Photoelectrochemical properties of PbS quantum dots sensitized TiO$_2$ nanorods photoelectrodes

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ABSTRACT

The semiconductor PbS quantum dots (QDs) were synthesized on TiO$_2$ nanorods (NRs) via successive ionic layer adsorption and reaction (SILAR) method. The deposition of PbS QDs on the TiO$_2$ NRs could enhance the ability of light absorption and improve the power conversion efficiency of solar cell. The morphological feature, crystal structures, optical properties, photoelectrochemical performances, electron transfer at the TiO$_2$-QDs/electrolyte interface and electron lifetime of the obtained PbS QDs/TiO$_2$ NRs photoelectrodes were characterized and discussed in detail. The results demonstrate that the photoelectrochemical performance of PbS QDs/TiO$_2$ NRs depends on the value of SILAR cycle number. The highest photoelectric conversion efficiency of 0.77% is achieved at the SILAR cycle number $n = 4$ under one sun illumination (AM 1.5, 100 mW cm$^{-2}$). The enlarge absorption edges to the visible region and the effective separation of photogenerated electron-hole pairs at the PbS QDs-TiO$_2$ NRs interface are attributed to the promotion of power conversion efficiency.

Keywords: successive ionic layer adsorption and reaction method; PbS quantum dot; semiconductor materials; quantum dot solar cells

1. Introduction

In recent decades, quantum dot sensitized solar cells (QDSSCs) as the third generation solar cells have attracted significant attention$^{1-4}$. Although the power conversion efficiencies of QDSSCs lag behind those of dye-sensitized solar cells (DSSCs)$^5$, the particular nature properties of quantum dots (QDs) have added impetus to their promising application. On the basis of the quantum size effect, optical band gap of QDs can be tuned by accommodating QDs size, which enhances their ability to exploit the NIR region of the sunlight spectrum$^2,6$. On the other hand, the impact ionization effect makes the quantum yield to be more than 100% by generating multi-excitons from single optical
photon absorption\textsuperscript{7}, which enable their theoretical maximum thermodynamic conversion efficiency can reach 44\% instead of the 31\% of the Schockley-Queisser detailed balance limit. These special properties make QDSSCs as promising novel highly-efficient photovoltaic (PV) devices.

At present, TiO\textsubscript{2} is one of the most commonly used photoanode material for solar cells\textsuperscript{8,9}. Among the TiO\textsubscript{2} nanostructured materials, well-aligned TiO\textsubscript{2} one-dimensional (1D) nanostructures, such as nanorod\textsuperscript{10,11}, nanotube\textsuperscript{12} and nanowire\textsuperscript{13}, exhibit high photoelectrochemical performance in solar cells, photocatalytic in water splitting\textsuperscript{14-16} and degradation of organic pollutants due to their highly well-defined 1D channel structure, relatively high surface area and unique charge transfer and transportation properties. However, TiO\textsubscript{2} has a large band gap of 3.26 eV, which limits its visible light utilization. Thereby, much effort has been devoted to construct novel hetero-composite structures to enlarge the absorption of solar spectrum. One effective strategy is to combine TiO\textsubscript{2} with chalcogenide semiconductor quantum dots, such as CdS\textsuperscript{17}, CdSe\textsuperscript{18}, Ag\textsubscript{2}S\textsuperscript{19}, PbS\textsuperscript{20}, Bi\textsubscript{2}S\textsubscript{3}\textsuperscript{21}, CuInS\textsubscript{2}\textsuperscript{22} and so on. As an important p-type chalcogenide compound, PbS QDs with high absorption coefficient, good photostability and bulk band gap of 0.41 eV, have been widely investigated for photoenergy conversion applications. PbS QDs have been prepared using several methods, including chemical bath deposition (CBD)\textsuperscript{23}, thermal evaporation\textsuperscript{24}, thermolysis\textsuperscript{25} and successive ionic layer adsorption and reaction (SILAR)\textsuperscript{26}. In both principle and practice, the SILAR method can be considered as the best way to deposit well-defined composition-modulated QDs layers onto metal oxides in the solution process with the advantage of being a faster, more reproducible, and less expensive way to deposit sensitizing materials\textsuperscript{27,28}.

