Journal of Power Sources 401 (2018) 255–262

Contents lists available at ScienceDirect

Journal of Power Sources

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

Hierarchical ZnO microspheres photoelectrodes assembled with Zn chalcogenide passivation layer for high efficiency quantum dot sensitized solar cells

Fei Huang[a,b], Hao Tang[b], Yuan Wang[b], Juan Hou[c], Zhaoyu Liu[b], Robert C. Massé[b], Jianjun Tian[a,*], Guozhong Cao[a,b,**]

[a] Advanced Material and Technology Institute, University of Science and Technology, Beijing, 100083, China
[b] Department of Materials Science and Engineering, University of Washington, Seattle, WA, 98195-2120, United States
[c] Key Laboratory of Ecophysics and Department of Physics, College of Science, Shihezi University, Xinjiang, 832003, China

HIGHLIGHTS

- A novel hierarchical ZnO microspheres photoelectrodes were fabricated.
- Zn chalcogenide (ZnS or ZnSe) passivation layers.
- Significantly reduced charge recombination and improved V_{oc} and FF.
- The PCE of the ZnO@ZnS and ZnO@ZnSe microspheres based QDSCs reached 5.13% and 5.20%.

ARTICLE INFO

Keywords:
Quantum dot sensitized solar cell
Hierarchical ZnO microspheres
Zn chalcogenide passivation layers
Reduced charge recombination
High efficiency

ABSTRACT

The power conversion efficiency of quantum dot sensitized solar cells with ZnO as photoelctrode is relatively low, largely due to high charge recombination rate at the ZnO surface. This paper reports high-efficiency hierarchical ZnO microspheres photoelectrodes with appropriate Zn chalcogenide passivation layers (ZnO@ZnS and ZnO@ZnSe) were constructed for reducing charge recombination of the resultant QDSCs. They were fabricated via a facile chemical solution route without any template or high temperature condition followed with controlled ion exchange. ZnS or ZnSe serves as passivation layer in CdS/CdSe QDSCs and their influences on the charge recombination as well as the light absorption were investigated. It was found that the ZnS or ZnSe passivation layer can effectively reduce charge recombination and significantly enhance the fill factor and open circuit voltage of the resulting QDSCs. Both of ZnS and ZnSe passivation layers enhanced the overall performance of the resultant QDSCs, which generated high power conversion efficiency of 5.13% and 5.20%, present 52% and 55% enhancement compared with 3.36% for the solar cell with hierarchical ZnO microspheres photoelectrode. ZnSe appears more favoring the deposition of QDs and enhancing the light absorbance than ZnS, resulting in an increased photocurrent density.

1. Introduction

Harvesting the abundant solar power from the sun is one of the most effective way to avoid severe environmental problems resulted from the use of fossil fuel. Quantum dot sensitized solar cells (QDSCs) benefited from low cost and high efficiency show promising future for solar power to electricity conversion and have attracted considerable attention from both scientific field as well as the industry. Narrow bandgap semiconductor quantum dots (QDs), such as CdS [1], CdSe [2–5], PbS [6,7], Ag_2S [8] and InAs [9] are used as the photosensitizer because of their extraordinary optical and electrical properties in terms of high flexibility in bandgap tuning, excellent light absorption coefficient, good stability as well as multiple exciton generation (MEG) with single-photon generation [10–12]. The theoretical photovoltaic conversion efficiency (PCE) of a QDSC can reach up to 40% in view of MEG effect of QDs, surpassing the 31% for semiconductor solar cells according to

* Corresponding author.
** Corresponding author. Advanced Material and Technology Institute, University of Science and Technology, Beijing, 100083, China.
E-mail addresses: tianjianjun@mater.ustb.edu.cn (J. Tian), gzcao@u.washington.edu (G. Cao).

https://doi.org/10.1016/j.jpowsour.2018.08.095
Received 15 February 2018; Received in revised form 5 August 2018; Accepted 30 August 2018
0378-7753/

the Schockley-Queisser limit [13,14].

