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Uncovering the charge transfer and recombination mechanism in ZnS-coated PbS quantum dot sensitized solar cells

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Abstract

In this work, the charge transfer and recombination mechanism is uncovered for the PbS/ZnS quantum dot sensitized solar cells (QDSSCs) based on nanoporous TiO_2 electrodes. PbS quantum dots (QDs) were in-situ grown on TiO_2 nanoparticles through the successive ionic absorption and reaction (SILAR) method, followed by the surface passivation of ZnS for the sensitized electrodes. It was observed that the ZnS coating cycles play a significant role in determining the photovoltaic parameters. The highest power conversion efficiency of 1.4% was achieved by coating 13 cycles of ZnS on TiO_2/PbS electrode. It is essential to understand why and how ZnS passivation layers improve the photovoltaic performance of PbS QDSSCs. All obtained solar cells were characterized thoroughly by optical and electrical techniques. The open-circuit voltage decay technique and electrochemical impedance measurements indicated that the ZnS passivation layers significantly suppressed the charge recombination at the TiO_2/electrolyte and TiO_2/QD interfaces. The transient grating measurements suggested that the electron injection from PbS QDs to TiO_2 was obviously enhanced by the ZnS coating layers. This could be attributed to the reduction of carrier trapping and recombination in PbS QDs after surface passivation. These beneficial effects of ZnS layers, therefore, resulted in the improved photovoltaic performances of PbS QDSSCs. This work provides better understanding on the passivation effect of ZnS layers in PbS QDSSCs, which would be beneficial for the further improvement of QDSSCs.

Keywords: Quantum dot sensitized solar cells; Charge transfer; Recombination; Transient grating

1. Introduction

Narrow-band-gap semiconductor quantum dots (QDs), such as CdS, CdSe, PbS, and $CuInS_2$ QDs are attracting growing attention as promising sensitizer candidates for solar cells (Chen et al., 2010; Diguna et al., 2007; Gonzalez-Pedro et al., 2013; Konovalov et al., 2015; Pan et al., 2014; Santra et al., 2013; Shen et al., 2010b; Zhang et al., 2012). In comparison with traditional dye sensitizers, QDs possess unique advantages such as high extinction coefficient, tunable band-gap structures, large intrinsic dipole, and the possibility of multiple exciton generation (MEG) (Shen et al., 2008b). The MEG effect can lead to

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over 100% quantum yield and enhance the performances of photovoltaic devices, which has been evidenced in previous literatures (Lin et al., 2011; Luque et al., 2007; Sambur et al., 2010). It was predicted that the power conversion efficiency (PCE) of photovoltaic devices could be increased up to 44% by tuning the band gap of QDs and generating multiple electron–hole pairs with one single photon absorption (Hanna and Nozik, 2006). However, the PCE of quantum dot sensitized solar cells (QDSSCs) is lagging behind that of dye-sensitized solar cells (DSSCs) (Emin et al., 2011; Yum et al., 2014). This is mainly attributed to the large amount of defects on QD surfaces, which serve as the trapping states for photoexcited carriers and thus lead to the poor photovoltaic performances (Prezhdo, 2009). To solve this problem, the surface of QD-sensitized electrodes are often modified by coating a wide band gap semiconducting material or exchanging the native long capping ligands with short ones. Our previous studies have demonstrated that coating ZnS layers over QD-sensitized electrodes was a powerful approach to improve the device stability and photovoltaic properties of quantum dot sensitized solar cells (Diguna et al., 2007; Guijarro et al., 2011; Shen et al., 2008b; Sixto et al., 2009). Although extensive effort has been devoted to investigate the role of passivation layers, the detailed mechanism is still not fully understood. In this work, therefore, the effects of passivation layers on the photovoltaic properties and charge transfer/recombination mechanism are investigated for PbS quantum dot sensitized solar cells. PbS QDSSCs with different ZnS passivation cycles were thoroughly characterized using the open circuit voltage decay (OCVD), electrochemical impedance spectroscopy (EIS), and an improved transient grating (TG) technique. It was revealed that the enhanced photovoltaic performances in PbS/ZnS QDSSCs were mainly attributed to the passivation effect of ZnS layers on TiO_2 photoanodes and PbS QD surface states, which prevented the electron trapping on QD surfaces, the electron back transfer from electrodes to electrolyte, and the interfacial recombination at TiO_2/PbS interfaces.

