Journal of Electroanalytical Chemistry 788 (2017) 131–136

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Enhanced light harvesting and charge recombination control with TiO_2/PbCdS/CdS based quantum dot-sensitized solar cells

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ARTICLE INFO

Article history:
Received 29 November 2016
Received in revised form 23 January 2017
Accepted 3 February 2017
Available online 04 February 2017

Keywords:
PbCdS
SILAR
Quantum dot sensitized solar cells
Charge recombination
Enhanced light

ABSTRACT

Charge recombination is considered as one of the most significant factors in hindering the photovoltaic performance of quantum dot-sensitized solar cells (QDSSCs). In addition, expand the light absorption range to the near-infrared region in QDSSCs increasing the generated photocurrent. A significant enhancement in the power conversion efficiency (PCE) of QDSSCs has been obtained by charge recombination control and enhanced light harvesting. In this respect, PbCdS layer is introduced between TiO_2 and CdS QDs via a facile successive ionic layer absorption and reaction (SILAR) method in order to further improve the cell performance. For the first time a photoanode assembly composed of TiO_2/PbCdS/CdS was prepared in QDSSCs. The photovoltaic parameters were significantly enhanced with the incorporation of a PbCdS intermediate layer between TiO_2 and CdS QDs but varied appreciably with the SILAR cycles of PbCdS. When four SILAR cycle layer was applied, the PCE is as high as 3.35%, which is higher than the efficiency of 1.84% for the solar cell without PbCdS layer. The improved performance of the TiO_2/PbCdS/CdS-based QDSSCs was attributed to the PbCdS layer can enhance the light harvesting to release more excitons. In addition, the PbCdS layer accelerates the electron injection kinetics and also functioning as a blocking layer to cover the TiO_2 core from the outer QDs and redox couple, thereby reducing the recombination of electrons from the TiO_2 with the electrolyte or with the QDs. Electrochemical impedance measurements has been measured and discussed in detail providing a detailed analysis of charge transport processes in QDSSCs.

1. Introduction

Developing low cost and high performance solar cells for harvesting and converting light energy to electricity is one of the most promising technologies to solve social concerns such as the exhaustion of fossil fuels, as well as global warming. As a promising low-cost candidate for third generation solar cells, quantum dot sensitized solar cells (QDSSCs) are attracting owing to their excellent properties of band gap tunability, high absorption coefficient, multiple exciton generation possibility, and solution processability [1–4]. The typical structure and principle of QDSSCs is similar to that of dye sensitized solar cells (DSSCs) in which the dye molecules replaced with the quantum dot (QD) sensitizer [5,6]. The QDSSC consists of a mainly concepts of mesoporous photoanode (TiO_2 film), a sensitizer (QDs), an electrolyte (polysulfide) and a counter electrode (CE). Under illumination, photons are captured by the sensitizer, which injects excited electrons into the conduction band (CB) of the TiO_2 film and the holes are released by the redox electrolyte and regenerated at the CE [7].

QD sensitizer materials including the conventional Cd-based (CdS, CdSe, $CdSe_xS_{1-x}$, $CdSe_xTe_{1-x}$), Pd-based (PdS, PdSe) and carbon QDs have been widely investigated for QDSSCs [8–16]. Even though QDs have tremendous properties, the QDSSCs performance is far lower than DSSCs [17] and perovskite solar cells [18]. The performance of QDSSCs is mainly depends on the factors including structure of mesoporous film for photoanode, the type of sensitizer, redox couples in electrolyte [19], and the electrocatalytic activity of the counter electrode. However, the lower power conversion efficiency was mainly attributed to high charge recombination at metal-oxide/electrolyte and QD/electrolyte interfaces [20,21]. Currently, several effective techniques have been evolved to suppress carrier recombination in QDSSCs: (1) wide-bandgap metal oxide layers were deposited (i.e. MgO, SiO_2 and amorphous TiO_2) on the TiO_2 surface to suppress the electron losses [22,23]; (2) passivation of QDs surface with ZnS (or ZnSe or ZnS/SiO_2) passivation layer to control charge recombination at interfaces of TiO_2/QDs/electrolyte [24–28]; (3) preparation of type II core/shell QD structure [29]; (4) fabricating new QD materials for enhancing light capturing