Herein, we report a facile method to deposit PbS QDs onto one-aligned TiO\textsubscript{2} nanorods for the first time and investigate their photoelectric performance in assembled QDSSCs. The synthetic process does
not use particular instrument and does not need any pre-synthesis of the precursors. The influence of SILAR cycle numbers for the photoelectrochemical performance of the assembled QDSSCs has been investigated in details. The photocurrent density of the composite photoelectrode enhanced by 3-5 times than that of the bare TiO$_2$ NRs. The composite electrode results in an energy conversation efficiency of 0.77% with a short circuit current density of 5.39 mA cm$^{-2}$ under illumination at 100 mW cm$^{-2}$.

2. Experimental section

2.1 Materials

Fluorine-doped tin oxide (FTO) glass (14 ohm per square), analytical-grade concentrated hydrochloric acid (HCl, 36.5%-38% by weight), lead nitrate (Pb(NO$_3$)$_2$, 99%), sodium sulfide (Na$_2$S·9H$_2$O, 99%), sulfur powder (S, 99.9%), sodium sulfite (Na$_2$SO$_3$, 99.5%), potassium chloride (KCl, 99.9%) and chloroplatinic acid (H$_2$PtCl$_6$·6H$_2$O, 99%) were purchased commercially. Titanium chloride (TiCl$_4$, 99.5%) was purchased from Alfa. All chemicals were used without further purification.

2.2 Fabrication of PbS/TiO$_2$ NRs photoelectrodes

TiO$_2$ nanorod arrays were prepared on fluorine-doped tin oxide (FTO) glass using a hydrothermal method that was described in detail elsewhere$^{29, 30}$. Typically, TiO$_2$ NRs film was dipped into 0.02 M Pb(NO$_3$)$_2$ aqueous solution for 60 s followed by deionized water washing, and dipped into 0.05 M Na$_2$S aqueous solution for 60 s followed by deionized water washing. The two-step dipping and rinsing procedure was termed as one SILAR cycle of PbS. The amount of PbS QDs can be increased by repeating the deposition cycle. In order to obtain optimized samples, different deposition cycles such as 3, 4, 5 and 6 times were applied to vary the amount of the PbS QDs assembled on the TiO$_2$ NRs. Finally, the obtained PbS QDs-TiO$_2$ NRs films were dried in nitrogen stream. The TiO$_2$ NRs
after n cycles of PbS QDs deposition was denoted as PbS(n)/TiO$_2$ NRs.

2.3 Cell fabrication

The Pt counter-electrode was prepared by spin-coating 5 mM H$_2$PtCl$_6$ 2-isopropyl solution onto a FTO glass substrate with a hole per-drilled, followed by heating at 400 °C for 20 min. The liquid-junction QDSSCs were fabricated by sandwiching the as-prepared PbS(n)/TiO$_2$ NRs photoanodes and Pt counterelectrodes by placing a 60 μm-thick hot-melt polymer (Surlyn, DuPont) material as a spacer. The inter-electrode space was filled with redox electrolyte consisting of 1.0 M Na$_2$S, 2.0 M sulfur and 0.2 M KCl in the mixture of methanol and water solution (7:3 by volume) by vacuum back-filling through a hole per-drilled in the counter electrode, and then the hole was sealed employing the hot-melt polymer and slide glass. The active area of QDSSCs was 0.5 cm$^2$.

2.4 Measurements

Field emission scanning electron microscope (FESEM, JSM-6701F, Japan), transmission electron microscope and high-resolution transmission electron microscope (TEM, JEOLJEM-1210) were employed for a close insight into the morphology of the PbS/TiO$_2$NRs. The structure and phase composition of the samples were studied by X-ray diffractometry (XRD) recorded using an X-ray diffractometer (Rigaku D/max-2400, Japan) with Cu-K$_α$ radiation ($λ = 0.15418$ nm ) at a speed of 5° min$^{-1}$. UV–visible absorbance spectra of the samples were obtained using a UV–visible spectrophotometer (Shimadzu UV-2600 spectrophotometer). The chemical states of the elements were determined using X-ray photoelectron spectrocope (XPS, ESCALAB 250Xi, Thermo Scientific), and the binding energy of contaminated carbon (C 1s = 284.8 eV) was used as reference. A computer controlled electrochemical workstation (CH Instruments, CHI 660d) was used for the photoelectrochemical (PEC) measurements, which were measured in an electrochemical cell under...
one sun illumination (AM 1.5, 100 mW cm\(^{-2}\)) in 0.05 M Na\(_2\)S and 0.95 M Na\(_2\)SO\(_3\) electrolyte solution with a three-electrode system, in which PbS/TiO\(_2\) NRs electrodes, a platinum wire and saturation mercury electrode (SCE) were used as the working electrode, the counter electrode and reference electrode, respectively. Photocurrent-voltage measurements were performed with a computer-programmed Keithley 2610 Sourcemeter at room temperature under illumination of simulated sunlight (CELL-S500, China, AM1.5, 100 mWcm\(^{-2}\)). The incident light was calibrated with a reference silicon solar cell (CEL-RCCO, China). All photoelectrochemical experiments were carried out under ambient conditions.

