Materials Research Express

PAPER

45% efficiency enhancement of ZnO nanorod bulk-heterojunction solar cells by PbS QDs

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Keywords: quantum dots, heterojunction, photovoltaic, power conversion efficiency

Abstract

Absorption of near-infrared (NIR) photons of solar energy which includes the ~40% of the sunlight energy is an effective approach to improve the photovoltaic performance of solar cells. In the present study, we have investigated PbS quantum dots (QDs) with different numbers of synthesis cycles (n) were introduced to ZnO nanorods (ZNRs) bulk-heterojunction (BHJ) solar cells. Our analysis revealed improving the power conversion efficiency (PCE) by absorbing the light in the visible and near-infrared regions. The light absorption of solar cells was enhanced by PbS QDs which led to an increase in the photocurrent. With increasing (n), the PCE increases at first, then it decreases because of the attenuation of possible facilitation of exciton dissociation. For this reason, the number of cycles was optimized. As a result, by optimizing the numbers of synthesis cycles (n), the PCE of PbS QD sensitized ZNR bulk heterojunction solar cells were improved from 2.76% to 4.01% by 1.45 times.

1. Introduction

Efficient harvesting of NIR sunlight is the most important issue for the effective use of solar energy. As compared to organic dyes, Quantum Dots (semiconductor nanoparticles) benefit individual properties such as tunable band gaps, high extinction coefficient and low processing cost; which make QDs to be attractive materials in solar cell applications. The band gap of colloidal PbS QDs may be changed from 0.7 to 1.3 eV [1–4].

QD solar cells containing a planar junction between a wide band gap n-type semiconductors and p-type PbS QDs have showed higher efficiencies, but their photocurrent in the NIR region is still low. The PCE of a solar cell could be improved by using a bulk heterojunction structure with an optimized thickness of QD layer. However, thicker QD layers would decrease the PCE by increasing the internal series resistance [5].

Quantum Dot Sensitized Solar Cells (QDSSCs) generally composed of wide band gap semiconductor, QD sensitizer, counter electrode and hole transport material. The role of wide band gap semiconductor is to collect photo-injected electrons from QD and provide electron transport barrier between the QD and the electrode. Wide band gap semiconductor could collect and transport electrons through its conduction band.

ZnO nanorod arrays were used as photo-anode owing to their large surface area for QDs adsorption. Photo electrons created in QD layer, have to travel across neighboring QDs by a series of either hopping steps between trap states on QDs or by diffusion phenomenon through extended states slowed down by trapping/ de-trapping events [6–8].

The presence of these surface traps attenuates the electron transport because these harmful events are unavoidable during electron diffusion through the nanoparticle network.

The advantage of using photo-anodes containing of semiconductor nanorods is to creation of excellent electron transport pathways to improve the electron collection. Although, the recombination process of photo-injected electrons by holes is the main factor limiting the overall performance of QDSSCs.
The performance of PbS QDSSCs is much lower than that of other QDSSCs based on CdS, CdSe and other similar QDS due to less injection of electrons to the electron transport layer and instability of PbS in redox electrolytes.

In present work, ZnO nanorods were grown through simple hydrothermal method and PbS QDs were synthesized by successive ion layer adsorption and reaction (SILAR) technique with different number of cycles on ZNRs, and a P3HT/PCBM polymeric layer was used as hole transport layer to protect the PbS QDs corrosion; the effect of number of SILAR cycles on performance of PbS QDSSC was analyzed in detail by photovoltaic studies.

### 2. Experimental methods

#### 2.1. Synthesis of PbS QD sensitized ZnO nanorod arrays

All chemical precursors used in this work were purchased from Sigma Aldrich and used without any further purification.

At first, a ZnO seed layer was spin coated on pre-patterned indium-doped tin oxide (ITO) glass substrate using 100μl of zinc acetate dissolved in ethanol and diethanolamine (DEA) at a speed of 4500 rpm for 30 s and was dried at 150 °C for 2 min on a hot plate. Then seeded substrate was annealed at 450 °C for 2 h in an electrical furnace. ZnO NRs were grown using the hydrothermal method by subjecting substrate facing downward in a kettle containing aqueous solution of 0.001 mol L$^{-1}$ Zn(NO$_3$)$_2$/0.1 mol L$^{-1}$ NaOH at 70 °C. The ZnO seed layer causes the regular growth of the ZnO NRs arrays on the ITO substrate [9].

PbS QDs were deposited on obtained ZnO NRs using the spin-assisted SILAR technique. To do this, first a 5 mmol L$^{-1}$ Pb(NO$_3$)$_2$ solution in water—methanol co-solvent (5:100 volume ratio) was dropped on the ZnO NRs and spin coated at 4500 rpm for 30 s. Then, a 5 mmol L$^{-1}$ Na$_2$S solution in water—methanol co-solvent (the same volume ratio) with previous conditions was spin coated on substrate. This two-step procedure was repeated (n) times to obtain PbS QDs sensitized ZNR electrode.

