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Optimizing the SILAR cycles for PbS/CdS quantum dots co-sensitized solar cells

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Abstract
Quantum dot-sensitized TiO_2 solar cells (QDSSCs) are photovoltaic devices with low fabrication cost and relatively high efficiency due to the high molar extinction coefficients, ability of multiple exciton generation and tunable energy gap of the quantum dots. Different types of quantum dots have the first excitonic peak at different wavelengths of the solar spectrum from visible to infrared regions. The absorption of the quantum dots is one of the main factors affecting the performance of QDSSCs. One type of quantum dots cannot absorb a wide range of the solar spectrum. To overcome this problem, usually, two or three different types or sizes of quantum dots are used to sensitize the photoanode of QDSSC. In the present study, TiO_2 electrodes were sensitized with PbS and CdS quantum dots separately and corresponding QDSSCs have been characterized. In order to get a high efficiency due to the co-sensitization, successive ionic layer adsorption and reaction (SILAR) cycle combinations of PbS/CdS quantum dots were optimized. Best combination of PbS/CdS solar cell shows an efficiency of 3.55% with short circuit current density of 12.10 mA cm^{-2} and open-circuit voltage of 0.6 V.

Keywords: Quantum dots, multiple exciton generation, tunable energy gap, SILAR

1. Introduction

Quantum dot – sensitized solar cells (QDSSCs) have gained more attention in the area of solar power conversion system due to their low production cost and the excellent properties of quantum dots such as the ability of multiple exciton generation (MEG), tunable energy gap due to the quantum confinement effect and high molar extinction coefficients [1,2]. In dye-sensitized solar cell (DSSC), dye molecules act as photon absorbers and in the case of QDSSC, dye molecules are replaced by the quantum dots. The energy conversion principle of the QDSSC also same as the DSSC with photon absorption, exciton generation, charge carrier injection and regeneration. But, quantum dots can convert a single photon to more than one electron-hole pair. photon absorption of quantum dots can be controlled by changing the size of the quantum dots and the combination of different types of quantum dots [3,4]. There are several types of QDSSCs have been reported with different types of quantum dots such as CdS, CdS/CdSe, PbS, CdTe and CdSe/CdS/PbS [4-8]. TiO_2 and ZnO semiconductor nanostructures are used to fabricate the photoanodes. Spin coating, ink-jet printing, chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) are commonly used techniques to deposit quantum dots in the semiconductor nanostructures [1,9,10].

Several studies have been done for utilizing visible to infrared light photons in QDSSCs, as described below. Huang *et al.* [11] reported CdS/CdSe QDSSCs with a high efficiency of 6.4 %. Here, they have passivated the quantum dots with ZnSe. Due to the co-sensitization, the absorption of the electrode has been increased and charge recombination has been

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reduced with the optimized thickness of the ZnSe passivation layer. CdTe/CdS QDSSCs have been fabricated using chemical bath deposition method by Yu *et al.* [12] with an efficiency of 5.25%. Here, absorption by the CdTe quantum dots is higher than the absorption by CdS quantum dots. CdS quantum dot layer (shell) protects the highly sensitive CdSe quantum dots (core) and plays a role in charge separation.

2. Experimental Methods

2.1 Preparation of TiO_2 electrode

A pin holefree compact layer of TiO_2 was first deposited on a pre-cleaned FTO glass substrate by the following method. 1 ml of titanium (IV) isopropoxide, 1 ml of propan-1-ol, 1 ml of glacial acetic acid and 1 drop of con. HNO_3 were added to 8 ml of ethanol and the mixture was mixed well. This solution was then spin-coated on the conducting side of FTO glass substrate at 3000 rpm for 1 minute. Substrate was sintered at 450 °C for 45 minutes. The above substrate with a compact layer was then covered with a paste prepared with P90 TiO_2 as follows. 0.25 g of TiO_2 P90 powder was ground well for 15 minutes with 1 ml of 0.1 M HNO_3. The paste was spin-coated on the TiO_2 compact layer at 3000 rpm for 1 minute and sintered at 450 °C for 45 minutes. For the preparation of TiO_2 P25 paste, 0.25 g of TiO_2 powder and 1 ml of 0.1 M HNO_3 were ground using mortar and pestle. Then, 0.02 g of Triton X-100 and 0.05 g of Poly ethylene glycol 1000 were used as the binder and the mixture was ground until it became a creamy paste. This TiO_2 P25 paste was spin- coated on TiO_2 P90 layer at 1000 rpm for 1 minute. Then the electrode was sintered at 450 °C for 45 minutes. The electrode was allowed to cool down to room temperature.