3 Results and discussion

![Cross-sectional view FESEM images](image1)

Fig. 1 Cross-sectional view FESEM images of (a) TiO\(_2\) NRs, (b) PbS(4)/TiO\(_2\) NRs (The insets show the top-view of the corresponding Cross-sectional view FESEM images). 3D schematic diagrams of (c) TiO\(_2\) NRs, (d) PbS(4)/TiO\(_2\) NRs.
Fig. 1 shows the FESEM images of the TiO$_2$ NRs and PbS(4)/TiO$_2$ NRs (a-b) and the corresponding 3D schematic diagrams (c-d). Almost all TiO$_2$ NRs are vertically aligned with relatively smooth sides and have a uniform length of 2 µm (Fig. 1a). The top-view shows that although the density of TiO$_2$ NRs is high, there is still obviously porosity between them (inset of Fig. 1a). The surface of TiO$_2$ NRs becomes rough after PbS QDs uniformly coated on the TiO$_2$ NRs and the deposition of PbS QDs does not destroy the morphology of TiO$_2$ NRs (Fig. 1b).

![Fig. 1](image1.png)

Fig. 2 TEM images of plain TiO$_2$ NRs (a) and PbS(4)/TiO$_2$ NRs (c). The inset in (a) is a bunch of TiO$_2$ NRs. HRTEM images of the corresponding TiO$_2$ NRs (b) and PbS(4)/TiO$_2$ NRs (d). The insets in (b) and (d) are the corresponding selected-area electron diffraction pattern, respectively.

![Fig. 2](image2.png)

The TEM and HRTEM images of TiO$_2$ NRs and PbS(4)/TiO$_2$ NRs are demonstrated in Fig. 2. The average diameter and length of TiO$_2$ NRs are 100 ± 5 nm and 2.1 ± 0.1 µm, respectively. It is completely crystalline along entire length (Fig. 2b), and the electron diffraction micrograph (inset)
confirming their single-crystalline nature. The observed distinguishable interplanar spacing of 0.25 nm and 0.35 nm are corresponded to the lattice fringe values for the (101) and (110) lattice planes of tetragonal rutile TiO$_2$, respectively. The PbS QDs with a size ranging from 5 nm to 8 nm are uniformly adsorbed on the TiO$_2$ NRs (Fig. 2c). The observed 0.289 nm lattice fringe in high-resolution TEM and selected area electron diffraction (Fig. 2d) can be assigned to the (220) planes of the cubic PbS.

![XRD and UV-Vis spectra](image)

**Fig. 3** Typical XRD patterns (a) and UV-Vis absorption spectra (b) of the bare TiO$_2$ NRs and as-prepared PbS(n)/TiO$_2$ photoelectrodes.