2. Experimental details

Nanoporous TiO_2 electrodes were prepared on precleaned FTO glasses by a doctor blading method as reported in previous literature (Shen et al., 2005; Shen and Toyoda, 2003). Anatase TiO_2 nanoparticles (DSL 18-NRT, 20 nm average diameter) were mixed with distilled water (30 wt.%), acetylacetone (10 wt.%) and polyethylene glycol (PEG, 40 wt.% relative to TiO_2) to form a white paste. The obtained pastes were deposited on fluorine-doped-tin-oxide (FTO) coated glasses (Pilkington, ~15 Ω/□ resistance) using a Scotch tape as the spacer. PbS/ZnS QDs layers were deposited on TiO_2 electrodes using the successive ionic-layer adsorption and reaction (SILAR) method, which involves the layer-by-layer growth of QDs by sequentially immersing substrates into ionic precursor solutions for 30 s. Here, a 0.05 M lead nitrate aqueous solution was used as the lead source for the deposition of PbS QDs, and a 0.1 M zinc acetate aqueous solution was used as the zinc source for the coating of ZnS passivation layers. The sulfide sources were 0.05 M and 0.1 M sodium sulfide aqueous solutions for deposition of PbS and ZnS, respectively. After each dipping step in a precursor solution, the electrodes were rinsed with distilled water to remove the excess of precursors. Two SILAR cycles were applied for the deposition of PbS QDs, while different cycles (4, 8, 13, 20) were carried out for the coating of ZnS layers. Quantum dot sensitized solar cells were fabricated by sandwiching the sensitized-TiO_2 electrodes with Cu_2S counter electrodes using a polysulfide aqueous solution as the redox electrolyte. The electrolyte was an aqueous solution containing 1 M Na_2S and 1 M S. The Cu_2S counter electrodes were prepared by immersing brass in 30% HCl at 70 °C for 5 min and subsequently dipping them into the polysulfide solution for 10 min (Toyoda et al., 2010). For the TG measurements, PbS-sensitized TiO_2 electrodes were prepared by coating 0, 5, and 13 cycles of ZnS on TiO_2/PbS electrodes. The morphology and composition of electrodes were investigated by a high-resolution transmission electron microscopy (HR-TEM, JEM-2100F) equipped with an energy dispersive X-ray (EDX) spectroscope.

The current density–voltage (*J–V*) measurements were performed under dark and AM 1.5G irradiation (100 mW/cm^2), respectively, using a Keithley 2400 source meter with a Peccell solar simulator PEC-L10. The active area of fabricated solar cells was 0.24 cm^2. The incident photon conversion efficiency (IPCE) spectra were measured under illustration using a Nikon G250 monochromator equipped with a 300 W Xe arc lamp. The open-circuit voltage decay (OCVD) measurements were carried out using a 405 nm diode laser and the voltage responses were recorded using an Iwatsu digital oscilloscope DS-5554. The OCVD measurements were performed without a background light bias. Electrochemical impedance spectroscopy measurements were performed under dark conditions using an impedance analyzer (BioLogic, SP-300) by applying a small voltage perturbation (10 mV rms) at frequencies from 1 MHz to 0.1 Hz for different forward bias voltages. The improved transient grating measurements were performed using a titanium/sapphire laser (CPA-2010, Clark-MXP Inc.) with a wavelength of 775 nm, a repetition rate of 1 kHz, and a pulse width of 150 fs. The light was separated into two beams. One beam was used as the probe pulse; the other one as the pump light to pump an optical parametric amplifier (TOAPS from Quantronix) and generate light pulses with wavelength tunable from 290 nm to 3 μm. In this work, the pump pulse wavelength was 520 nm and the probe pulse wavelength was 775 nm. Typical laser pulse intensity used in the TG measurement was 2.0 mW or less than it. The area of the laser beam was around 0.2 cm^2. All the TG measurements are carried out in N_2 atmosphere. All tested samples showed negligible photo-damage during the TG measurements. The detailed principle of the