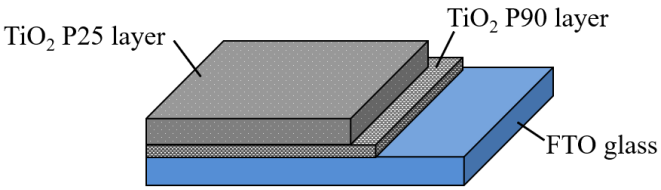

Figure 1: Schematic diagram of the fabricated TiO_2 electrode

2.2 Deposition of quantum dots on TiO_2 electrode

Incorporation of PbS/CdS quantum dots into the TiO_2 electrodes was done by using SILAR method. To get higher efficiency, the number of SILAR cycles were optimized for PbS/CdS combination. For the deposition of PbS quantum dots, aqueous solutions of 0.1 M $Pb(NO_3)_2$ and 0.1 M Na_2S were used as cationic and anionic precursor solutions. Two SILAR cycles were done with 1 minute per dipping for PbS quantum dots. For the deposition of CdS quantum dot shell structure over the PbS quantum dots, aqueous solutions of 0.1 M $CdCl_2$ and 0.1 M Na_2S were used as cationic and anionic precursor solutions. Four SILAR cycles were done with 1 minute per dipping for CdS quantum dots. Finally, the photoanodes were dried at 80 °C for 10 minutes.

2.3 Preparation of electrolyte

2 M S, 2 M Na_2S, and 0.2 M KCl were dissolved in a mixture of deionized water and methanol in the ratio of 3:7 (v/v). The mixture was continuously stirred until getting the clear solution.

2.4 Preparation of counter electrode

Cu_2S was formed on the surface of the cleaned brass plate by applying appropriate amount of polysulfide.

2.5 Optical absorption measurements

Optical absorption spectra of PbS/CdS quantum dot-sensitized TiO_2 electrodes and pristine TiO_2 electrode were obtained using Shimadzu 2450 spectrophotometer.

2.6 Morphology analysis and energy-dispersive X-ray spectra

SEM images of the TiO_2 nanoparticle layer were obtained by using ZEISS EVO scanning electron microscope. Energy-dispersive X-ray (EDX) spectrum was obtained by using Ametek EDAX module with Octane T Optima-60 EDX detector in TEM (JEOL JEM-2100) mode.

2.7 Cell assembly and current-voltage characterization

An appropriate amount of polysulfide electrolyte was applied on the unmasked area of the Cu_2S counter electrode. TiO_2 photoanode was placed on the electrolyte so that the active sides of both electrodes were facing each other with the electrolyte in between them and held together using steel clips as shown in figure 2.

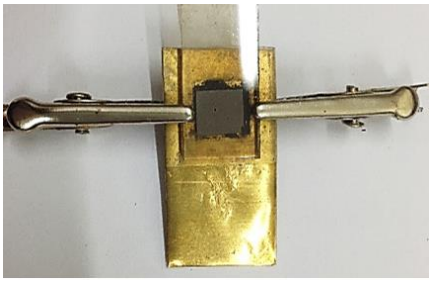

Figure 2: Fabricated PbS/CdS QDSSC with liquid polysulfide electrolyte

Current-voltage measurements of each QDSSCs were done under the illumination of 100 mW cm^{-2} with AM 1.5 spectral filter using a computer-controlled multi-meter (Keithley 2000 model) coupled with potentiostat/galvanostat unit (HA-301). The active area of the QDSSC was 0.12 cm^2.

3. Results and Discussion

Figure 3 displays the optical absorption spectra of TiO_2 electrode and TiO_2 electrode with PbS/CdS quantum dots. PbS/CdS quantum dot - sensitized TiO_2 electrode clearly shows enhancement in optical absorption throughout the entire wavelength region due to the incorporation of CdS and PbS in the photoanode.

