Electrochemistry Communications 20 (2012) 97–100

Contents lists available at SciVerse ScienceDirect

Electrochemistry Communications

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

Highly efficient PbS/CdS co-sensitized solar cells based on photoanodes with hierarchical pore distribution

Na Zhou, Guoping Chen, Xiaolu Zhang, Luyao Cheng, Yanhong Luo, Dongmei Li *, Qingbo Meng *

Key Laboratory for Renewable Energy, Chinese Academy of Sciences, Beijing 100190, China
Beijing Key Laboratory for New Energy Materials and Devices, Beijing 100190, China
Beijing National Laboratory for Condense Matter Physics, Beijing 100190, China
Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

ARTICLE INFO

Article history:
Received 28 February 2012
Received in revised form 21 March 2012
Accepted 22 March 2012
Available online 29 March 2012

Keywords:
Quantum dots
Lead sulfide
Dye-sensitized solar cells
Diffusion reflection spectrum

ABSTRACT

A new TiO_2 photoanode with hierarchical pore distribution was first employed to fabricate PbS/CdS co-sensitized quantum dot-sensitized solar cell (QDSC). Under AM 1.5 illumination of 100 $mW \cdot cm^{-2}$, up to 3.82% of light-to-electricity conversion efficiency has been achieved, higher than the reported results of PbS/CdS QDSCs so far. The effects of PbS SILAR cycles, CdS deposition time and film thickness on cell performance were investigated. Furthermore, comparison between this photoanode with large spherical voids and conventional photoanode with large size TiO_2 scattering layer was carried out. This kind of photoanode can provide good scattering ability and large surface area, which is suitable for QDs efficient deposition and electrolyte penetration, exhibiting potential application in highly efficient QDSCs especially with high photocurrent.

1. Introduction

Quantum dot-sensitized solar cells (QDSCs) are interesting energy devices because quantum dots (QDs) exhibit some attractive advantages, such as high extinction coefficients, tunable bandgaps simply by controlling the QDs sizes, low cost and so on [1,2]. Especially, the application of multiple exciton generation (MEG) into QD solar cells may potentially give about 44% of conversion efficiency, higher than Shockley–Queisser efficiency limit [3]. At present, different kinds of QDs have been attempted to fabricate QDSCs, among which PbS with a considerably lower bulk bandgap of 0.37 to 0.41 eV has received more attention since it can allow the absorption band extending to the NIR region of the solar spectrum. Very recently, Parkinson et al. experimentally demonstrated the collection of photocurrents with quantum yields greater than one electron per photon in the PbS QDs sensitized planar TiO_2 single crystal, which is undoubtedly encouraging to the future photovoltaics development [4]. Despite of these advantages, however, the photovoltaic performance of PbS/CdS QDSCs is much lower than those CdS/CdSe co-sensitized QDSCs [5,6]. This is mainly ascribed to electron losses from recombination reactions at TiO_2/PbS QDs/electrolyte interfaces as well as inner energy losses at electrolyte/counter electrode interface [7]. Therefore, in order to improve the performance of PbS QDSCs, optimizing the structure of photoanode and effective surface treatment methods are necessary [8].

Herein, a new kind of TiO_2 photoanode with hierarchical pore distribution has been employed in PbS/CdS QDSCs, consisting of a transparent layer with small pores and a light scattering layer derived from large nano-embossed hollow sphere. Meanwhile, a screen-printable Cu_2S/carbon composite counter electrode was used to fabricate PbS/CdS QDSCs. Nearly 20 $mA \cdot cm^{-2}$ of the photocurrent density can be achieved, over 70% higher than those similar PbS/CdS QDSCs [7]. An overall conversion efficiency of 3.82% has been reached, which is, to the best of our knowledge, the highest efficiency of this kind of PbS QDSCs with the polysulfide electrolyte. This PbS/CdS QDSC exhibits some attractive advantages, such as extraordinarily high photocurrent and lost-cost as well as promising application in the future.