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http://dx.doi.org/10.1016/j.jelechem.2017.02.005
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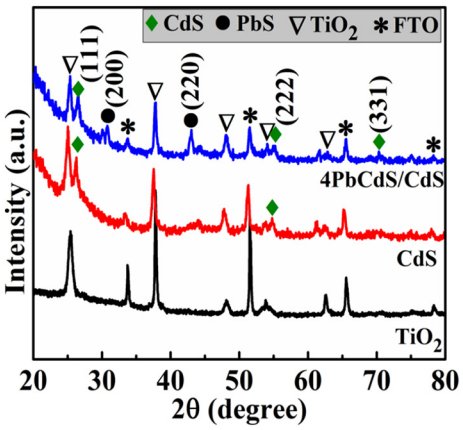

Fig. 1. XRD patterns of the TiO_2, CdS (0PbCdS/CdS) and 4PbCdS/CdS samples.

efficiency [30–33]; and (5) introducing mid-gap states in sensitizers with the dopant materials [34]. Anyway, developing new QD sensitizers with interfacial modification is important to elevate the device performance of the QDSSCs in essence.

Here, we describe QDSSCs consisting of a CdS QDs with a buffer layer (PbCdS) prepared by using the successive ionic-layer adsorption and reaction (SILAR) process. To our best knowledge, the utilization of PbCdS/CdS as sensitizer in QDSSC has not been reported. The TiO_2/PbCdS/CdS electrode shows a complementary effect in light harvesting, and also illustrates efficient charge transport with reduced recombination, which may further elevate its device performance. Thus, it was found that the QDSSC performance is depends on the deposition of SILAR cycles on the surface of TiO_2. Ultimately, the four SILAR cycles of PbCdS with CdS (TiO_2/PbCdS/CdS) structure delivers a superior PCE of 3.35% than the CdS QDSSCs (PCE = 1.84%) under simulated AM 1.5100 mW cm^{-2} illumination

2. Experimental section

2.1. Fabrication of TiO_2/PbCdS/CdS photoelectrodes and QDSSC assembly

TiO_2 paste (Ti-Nanoxide HT/SP) was purchased from Solaronix and the other all chemicals were received from Sigma-Aldrich. Fluorine-doped tin oxide (FTO, 13 Ω $sq.^{-2}$, Hartford Glass Co. Inc.) substrate is used to fabricate the mesoscopic TiO_2 films. A thick layer of 20 nm anatase TiO_2 particles (Ti-Nanoxide HT/SP, Solaronix) was coated on the FTO by the doctor blade method with an active area of 0.27 cm^2. To remove impurities and improve the crystallinity, the films were annealed at 450 °C for 30 min.

Facile SILAR method was used to deposit PbCdS seed layer on the mesoporous TiO_2 surface to facilitate the subsequent CdS growth. The substrate was first dipped into an aqueous 0.1 M $Cd(CH_3COO)_2 \cdot 2H_2O$ and 25 mM $Pb(NO_3)_2$ solution for 2 min to allow Cd^{2+} and Pb^{2+} to adsorb onto the TiO_2. After rinsed with DI water and ethanol, the film was immersed into a 0.1 M Na_2S solution for another 2 min, followed by rinsing with DI water and ethanol and dried with a drier. The two-step immersion procedure is one SILAR cycle. 0, 2, 4, 6, and 8 SILAR cycles of PbCdS was deposited on the TiO_2 surface and the corresponding samples are named as 0PbCdS, 2PbCdS, 4PbCdS, 6PbCdS, and 8PbCdS, respectively. For preparing PbCdS/CdS QDs, the above prepared TiO_2/PbCdS films were dipped in 0.1 M $Cd(CH_3COO)_2 \cdot 2H_2O$ and 0.1 M Na_2S aqueous solutions for 5 min respectively, rinsing with DI water and ethanol between the two immersion steps and repeat the 8 CdS SILAR cycles. The as-prepared photoanode is denoted as TiO_2/PbCdS/CdS. CuS CEs were fabricated using a previous literature method [35].

