The effect of CdS on the charge separation and recombination dynamics in PbS/CdS double-layered quantum dot sensitized solar cells

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Abstracts

Quantum dot sensitized solar cells (QDSSCs) have attracted much interest due to their theoretical efficiency, predicted to be as high as 44%. However, the energy conversion efficiency of QDSSCs is still a lot lower than the theoretical value, one reason for which is the number of surface defects on the QDs. In order to improve the conversion efficiency, surface passivation of the QDs has been applied to QDSSCs. Studying the mechanism of how the surface passivation influences the photoexcited carrier dynamics is very important. In this paper, we clarify the effects of CdS passivation on electron injection, trapping and recombination in CdS passivated PbS QDSSCs (called PbS/CdS double-layered QDSSCs). We found that electron trapping and recombination can be suppressed effectively, and that the electron injection efficiency can be increased significantly by surface passivation with CdS on PbS QDSSCs. Our findings provide a better understanding of the effects of surface passivation on QDSSCs, which will prove beneficial for making further improvements in the photovoltaic properties of QDSSCs.

1. Introduction

Quantum dots (QDs) can be used as excellent light harvesting materials, because of their unique properties, such as the capability of tuning the optical absorption spectrum by controlling their size, the large optical absorption coefficient, and the possibility of multiple exciton generation (MEG) [1-3]. The maximum theoretical efficiency of QD based solar cells is expected to be as high as 44% [4], which is about 15% higher than the theoretical efficiencies of dye sensitized solar cells (DSSCs) [5] and traditional silicon solar cells [6]. QD sensitized solar cells (QDSSCs) have attracted much attention because they are easy to produce. However, the energy conversion efficiency of QDSSCs is still less than 12% [7-8]. One of the reasons for the low energy conversion efficiency is the defect levels on the QD surfaces. Therefore, QD surface passivation is crucial for decreasing the surface defect levels and improving the energy conversion efficiency of QDSSCs [9]. In our earlier studies, our group and several others have found that CdS passivation on PbS QDSSCs can greatly improve the photocurrent and energy conversion efficiency [10-13]. Nevertheless, the mechanisms for the effects of CdS, especially how CdS passivation affects the photoexcited carrier dynamics, such as charge separation and recombination in the PbS QDSSCs, are still not very clear.

Generally, the photovoltaic properties of solar cells, such as the short circuit current and the open circuit voltage, are very dependent on the photoexcited carrier dynamics. To improve the photovoltaic properties of QDSSCs, it is vital to understand the mechanisms of the charge transfer dynamics at the TiO₂/QDs, TiO₂/redox, and QDs/QDs interfaces on different timescales. In the timescales from femtoseconds to nanoseconds, there are several relaxation processes for photoexcited electrons, such as electron injection from the QDs to the TiO₂ electrode [14-15], electron trapping at the defect levels [16-17], and recombination of the electrons with holes in the QDs [18]. On the other hand, in the timescales from microseconds to milliseconds, there are some charge recombination processes, such as recombination of electrons injected into the TiO₂ with holes remaining in the QDs and/or in the electrolyte. Up till now, we have succeeded in measuring the photoexcited carrier dynamics in various kinds of solar cells such as QDSSCs, DSSCs, inorganic-organic hybrid solar cells and

perovskite solar cells [19-25] using the transient grating (TG) and transient absorption (TA) methods.

In this study, we studied the photoexcited carrier dynamics in both PbS and PbS/CdS double-layered QDSSCs, including electron injection and charge recombination, using TA measurements. We clarified how the CdS outer layer affects the charge separation and recombination processes as well as the photovoltaic properties of PbS QDSSCs.

2. Experimental

The method used to prepare the TiO₂ electrodes was reported in a previous paper [26]. An anatase TiO₂ paste (PST-18NR, diameter 20 nm, JGC Catalysts and Chemicals Ltd.) was cast onto a glass substrate coated with fluorine doped tin oxide (FTO, 10 Ohm, Asahi Glass) using scotch tape as a frame and spacer, and raking off the excess solution with a glass rod (Squeegee technique). The TiO₂ electrodes were dried in air at room temperature for 10 min, and annealed at 450°C for 30 min in a furnace, before being cooled down to room temperature. The TiO₂ film thickness was around 6 ± 1 μm measured by a contact profilometer (Dektak, Ulvac).