2. Experimental

2.1. Fabrication of PbS/CdS electrode and counter electrodes

The TiO_2 photoanode was deposited on fluorine-doped tin oxide conducting glass (FTO, thickness: 2.2 mm, Pilkington, 14 Ω/square) by doctor blading technique. The double-layer TiO_2 film consists of a transparent layer with 20 nm anatase TiO_2 nanoparticles and an 11 μm-thickness large pore scattering layer with 60 nm anatase TiO_2 nanoparticles [6,9]. The scattering layer is obtained by twice deposition and calcination at 450 °C. The paste for the scattering layer was prepared by using 60 nm TiO_2 nanoparticles dispersed in terpineol with polystyrene spheres of diameters about 1 μm in a weight ratio of 2:1 (TiO_2:polystyrene spheres).

* Corresponding authors. Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China. Tel./fax: +86 10 82649242.
E-mail addresses: dmli@iphy.ac.cn (D. Li), qbmeng@iphy.ac.cn (Q. Meng).

1388-2481/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.elecom.2012.03.032

The successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition (CBD) techniques were employed to assemble PbS and CdS on the photoanode, respectively [6,8]. Briefly, the photoanode film was dipped into 0.02 M Na_2S aqueous solution for 30 s, thoroughly rinsed with Milli-Q ultrapure water, then dipped into 0.02 M $Pb(NO_3)_2$ solution for another 30 s, rinsed with Milli-Q water again, which was defined as one SILAR cycle. Subsequently, CdS was deposited on PbS sensitized films by CBD method at 10 °C [6]. The amount of QDs on the TiO_2 photoanode was controlled by SILAR cycles and CBD deposition time. Finally, the photoanode was passivated with ZnS by twice dipping into 0.1 M $Zn(CH_3COO)_2$ and 0.1 M Na_2S aqueous solutions for 1 min alternately. Cu_2S/carbon (Cu_2S/C) composite counter electrode was prepared according to our previous work [10].

2.2. Characterization

The surface morphologies were obtained using a scanning electron microscope (SEM, FEIXL30S-FEG). The cells were irradiated by an Oriel solar simulator 91192 under AM 1.5 illumination (100 $mW \cdot cm^{-2}$), and photocurrent–voltage (*J–V*) characteristics of the cells were recorded on Princeton Applied Research, Model 263A. The PbS/CdS-coated TiO_2 film, polysulfide electrolyte (1 M Na_2S and 1 M S) and Cu_2S/C electrode were assembled into a sandwich-type cell. A mask with a window of 0.15 cm^2 was clipped on the TiO_2 side to define the active area of the cell. The incident photon-to current conversion efficiency (IPCE) was measured by using a homemade IPCE setup illuminated under 0.3–0.9 $mW \cdot cm^{-2}$ monochromic light [11,12]. Reflectance spectra of TiO_2 films were carried out on Shimadzu UV-2550 equipped with an integrating sphere in the wavelength range of 350–800 nm.

3. Results and discussion

Fig. 1(a) shows the typical cross-section SEM image of the as-prepared double layer TiO_2 film. Its top layer (TL) is composed of 60 nm-size TiO_2 nanoparticles with large spherical voids, which average pore sizes are around 1 μm, as shown in Fig. 1(b) and (c). These hollow spheres embedded in the TiO_2 matrix act as scattering centers for QDSCs. In the meantime, about 100 nm-sized pores generate between the 60 nm particles. The bottom transparent layer (NL) is composed of 20 nm nanocrystals with about 30 nm pore size, as shown in Fig. 1(d). Accordingly, a hierarchical pore distribution is obtained in the TiO_2 photoanode, favoring large surface area and easy electrolyte penetration.