#### 2.2. Fabrication of PbS SSC

Fabricated photo-anode layer was then covered with a mixture of P3HT/PCBM hole transport layer dissolved in 1,2-dichlorobenzene (ODCB) by spin-coating at 600 rpm for 50 s and dried at 150 °C for 30 min in the presence of nitrogen. Eventually, a 100 nm thick silver as the counter electrode was deposited on top of the fabricated film via vacuum evaporation at the pressure of 4 × 10$^{-6}$ mb. The active area of the device was fixed at 6 mm$^2$.

### 3. Results and discussion

#### 3.1. Morphological studies

The scanning electron microscopy (SEM) top view images of ZnO NRs uncovered and covered by PbS QDs are shown in figure 1. In figure 1(a), the bare ZnO NRs could be seen. The number of PbS QDs covering the ZnO NRs is enhancing with increasing the number of SILAR cycles (n). It is clear that large number of QDs is adsorbed over the surface of the ZnO NRs, as shown in figure 1(f). It also could be seen that for n=5, the surface of ZnO NRs is covered completely by PbS QDs.

#### 3.2. Optical studies

The UV–vis absorption spectrum of the ZnO NR/PbS(n), for different number of cycles is depicted in figure 2(a).

The absorption onset of ZnO NRs covered by PbS QDs with different number of (n) is listed in table 1 and corresponding diagram is shown in figure 2(b).

It could be observed that addition of PbS QDs on ZnO NRs leads to decrease the light harvesting efficiency (from n = 0 to n = 4), reaches to its minimum and then begin to increase again (for n = 5), as shown in figure 2(b). Changing the number of cycles has two opposite effects on the light harvesting process. The main factor that impacts the light absorption of layers is surface scattering centers formed as a consequence of QDs aggregation and sticking to each other. Due to increasing the number of cycles, PbS QDs are sticking to each other on ZnO NR arrays, although with a further increase of cycles, a smooth layer of PbS QDs could be created on ZnO NRs which improves light absorption.

#### 3.3. Photovoltaic analysis

The schematic diagram of device structure is shown in figure 3.

Figure 4 shows the current density–voltage (I–V) curves of devices with different number of cycles (n) measured under a stimulated light source of 100 mW cm$^{-2}$ power density. The detailed values of these...
parameters are given in table 2. It could be observed that the device without PbS QDs (n=0), shows an open-circuit voltage, a short-circuit current density and PCE of 0.55 V, 9.49 mA cm\(^{-2}\) and 2.76%, respectively.

Introducing the PbS QDs with 1 cycle leads to increase all photovoltaic parameters (\(V_{OC} = 0.61\) V, \(J_{SC} = 10.47\) mA cm\(^{-2}\), FF = 58.38% and PCE = 3.81%). Further increasing (n) (up to 2) leads to increase in all parameters except \(V_{OC}\) which refers to increasing the electron-hole recombination in interfaces. In this conditions, the PCE of device reaches to its maximum value of 4.01%. In this device the current density reaches
to its maximum value (10.94 mA cm$^{-2}$). This increase in current density is responsible for the enhancement of PCE. This depicts the positive influence of PbS QDs in PCE of device by improving the performance of photoelectrons harvesting of the ZnO NR/PbS QDs [10].

For n = 3 although the recombination process decreases (leads to increase in $V_{oc}$ to 0.61V), short-circuit current density and FF decreases down to 9.54 mA cm$^{-2}$ and 57.01% because of aggregation of PbS QDs and forming a thick layer. The thicker layer of QD attenuates electron-hole separation at the interfaces and leads to decrease in $J_{sc}$ and FF.

External quantum efficiency (EQE) or photon-to–current efficiency, of solar cell with ITO/ZnO/ZNR/PbS (2) QD/P3HT&PCBM/Ag structure in the spectral range of 350 to 850 nm is depicted in figure 4(b), which could be attributed to the ratio of optical output power to electrical input power.
It could be observed that EQE reaches to its maximum value of 70% in 800 nm (corresponding to 1.55 eV). That is, photons at this wavelength are converted and extracted more efficiently as light is absorbed in active layer.

4. Conclusions

In summary, solar cells with ITO/ZnO NR/PbS(n)/P3HT&PCBM/Ag structures were fabricated using SILAR technique, including a different number of cycles (n). Maximum values of short circuit current density, filling factor and power conversion efficiency under one sun illumination were achieved by two cycles of PbS QDs (n = 2). Experimental data confirmed that PbS layer acts as a promising absorber layer with the optimized number of SILAR cycles.

The weaker separation of photo-injected electrons and holes at the interfaces leads to a decrease in photovoltaic properties with increasing (n). Our results in this work confirmed that Optimizing the PbS QD layer over ZnO NRs could be considered as a potential approach to fabricate PbS QDs sensitized solar cells.

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