The PbS QDs and the CdS were adsorbed by the successive ionic layer adsorption and reaction (SILAR) method. This method for adsorption and coating was reported in previous papers [9, 13]. The TiO₂ electrodes were immersed in (CH₃COO)₂Pb solution (0.02 M in methanol) for 1 min and then rinsed with solvent. Next they were immersed in Na₂S solution (0.02 M in pure water and methanol mixed solvent (v/v=0.5)) for 1 min and then rinsed with solvent again. This immersion cycle was carried out just once. The PbS/TiO₂ and TiO₂ electrodes were immersed in (CH₃COO)₂Cd solution (0.05 M in methanol) for 1 min then rinsed with solvent. Next they were immersed in Na₂S solution (0.05 M in pure water and methanol mixed solvent (v/v=0.5)) for 1 min and then rinsed with solvent again. This immersion cycle was repeated 5 times. After adsorption of the PbS QDs and the CdS, all the electrodes were coated with zinc sulfide (ZnS), again using the SILAR method. The electrodes were immersed in (CH₃COO)₂Zn solution (0.1 M in methanol) for 1 min and rinsed with solvent. Next they were immersed in Na₂S solution (0.1 M in pure water and methanol mixed solvent (v/v=0.5)) for 1 min and then rinsed with solvent again. This immersion cycle was repeated 6 times in the case of the PbS/TiO₂ electrodes and twice in the case of the CdS/PbS/TiO₂ electrodes. A polysulfide solution was used as the electrolyte with 1M concentrations of S and Na₂S in pure water, through which N₂

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was bubbled. The counter electrode was made of Cu_2S .

Two kinds of TA setup were used to characterize the charge separation (relaxation of photoexcited electrons in the QDs) (a fs TA technique: fs-TA) [22-25], and the charge recombination dynamics (relaxation of the electrons injected into the TiO_2) (a ns TA technique: ns-TA) [20, 21, 24, 25] in the samples. In the fs-TA setup, the laser source was a titanium/sapphire laser (CPA-2010, Clark-MXR Inc.) with a wavelength of 775 nm, repetition rate of 1 kHz, and a pulse width of 150 fs. The light was separated into two parts by a beam splitter. One part entered the sapphire crystal to be used as a white light probe pulse. The other part was used to pump an optical parametric amplifier (OPA) (s TOPAS from Quantronix) to generate light pulses with a wavelength tunable from UV to NIR. This was used as the pump light to excite the sample. The wavelength used was 470 nm. In the ns-TA setup, the pump light source was an optical parametric oscillator (OPO) (Panther, Continuum, Electro-Optics Inc.) excited by a Nd:YAG nanosecond pulse laser (Surelite II-10FR). The pulse width was 5 ns and the repetition rate was 0.5 Hz. We used the pulsed light with a wavelength of 470 nm to excite the samples. The probe light came from a fiber coupled CW semiconductor laser. According to the previous reports, the TA signal resulting from optical absorption of the electrons injected into the TiO_2 can be observed in the vis-NIR region [27]. We also succeeded in observing the relaxation of electrons injected into TiO_2 in DSSCs [19, 28], QDSSCs [20, 21] using probe light with wavelengths of 658 nm and 785 nm. In this study, a probe light wavelength of 785 nm was used to investigate the relaxation of electrons injected into TiO_2 . For all the measurements, the pump and probe lights were incident from the FTO substrate side.

Photoacoustic (PA) spectra were measured using home-built apparatus covering the wavelength region of 270-1200 nm [29]. The photocurrent density-voltage (J-V) curves were measured under A.M. 1.5 over an area of 0.24 cm^2 using a solar simulator (Pacell: PEC-L10). The incident photon to current conversion efficiency (IPCE) spectra were measured using home-built IPCE equipment covering the wavelength region of 450-1200 nm.

