47.86%, and 5.48% in PbS/In-CdS QDs; and 6.49%, 49.62%, and 5.49% in In-PbS/In-CdS QDs. This indicates the incorporation of Indium into PbS and CdS quantum dots by

FIGURE 2: The XRD patterns of (a) four QDs and TiO₂ and (b) four heterojunctions and TiO₂; the HRTEM of (c) PbS, (d) In-PbS; (e) CdS, and (f) In-CdS.

SILAR method. In addition, the concentration of PbS and CdS which was doped In atoms has no significant increase or decrease, while the concentration in solid film of In atoms would vary with SILAR cycles.

The X-ray diffraction (XRD) patterns are shown in Figure 2. The XRD patterns show the PbS and CdS all are

cubic structure. The diffraction maximum peak of PbS is (200) at 27.834° , while the higher peaks of In-PbS are (111) and (200) at 26.76° and 27.834° , respectively. However, the major peaks of CdS and In-CdS both are (220) at 43.972° , but a broadening of the peak of In-CdS relative to CdS is seen. Figure 2(b) is the XRD patterns of four heterojunctions.

FIGURE 3: (a) The HRTEM of In-PbS/In-CdS and (b) the EDX mapping of the cross section In-PbS/In-CdS QD sensitized TiO_2 film.

FIGURE 4: (a) Diffuse reflectance absorbance spectra of different QD sensitized films; (b) $J-V$ characteristics of different working heterojunctions.

If In atoms were incorporated into PbS (In-PbS/CdS), the peak is moved to 26.76° from 27.834° ; this is because of the appearance of (111) peak of In-PbS at 26.76° , while the peak is broadened at 43.972° after incorporating In atom into CdS (PbS/In-CdS); this is because of the broadening of the (220) peak of In-CdS. When both incorporate In atom into PbS and CdS (In-PbS/In-CdS), the peak is moved from 27.834° to 26.76° and is broadened at 43.972° . Because of lattice distortions or changes as a result of In doping, it can be confirmed that PbS or CdS has been incorporated. The high-resolution electron transmission electron microscopy (HRTEM) images of QDs also are shown in Figure 2. We can reckon that the particle size of PbS and In-PbS is about 10 nm and 5 nm, respectively, while the major peaks is different, that matches the change of XRD patterns. The particle size of PbS or In-PbS is surprisingly smaller than their Bohr radius [17]. The particle sizes of CdS and In-CdS are all about 5 nm, which is bigger than their Bohr radius and smaller than 10 nm [18].

The HRTEM image of In-PbS/In-CdS QDs is shown in Figure 3(a). The information obtained from Figure 3(a) agrees with Figures 2(d) and 2(f). The EDX mapping of the cross section In-PbS/In-CdS QD sensitized TiO_2 film is shown in Figure 3(b). The In element not only exists in film, but also is evenly distributed along depth. Such a distribution is not only because In-PbS or In-CdS were assembled in the TiO_2 mesoporous by using SILAR but because same proportion indium chloride was mixed with lead nitrate or cadmium nitrate as a cation source.

The light absorption property of PbS/CdS without or with In dopant sensitized TiO_2 film is assessed by UV-vis absorption spectra, Figure 4(a). The absorption property in the visible range increased when the CdS was doped (PbS/In-CdS); however, no apparent contrast increase was found in the long wavelength region. The absorption property for wavelength longer than 1000 nm increases greatly when the PbS was doped (In-PbS/CdS). But the absorption of

FIGURE 5: (a) IPCE spectra for four devices; (b) EIS spectra of QDSSCs measured in the dark at -0.4 V bias voltages. The inset illustrates the equivalent circuit simulated. R_{rec} and $CPE1$ represent the charge transfer resistance and capacitance at TiO_2 /electrolyte interface, respectively; R_s is a series resistance.

TABLE 1: Different photovoltaic parameter for different working heterojunctions.

Samples	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)
TiO_2 /PbS/CdS	13.61	0.37	0.25	1.26
TiO_2 /In-PbS/CdS	23.4	0.44	0.23	2.36
TiO_2 /PbS/In-CdS	11.6	0.45	0.32	1.69
TiO_2 /In-PbS/In-CdS	27.01	0.43	0.29	3.42

In-PbS/CdS deposited film also increased in the visible range, which is due to the diffusion of indium atoms from In-PbS/CdS interface where In is not stable into CdS quantum dot [19]. Both the PbS and CdS were incorporated with indium (In-PbS/In-CdS), not only increased the light absorption in the visible range, and an absorption peak has emerged in the near-infrared portion. ICP-OES analysis illustrates that the concentration of PbS and CdS has no significant increase or decrease; it is excluded that the higher light adsorption was attributed to the possibility of the increase of PdS or CdS for the “doped” samples compared with the undoped ones fabricated via SILAR process, while, the absorption peak emerged in the near-infrared portion is the absorption peak of the exciton of the In-PbS QD.