First, optimal PbS SILAR cycles and CdS CBD deposition time on this photoanode, were investigated. As we can see from Fig. 1(e), with increasing PbS SILAR cycles, the color of the PbS–TiO_2 photoanode changes from yellow to black, indicating that the QD sizes are increasing. When incorporated with polysulfide electrolyte and Cu_2S/C electrode to give a sandwich-type cell, the effects of PbS SILAR cycles and CdS deposition time on the cell performance were clearly distinguished at a fixed 9 μm-thickness NL film, respectively, as presented in Table 1. It is found that the short-circuit photocurrent density (J_{sc}) enhances from 7.98 to 18.84 $mA \cdot cm^{-2}$ with increasing the number of SILAR cycles. However, open-circuit photovoltage (V_{oc}) and fill factor (*FF*) are simultaneously observed lower with increasing PbS SILAR cycles, mainly due to higher recombination between photo-generated electrons and polysulfide, further in accordance with I. Mora-Seró's work about impedance spectroscopy [7]. Therefore, the optimal PbS SILAR cycles are three. Under the same PbS deposition cycles, the cell without CdS presents both low J_{sc} and V_{oc}, indicating that CdS QDs is indispensible to highly efficient PbS-sensitized solar cells. Furthermore, CdS deposition time is investigated. When prolonging CdS adsorption time from 1 h to 3 h, the efficiency of PbS/CdS QDSCs obviously decreases since too much CdS QDs on the TiO_2 electrodes may hinder QDs regeneration by the electrolyte and enhance the recombination reaction [13]. Similarly, the CdS sensitized solar cells with 1 h deposition can only present 1.19% efficiency, due to very narrow absorption band. Consequently, for PbS/CdS co-sensitized solar cells,

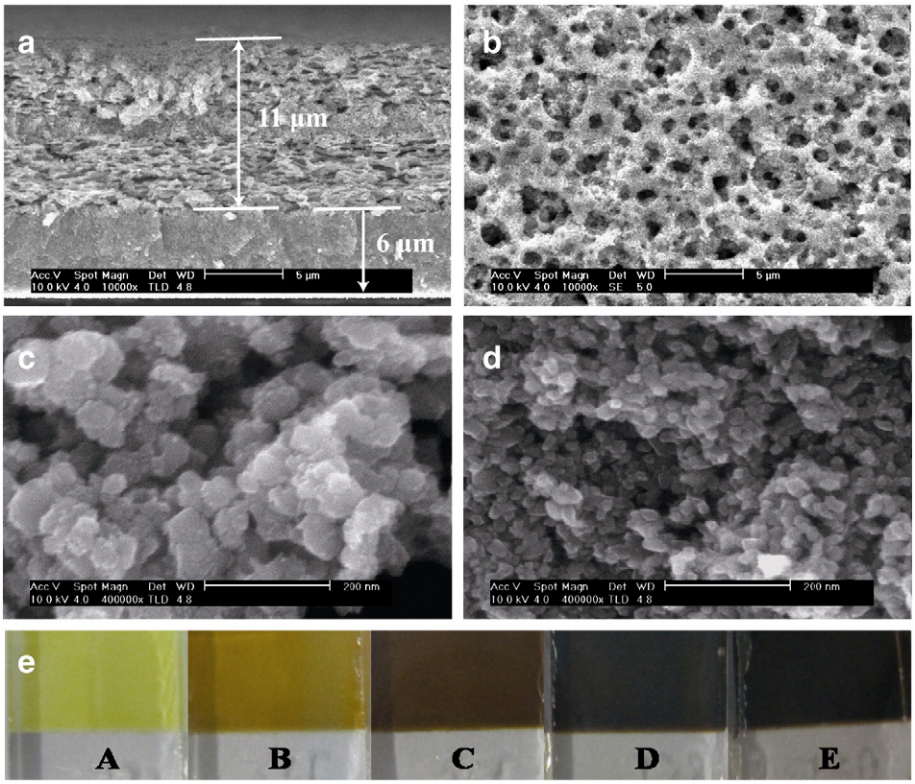

Fig. 1. SEM images of (a) the cross section of the whole film, (b) the vertical section of TL (top layer), (c) and (d) the magnified images of TL and NL (nanocrystal layer). (e) The photos from A to E orderly representing TiO_2/PbS/CdS films with PbS SILAR cycles for 0, 2, 3, 4, 5 and the same 1 h CdS deposition.