3. Results and Discussion

We prepared three different types of sample, CdS/TiO_2 , PbS/TiO_2 , and $\text{CdS}/\text{PbS}/\text{TiO}_2$ samples. The optical absorption spectra of these were measured using a PA technique and the PA spectra are shown in Fig. 1. The PA signal intensities for PbS/TiO_2 and $\text{CdS}/\text{PbS}/\text{TiO}_2$ increase from about 1.0 eV. Since the band gap energies of TiO_2 (3.0 eV) and CdS (2.42 eV) are higher than 1.0 eV, the PA signals for PbS/TiO_2 and $\text{CdS}/\text{PbS}/\text{TiO}_2$ result from the PbS QDs. As shown in Fig. 1, PbS/TiO_2 and $\text{CdS}/\text{PbS}/\text{TiO}_2$ have almost the same optical absorption spectra.

Fig. 1 PA spectra of CdS/TiO_2 , PbS/TiO_2 and $\text{CdS}/\text{PbS}/\text{TiO}_2$

The J-V curves of the PbS and PbS/CdS double-layered QDSSCs are shown in Fig. 2. Table I shows typical photovoltaic properties

of the two kinds of QDSSC. Both the short circuit current density (J_{sc}) and the open circuit voltage (V_{oc}) increase greatly after CdS passivation. The conversion efficiency of the $\text{CdS}/\text{PbS}/\text{TiO}_2$ sample (2.45%) is 25% higher than that of the PbS/TiO_2 sample (1.96%). Especially, J_{sc} for the $\text{CdS}/\text{PbS}/\text{TiO}_2$ sample is 30% higher than that for the PbS/TiO_2 sample. These results indicate that CdS surface passivation can effectively improve the photovoltaic performance of PbS QDSSCs.

Fig. 3 shows the IPCE spectra of PbS and PbS/CdS double-layered QDSSCs. The optical absorption region is the same for both of these. However, the IPCE intensity increases considerably after CdS passivation. For example, the IPCE value increases by about 20% at 550 nm due to the CdS surface passivation, at which wavelength CdS has almost no optical absorption. This result indicates that the increased photocurrent is mostly due to the surface passivation effects of CdS rather than optical absorption of the CdS outer layer. On the other hand, for the increase in the IPCE values at the shorter wavelength region (the photon energy larger than 2.4 eV (bandgap of bulk CdS)), there is also the possibility of the direct injection of electrons from CdS to TiO_2 besides the passivation effect of CdS. This is because that some CdS probably deposited directly on the TiO_2 surface since the PbS QDs may not cover the TiO_2 completely.

Fig. 2 J-V curves of PbS and PbS/CdS double-layered QDSSCs

Table I Photovoltaic parameters of PbS and PbS/CdS double-layered QDSSCs

samples	J_{sc} [mA/cm ²]	V_{oc} [V]	FF [-]	η [%]
PbS/ TiO_2	10.7	0.42	0.43	1.96
CdS/ PbS/ TiO_2	12.9	0.46	0.41	2.45

Fig. 3 IPCE spectra for the samples: PbS/TiO_2 , $\text{CdS}/\text{PbS}/\text{TiO}_2$ samples

Next, to clarify the mechanism by which CdS passivation improves the photocurrent and energy conversion efficiency, we used TA measurements to study the photoexcited carrier dynamics in the two kinds of QDSSC with and without CdS passivation.

The time-resolved TA spectra of each sample without the electrolyte are shown in Fig. 4 (a: PbS/TiO₂, b: CdS/PbS/TiO₂). The TA spectra of both samples showed absorption signals at wavelengths from 680 nm to 770 nm. According to the earlier studies, electron injection from the PbS QDs into the TiO₂ electrodes occurred on a timescale of 100 ns when the PbS QDs were adsorbed onto the TiO₂ using the SILAR method, and the radiative lifetime of the photoexcited carriers in the PbS QDs was of the order of microseconds [17, 30, 31]. Based on these results, it can be inferred that the TA signals for timescales up to 1 ns (Fig. 3) are due to optical absorption of photoexcited electrons in the PbS QDs.