During the past twenty-five years, pioneers have spent tons of efforts on improving the photovoltaic performance of QDSCs. However, there is still no remarkable breakthrough on that and the current power conversion efficiency is still far below its theoretical efficiency [15,16]. Constructing a high-performance photoanode is critically important on facilitate the improvement on the photovoltaic performance of QDSCs. As wide band gap metal oxide semiconductors, TiO_2 and ZnO are the most intensely used to make mesoporous 1thin films as photoanodes in dye sensitized solar cells (DSCs) and QDSCs [13,17–19]. Comparing with TiO_2, ZnO has a similar energy-band structure, a higher conduction band edge and a much faster electron transfer mobility (about four orders of magnitude larger than that of TiO_2) [20,21]. Moreover, ZnO is easier to synthesize and to form anisotropic structures such as nanorods, nanowires and nanotubes which present unique electronic and optical properties [22–24]. The hierarchical structured ZnO have also been fabricated as an excellent candidate material as photoelectrode for quantum dot sensitized solar cells (QDSCs), due to its high diffuse reflection, large surface areas and suitable porosity for loading QDs [17,25,26]. Despite of the unique properties of ZnO with various morphologies and structures, ZnO based QDSCs still hold to a relatively low PCE comparing to that of TiO_2, mainly due to the instability and defects on the surface of the ZnO photoanodes [27–29].The instability and defects of the ZnO could be reflected by a higher charge recombination rate, which results in lower photovoltaic performance of the devices [30–32]. Lots of investigations have be conducted on passivation of the surface defects, and it has been demonstrated that the charge recombination rate can be effectively reduced by introducing a thin shell on the ZnO surface, which serves as a sort of passivation layer [33]. For example, Tian et al. applied a facile solution processing to introduce a thin shell of TiO_2 on the surface of ZnO [19,34]. Which have remarkable influence on the quantum dot sensitized solar cells (QDSCs), on the one hand, increasing the surface area of ZnO for adsorbing more quantum dots (QDs), which led to high short current density; on the other hand, forming an energy barrier that reduced the charge recombination rate, resulting in prolonged electron lifetime and enhanced open circuit voltage. Other materials, such as Al_2O_3 [35,36], and Cu_2O [37] have been investigated for the same purpose.

Among the passivation materials in QDSCs, both ZnS and ZnSe have been extensively explored [38,39]. Both of them are wide bandgap semiconductors which have higher conduction band edges than the commonly used oxides (ZnO, SnO_2, TiO_2) and QDs. They can effectively passivate the surface defects of the oxides and prevent charge back transfer from QDs and the oxides to electrolyte. In this article, we synthesized a hierarchical ZnO microsphere through a chemical solution route. The Zn chalcogenide passivation layer were in-situ constructed on the ZnO surface by a facile ion exchange process. The ZnO hierarchical microspheres are composed of packed nanosheets with ~20 nm thickness. Such a structure not only show the direct charge transfer properties of two dimensional materials, but also allows the efficient light harvesting due to the light scattering of ZnO microspheres [17,25,26]. The composition of ZnS or ZnSe passivation layer and its effect on the charge collection, light absorption as well as the energy band alignment within the CdS/CdSe QDSCs were systematically investigated. The ZnS or ZnSe passivation layer can significantly reduce charge recombination resulting in improved open circuit voltage and fill factor. ZnSe appeared to be more effective in enhancing the deposition amount of QDs and leading to increased photocurrent density. The champion QDSCs based on the ZnO@ZnS and ZnO@ZnSe hierarchical microspheres photoelectrodes exhibits PCE of 5.13% and 5.20%, which is among the best performances of CdS/CdSe QDSCs with ZnO photoanode.