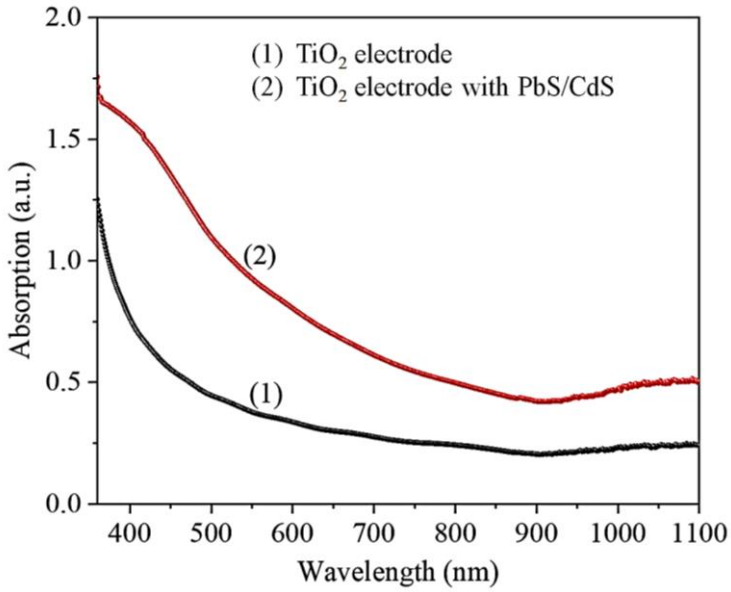

Figure 3: Optical absorption spectra of TiO_2 electrode and PbS/CdS quantum dot-sensitized TiO_2 electrode

Figure 4 shows the SEM image of the fabricated TiO_2 P25 nanoparticle layer on top of the TiO_2 P90 layer. The average particle size of the TiO_2 appears to be in the 25-45 nm range.

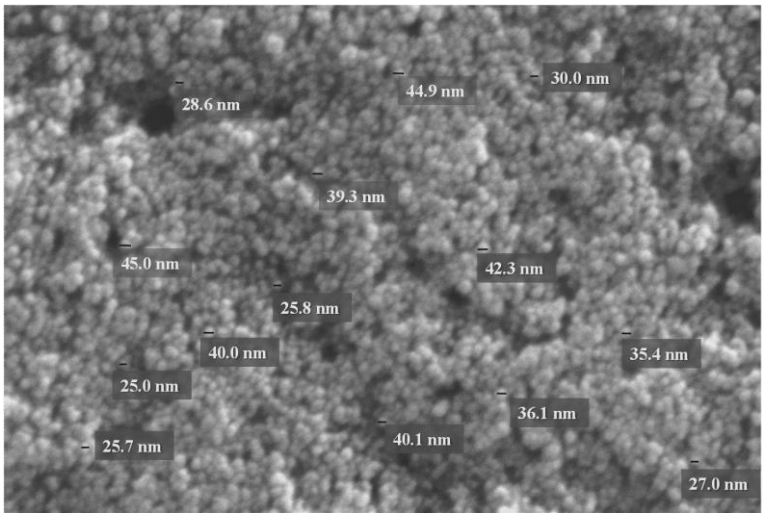

Figure 4: SEM image of TiO_2 nanoparticle layer after sintering at 450 ºC for 45 minutes

EDX spectra and elemental mapping of PbS/CdS quantum dot-sensitized TiO_2 electrode are shown in figures 5 and 6 respectively. These results confirm the coexistence of Pb, Cd and S in the synthesized TiO_2 photoanode.

