



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



Koki Sato^{a,b}, Keita Ono^a, Takuya Izuishi^a, Shota Kuwahara^b, Kenji Katayama^{b,1}, Taro Toyoda^a, Shuzi Hayase^c, Qing Shen^{a,*}

^a Department of Engineering Science, The University of Electro-Communications, 1-4-1 Chofugaoka, Chofu, Tokyo 182-8585, Japan

^b Department of Applied Chemistry, Chuo University, 1-13-27, Kasuga, Bunkyo, Tokyo 112-8551, Japan

^c Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, 2-4 Hibikino, Wakamatsu, Kitakyushu 808-0196, Japan

ARTICLE INFO

Article history:

Available online 24 April 2016

Keywords:

Quantum dot
Sensitized solar cell
Surface passivation
Electron injection
Charge recombination

ABSTRACT

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.

© 2016 Elsevier B.V. All rights reserved.

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 con-

version 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.

* Corresponding author. Tel.: +81 424435471; fax: +81 424435501.

E-mail addresses: kkata@kc.chuo-u.ac.jp (K. Katayama), shen@pc.uec.ac.jp (Q. Shen).

¹ Co-corresponding author.

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 $6 \pm 1 \mu\text{m}$ 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 1 M concentrations of S and Na₂S in pure water, through which N₂ was bubbled. The counter electrode was made of Cu₂S.

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 TiO₂) (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 TiO₂ can be observed in the vis–NIR region [27]. We also

succeeded in observing the relaxation of electrons injected into TiO₂ 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 TiO₂. 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 cm² 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/TiO₂, PbS/TiO₂, and CdS/PbS/TiO₂ 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/TiO₂ and CdS/PbS/TiO₂ increase from about 1.0 eV. Since the band gap energies of TiO₂ (3.0 eV) and CdS (2.42 eV) are higher than 1.0 eV, the PA signals for PbS/TiO₂ and CdS/PbS/TiO₂ result from the PbS QDs. As shown in Fig. 1, PbS/TiO₂ and CdS/PbS/TiO₂ have almost the same optical absorption spectra.

The *J*–*V* curves of the PbS and PbS/CdS double-layered QDSSCs are shown in Fig. 2. Table 1 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 CdS/PbS/TiO₂ sample (2.45%) is 25% higher than that of the PbS/TiO₂ sample (1.96%). Especially, *J*_{sc} for the CdS/PbS/TiO₂ sample is 30% higher than that for the PbS/TiO₂ 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 TiO₂ besides the passivation effect of CdS. This is because that some CdS probably deposited directly on the TiO₂ surface since the PbS QDs may not cover the TiO₂ completely.

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.

Download English Version:

<https://daneshyari.com/en/article/5372883>

Download Persian Version:

<https://daneshyari.com/article/5372883>

[Daneshyari.com](https://daneshyari.com)