2. Materials and experimental methods

2.1. Materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, 99%, Sigma Aldrich), Sodium hydroxide (NaOH, 98%, Sigma Aldrich) α − terpineol ($C_{10}H_8O$, 96%, Sigma Aldrich), ethyl cellulose ($[C_6H_7O_2(OC_2H_5)_3]n$, 48.0–49.5% (w/w) as ethoxyl, Sigma Aldrich), cadmium acetate dihydrate ($Cd(CH_3COO)_2{\cdot}2H_2O$, 98%, Sigma Aldrich), cadmium nitrate tetrahydrate ($Cd(NO)_3{\cdot}4H_2O$, 98.0%), sodium sulfide Nonahydrate ($Na_2S{\cdot}9H_2O$, ≥98.0%, Sigma Aldrich), sulfur (S, purified by sublimation, Sigma Aldrich), sodium sulfide anhydrous (Na_2SO_3, 99.1%, Italy), trisodium salt of nitrilotriacetic acid ($N(CH_2COONa)_3$, ≥98.0%, Aldrich), zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, ≥99.0%, Aldrich), selenium powder (Se, 99.5%, Alfa Aesar), sodium borohydride ($NaBH_4$, 98%, Alfa Aesar), brass foil (alloy 260, 0.3 mm thick, Alfa Aesar), hydrochloric acid (HCl, 37%, USA), methanol (CH_3OH, ≥99.5%, Sigma Aldrich), and ethanol (CH_3CH_2OH, ≥99.5%, Decon Labs) were all used as received without further purification.

2.2. Preparation of the hierarchical ZnO@ZnS and ZnO@ZnSe microsphere films

The hierarchical ZnO microspheres were obtained from the previous work [40]. The synthesis procedure is described as follows. First, zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, Aldrich) was dissolved in deionized water with a continuous stirring process in order to form a homogenous clear solution. Then, sodium hydroxide flakes were added into the prepared zinc nitrate solution to maintain its pH to be around 13. Continuous stirring was kept for another 3 h at room temperature. The final ZnO product was obtained via centrifuging, rinsing with ethanol twice and drying at 60 °C in air for 12 h. For the fabrication of ZnO microspheres film, well-cleaned fluorine-doped tin oxide coated (FTO, 6-8 Ω/square) glass was used as substrate. The ZnO paste was prepared by mixing the synthesized ZnO microspheres, ethyl cellulose and α − terpineol together with a mass ratio of 2.5:1:7 in ethanol. A two-day continuous stirring was followed to allow the evaporation of excess ethanol. Doctor blade method was used throughout the ZnO film fabrication process. A Scotch tape was used to fix the substrate and control the film thickness. The ZnO paste was placed in front of the blade. Then move the blade linearly across the substrate. A thin wet film was formed after the blade. Finally, the thin wet film was sintered at 450 °C for 120 min to remove impurities and to form the crystallinity.

The hierarchical ZnO@ZnS microspheres film was prepared by ion-exchange method. The ZnO microspheres film was immersed into a 0.05 M Na_2S solution for different times in a water bath at 60 °C, then the photoanode was rinsed with deionized water and followed with air drying. The optimization of the performance of the QDSCs with different thickness of the ZnS layer is shown in Figure S1 (ESI†). This process needs 2 min to obtain an optimal thickness.

The hierarchical ZnO@ZnSe microsphere film was prepared by the same ion-exchange method. While, the ZnO microspheres film was immersed into a 0.01 M NaHSe solution for different times in a water bath at 50 °C, and then followed with rinsing by deionized water and air drying. The NaHSe solution was prepared by dissolving sodium borohydride ($NaBH_4$, AR, 98.0%) into deionized water firstly with continuous stirring, and then addition of selenium powder into the clear $NaBH_4$ solution. The obtained NaHSe solution is a clear solution. The optimization of the performance of the QDSCs with different thickness of the ZnSe layer is shown in Figure S2 (ESI†). This process needs 1 min to obtain an optimal thickness.