Fig. 5 shows the normalized TA responses with a probe light wavelength of 760 nm for the PbS/TiO₂ and CdS/PbS/TiO₂ samples. The TA response can be well fitted to the following biexponential function

$$Y = A_1 e^{-t/t_1} + A_2 e^{-t/t_2} + A_3 \quad (1)$$

where t_1 and t_2 are time constants, and A_1 , A_2 and A_3 are the contributions from the corresponding components. The parameters obtained by the fit are shown in Table. 2. In a previous report [17], we succeeded in observing three components in PbS QDSSCs with timescales of less than 1 ns, where the first two decay processes were assigned to electron trapping at interfacial defects or surface defects (A_1 , A_2) and the third process (A_3) was considered to be electron injection into the TiO₂ electrode from the PbS QDs. As shown in Table 2, after CdS passivation, there was little change in the time constants, but the corresponding components, A_1 , A_2 , and A_3 , changed considerably. Next, we calculated the ratio of the electrons trapped at the defects to the total number of electrons excited in the PbS QDs using equation (2)

$$\frac{A_1 + A_2}{A_1 + A_2 + A_3} \times 100 [\%] \quad (2)$$

From eq. (2), we found that 87% of the photoexcited electrons in the PbS QDs were trapped in the case of the PbS/TiO₂ sample. In contrast, only 58% of the photoexcited electrons were trapped in the case of the CdS/PbS/TiO₂ sample. Photoexcited electron trapping at the surface and the interfacial defects were suppressed greatly by the CdS coating and as a result higher photocurrents were obtained after CdS passivation. Figure 6 schematically illustrates the electron injection and trapping processes for PbS and PbS/CdS QDSSCs.

Fig. 4 fs-TAS responses for the electrodes: a) PbS/TiO₂, b) CdS/PbS/TiO₂ electrodes

Fig. 5 TA responses measured with a probe wavelength of 760 nm for the PbS/TiO₂ and CdS/PbS/TiO₂ samples, for timescales of (a) 1~10 ps and (b) 10~1000 ps.

Table. 2 Fitted parameters of the fs-TA responses for electrodes

samples	A_1 [-]	A_2 [-]	A_3 [-]	t_1 [ps]	t_2 [ps]
PbS/TiO ₂	0.62	0.23	0.12	0.59	12
CdS/ PbS/TiO ₂	0.40	0.17	0.41	0.37	12

Fig. 6 Schematic illustration of the photoexcited electron dynamics in PbS and PbS/CdS QDSSCs without an electrolyte solution

The TA responses obtained on timescales from 0.1 ms to 500 ms for the PbS/TiO₂ and CdS/PbS/TiO₂ samples without an electrolyte are shown in Fig. 6. For such longer timescales, the TA signals result from absorption of the electrons in the TiO₂ injected from the PbS QDs. The TA intensity of the CdS/PbS/TiO₂ sample is 1.5 times larger than that of the PbS/TiO₂ sample. This result means that the ratio of electrons injected into the TiO₂ electrode increase considerably after CdS passivation, which is in good agreement with the decrease in electron trapping shown in Figs. 4 and 5. On the other hand, the TA responses shown in Fig. 6 couldn't be well fitted by an exponential or bi-exponential function. In order to see how CdS passivation affects the lifetimes of the injected electrons in TiO₂, we compared the effective lifetimes $\tau_{1/2}$ at which the TA signal intensity is half that at 0.1 ms for QDSSCs before and after CdS passivation. As shown in Fig. 7, $\tau_{1/2}$ for the CdS/PbS/TiO₂ sample is 2 ms, which is four times longer than that of the PbS/TiO₂ sample (0.5 ms). This result indicates that CdS passivation considerably increases the lifetime of electrons injected into TiO₂ due to it decreasing the surface defect levels. These results indicate that the electron collection efficiency can be improved by CdS passivation.

Fig. 7 TA responses of PbS/TiO₂ and CdS/PbS/TiO₂ for timescales from 0.1 ms to 500 ms.

4. Conclusion

We studied the photoexcited carrier dynamics of PbS and PbS/CdS double-layered QDSSCs over timescales from ps to ms. We found that CdS passivation reduces the photoexcited electron trapping and increases the efficiency of the electron injection from the PbS QDs to the TiO₂ electrode. In addition, charge recombination at the interfaces between the QDs and the TiO₂ electrodes was suppressed greatly by the CdS passivation. As a result, the charge separation

efficiency and the charge collection efficiency can be considerably enhanced by passivation of this kind. Therefore, the photovoltaic properties can be correspondingly improved by surface passivation. These results provide a better understanding of the passivation effects in QDSSCs, which will benefit research being carried out into making further improvements in the energy conversion efficiency of QDSSCs.

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6. References

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