Devices were fabricated by assembling the CEs and photoanodes and sealed at 100 °C using sealant (SX 1170-60, 60 μm thickness, Solaronix). The gap between the electrodes was filled with polysulfide electrolyte (1 M Na_2S, 2 M S and 0.1 M KCl in a solution of methanol:water is 7:3).

2.2. Characterization

The crystalline structure of the electrodes was investigated by X-ray diffraction (XRD, D/Max-2400, Rigaku using a Cu Kα, 40 kV and 30 mA). The surface morphologies of the electrodes were analyzed by a scanning electron microscope (SEM, S-2400, Hitachi). X-ray photon spectroscopy (XPS) was performed using a VG Scientific ESCALAB 250. Atomic force microscope (AFM) analysis was carried out in a JPK NanoWizard II AFM, JPK instruments, Berlin, Germany. The UV–visible absorption spectra are collected from the OPTIZEN 3220UV system. The photocurrent density-voltage (J–V) curves were measured under AM 1.5G using an ABET Technologies (USA) solar simulator. The incident photon-to-current conversion efficiency (IPCE) characteristics were analyzed by an Oriel® IQE-200™ system. Electrochemical impedance spectra (EIS) are examined using a BioLogic potentiostat/galvanostat/EIS analyzer (SP-150, France) and the curves are recorded in the

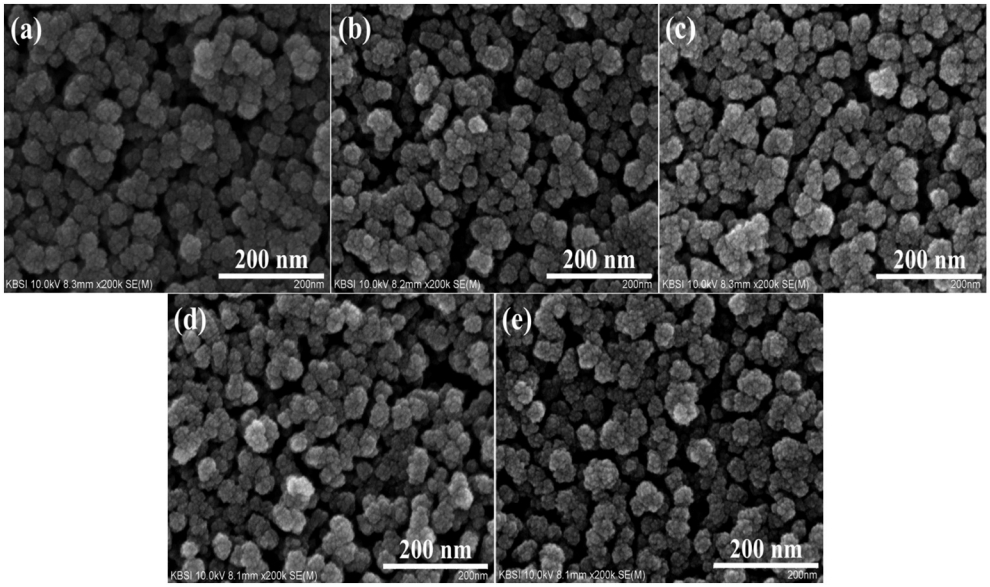

Fig. 2. Surface SEM images of the (a) 0PbCdS/CdS, (b) 2PbCdS/CdS, (c) 4PbCdS/CdS, (d) 6PbCdS/CdS and (e) 8PbCdS/CdS QD-sensitized electrodes on the surface of TiO_2.