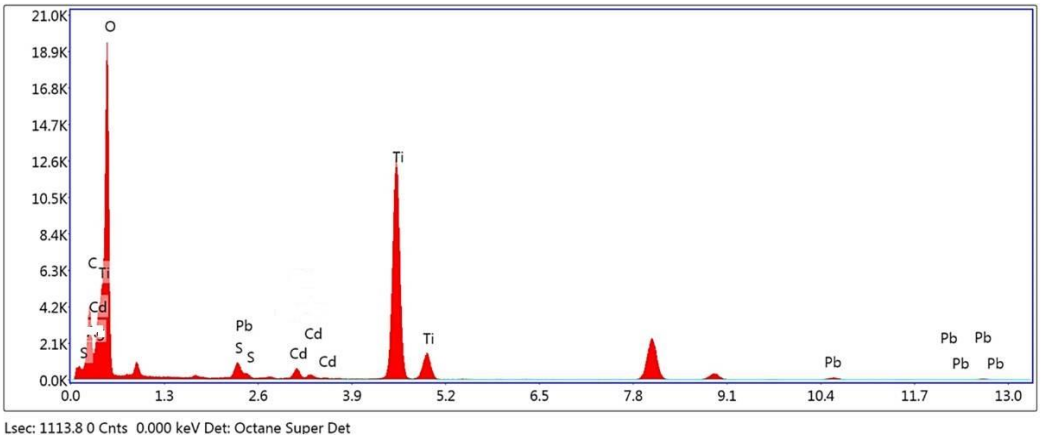

Figure 5: EDX spectrum of PbS/CdS quantum dot-sensitized TiO_2 electrode

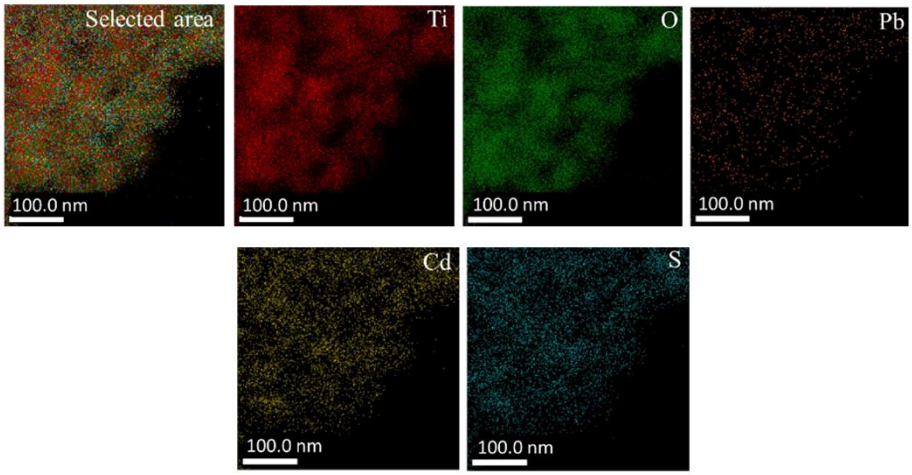

Figure 6: Elemental mapping of PbS/CdS quantum dot-sensitized TiO_2 electrode

Variation of power conversion efficiency of the solar cells with the number of SILAR cycles is given in table 1. Photoanode sensitized with 2 SILAR cycles of PbS and 4 SILAR cycles of CdS shows better efficiency. According to the quantum confinement effect, energy gaps of the PbS and CdS quantum dots decrease with the number of SILAR cycles. When the number of PbS SILAR cycles increased beyond 2, the efficiency decreases as it occupies available nanoporous space in the TiO_2 electrode and not enough space for the formation of CdS quantum dots. The efficiency of the solar cell increases with CdS SILAR cycles and reaches a maximum efficiency of 3.55% corresponding to the 4^{th} cycle.

Table 1: Variation of efficiency of PbS/CdS QDSSCs with the number of SILAR cycles under the illumination of 100 mW cm^{-2} with AM 1.5 spectral filter

SILAR cycles for PbS	SILAR cycles for CdS	Current density (mA cm^{-2})	Efficiency (%)
0	10	10.58	**3.07**
0	11	10.41	2.95
2	0	8.32	1.52
2	1	9.12	2.13
2	2	10.53	2.86
2	3	11.48	3.41
2	4	12.07	**3.55**
2	5	11.96	3.48
3	0	8.56	2.02
3	1	9.04	2.98
3	2	10.24	3.01
3	3	11.01	3.12
3	4	10.11	3.28
3	5	9.89	3.06
4	0	8.63	2.11
4	1	8.98	2.32
4	2	8.51	2.25
5	0	8.82	2.20
5	1	8.70	2.14
6	0	9.01	**2.34**
6	1	8.83	2.29
7	0	8.74	2.17

Beyond 4 cycles, the efficiency decreases. A larger deposited amount of CdS quantum dots increases the light absorption. On the other hand, the increase of CdS quantum dot size would decrease the driving force for the interfacial electron transfer due to the lower conduction band [13]. Further deposition of CdS quantum dots did not further enhance the efficiency, perhaps because of increased pore filling, which would affect the diffusion of the electrolyte within the TiO_2 electrode.

Conclusion

PbS/CdS quantum dot co-sensitized solar cells were fabricated with optimized size and amount of PbS and CdS quantum dots on the TiO_2 electrode. The QDSSC with TiO_2/CdS photoanode shows an efficiency of 3.07% while that with TiO_2/PbS electrode shows 2.34% efficiency. As a result, the overall efficiency increases noticeably after introducing optimized

amounts of quantum dots in TiO_2/PbS/CdS photoanode, and maximum efficiency of 3.55% is obtained. The larger deposited amount of CdS quantum dots increases the light absorption. On the other hand, the increase of CdS quantum dot size would decrease the driving force for the interfacial electron transfer due to the lower conduction band.

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