The J - V characteristics of these four QDSCs are presented in Figure 4(b). The J_{sc} , V_{oc} , fill factor (FF), and power conversion efficiency (η) are summarized in Table 1. An increase of V_{oc} is seen in the cells that incorporate foreign atoms. Similarly, cells that the PbS with indium atoms exhibited a significant increase in the photocurrent as compared to the corresponding cells without indium atoms. The absorption property has been able to explain why the higher J_{sc} was achieved in this study. However, PbS/In-CdS films exhibited decrease in the photocurrent and great increase in the J_{sc} ,

which is due to an accumulation of photo-generated electron in QD layers, but improve the V_{oc} . As we expect, doped heterojunction used in solar cells can significantly increase J_{sc} and the V_{oc} was improved at the same time; an energy conversion efficiency of 3.42% was achieved.

The incident photon to carrier conversion efficiency (IPCE) recorded at different incident light wavelengths for QDSC that employ four different photo-anodes is shown in Figure 5(a). The overall photocurrent response matches the absorption features; IPCE values as high as 70% can be achieved by the TiO_2 /In-PbS/In-CdS device. Significant retaining in IPCE is seen for TiO_2 /In-PbS/In-CdS device with 10% at 1100 nm. It is worth noting that the IPCE of TiO_2 /PbS/In-CdS is higher than undoped ones, but the J_{sc} is lower. As we know, the IPCE represents how many electrons were generated when a photon was absorbed. So the TiO_2 /PbS/In-CdS generated more electrons, but they could not transport completely to FTO. There are two reasons; the impurity energy level is lower than conduction band of TiO_2 /PbS/CdS; some of the electrons accumulated on the impurity energy level to improve V_{oc} . On the other hand, the electron on the conduction band of In-CdS would be back to impurity energy level to combine with the hole. As we expect, doped heterojunction used in solar cells can significantly broaden scope of light harvest into near-infrared portion and promote IPCE at long wavelength. Figure 5(b) shows the electrochemical impedance spectroscopy (EIS) of QDSSCs based on PbS/CdS, In-PbS/CdS, PbS/In-CdS, and In-PbS/In-CdS electrodes measured in the dark at -0.4 V bias voltages. The equivalent circuit simulated which applies to the impedance spectroscopy was inset of Figure 5(b); R_{rec} and $CPE1$ represent the charge transfer resistance and capacitance at TiO_2 /electrolyte interface, respectively; R_s is series resistance that would account for the transport

FIGURE 6: The schematic illustration of the carrier transfer in the (a) TiO₂/PbS/CdS film and (b) TiO₂/In-PbS/In-CdS film. Black arrow showed the electron transport; red arrow showed the electron transition.

resistance of FTO and the connection setup. It can be noticed that incorporating of indium atoms would enhance the value of the R_{rec} , which indicates that the recombination rate of electrons is slower than undoped ones. But seldom is a major change in the value of the R_s .

Figure 6(a) shows the schematic illustration of the electron transfer model for TiO₂/PbS/CdS film. PbS QDs and CdS QDs absorb photon to create pairs of electrons and holes, the electron transports to TiO₂ from QDs, and then the electron transports to FTO from TiO₂. The hole transports to electrolyte from QDs. The TiO₂ particles are designed to give a large surface area for QDs to grow on. In addition, TiO₂ particles are the transporting layer of the electron. As shown in Figure 5(b), the impurity energy level is the presence in PbS or CdS QD. The presence of impurity energy level not only increased the light absorption in the near-infrared portion, but also improves transmission dynamics of electron and transport path between two nanoparticles. Most electrons were transport to FTO; the combination rate of electrons in film would be slower. So the J_{sc} ballooned to 27.01 mA/cm² of TiO₂/In-PbS/In-CdS devices. The presence of impurity energy level will accumulate electron within the QD layers, thus shifting the Fermi level to more negative potentials and increasing the conduction band of CdS. The V_{oc} of TiO₂/In-PbS/In-CdS device was improved.

There is no doubt that incorporated heterojunction used in QDSCs would significantly increase the J_{sc} ; the V_{oc} have an improvement at the same time. Although such a high J_{sc} is rare, it can be further increased to prevent exciton fast recombining to, such as coat with ZnS or dyes at the outer surface of CdS [20]. In addition, the power conversion efficiency can be also enhanced by improve electrolyte and counter electrode [8, 9].

4. Conclusion

A foreign atom—indium atom was incorporated into PbS/CdS QDs to prepare In-PbS/In-CdS heterojunction by successive ionic layer adsorption and reaction method which is a chemical method. Experimental results indicate that PbS or CdS has been doped with In by SILAR method; the concentration of PbS and CdS which was doped In

atoms has no significant increase or decrease. In addition, incorporating of indium atoms has resulted in the lattice distortions or changes of PbS or CdS and improved the light harvest of heterojunction. Using this heterojunction, Pt counter electrode and polysulfide electrolyte to fabricate quantum dot sensitized solar cells, the short circuit current density ballooned to 27.01 mA/cm² from 13.61 mA/cm², and the open circuit voltage was improved to 0.43 V from 0.37 V at the same time.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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