Fig. 3a shows typical XRD spectra of the bare TiO$_2$ NRs and as-prepared PbS(n)/TiO$_2$ photoelectrodes. Apart from the FTO substrate, the rest of the diffraction peaks match well with the tetragonal rutile TiO$_2$ (JCPDS file No. 71-0650) and cubic PbS (JCPDS file No. 78-1057), respectively. The main diffraction peaks located at 36.1° and 62.7° are assigned to the crystal planes of (101) and (002) of TiO$_2$ NRs. Meanwhile, the main diffraction peaks located at 30.1° can be ascribed to the crystal planes of (200) of PbS QDs. It can also be seen that the main peak of PbS phase enhances gradually along with the increase of SILAR cycle. The XRD peaks of cubic PbS phase are broad, suggesting that the size of the deposited PbS crystallites on the surface of TiO$_2$ NRs is very small. The average diameter of PbS QDs estimated by Scherrer’s equation is about 8 nm, which is accordance with the
HRTEM result shown in Fig. 2d. Fig. 3b shows the UV-Vis absorption spectra of PbS/TiO$_2$ NRs fabricated with different SILAR cycles. The TiO$_2$ NRs only absorb the high energy light with a wavelength shorter than 400 nm, while the deposition of PbS QDs on TiO$_2$ NRs enlarged the absorption edges from 400 nm to 700 nm due to the narrow bandgap of PbS. The increasing in absorption for the visible light after each SILAR cycle are corresponding to that the amount increasing of deposition PbS nanoparticles. However, given that most II-VI semiconductor materials have large hole masses, strong quantum confinement can be difficult to achieve$^{25}$. And the devoid of significant absorption peak indicates the absorption is negligible band-edge absorption.

Fig. 4 XPS spectra of PbS(4)/TiO$_2$: (a) survey spectrum, (b) Ti 2p, (c) O 1s, (d) Pb 4f, (e) S 2p. The deconvolution of O 1s, Pb 4f and S 2p spectras were performed by fitting a sum of Gaussian-Lorentzian functions to the experimental data on Multipak software. The black curves are the experimental data and the red curves are the sum of curve fitting.

Table 1 Binding energy, chemical species and atomic percentages of as-prepared PbS(4)/TiO$_2$.\[\text{Table 1 Binding energy, chemical species and atomic percentages of as-prepared PbS(4)/TiO}_2.\]
<table>
<thead>
<tr>
<th>Elements</th>
<th>Binding Energy (eV)</th>
<th>Species</th>
<th>Atomic(%)</th>
</tr>
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<tbody>
<tr>
<td>Pb</td>
<td>137.4</td>
<td>PbS</td>
<td>74.3</td>
</tr>
<tr>
<td></td>
<td>138.4</td>
<td>PbSO$_3$</td>
<td>23.6</td>
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<tr>
<td></td>
<td>139.0</td>
<td>PbSO$_4$</td>
<td>2.1</td>
</tr>
<tr>
<td>S</td>
<td>160.6</td>
<td>PbS</td>
<td>42.6</td>
</tr>
<tr>
<td></td>
<td>161.8</td>
<td>PbS</td>
<td>21.5</td>
</tr>
<tr>
<td></td>
<td>163.6</td>
<td>S-S</td>
<td>21.8</td>
</tr>
<tr>
<td></td>
<td>164.8</td>
<td>PbSO$_3$</td>
<td>8.7</td>
</tr>
<tr>
<td></td>
<td>168.0</td>
<td>PbSO$_4$</td>
<td>5.3</td>
</tr>
</tbody>
</table>

The surface composition as well as valence state of as-prepared PbS(4)/TiO$_2$ were determined by XPS (Fig. 4 a-e). The survey spectrum confirms the existence of Pb, S, Ti and O elements in the sample (Fig. 4a). The peaks of the binding energies at 464.40 eV and 458.71 eV are assigned to the 2p$_{1/2}$ and 2p$_{3/2}$ of Ti$^{4+}$ (Fig.4d). The characteristic peaks at 531.6 eV and 529.9 eV can be seen in the high-resolution O1s spectra (Fig. 4c). The former peak is closely related to the hydroxyl groups (-OH) resulting mainly from the chemisorbed water$^{31}$, and the later peak is described to the O atom bound to Ti$^{3+}$. As we all known, the surface energy of quantum dots is high, which make them can be oxidized easily in the ambient conditions. To evaluate the Pb-S species, we focused on the Pb 4f and S 2p XPS to analyze oxidation species (Fig. 4d-e). Detailed spectral deconvolution of the high resolution XPS spectra allowed us to distinguish the sulfur-containing oxidation species such as lead sulfite (PbSO$_3$), lead sulfate (PbSO$_4$) and polythiol (S-S)$^{32}$. The abundance ratio of the sulfur-containing oxidation products were presented in table 1. The QDs consisted of 74.3% PbS, 23.6% PbSO$_3$ and 2.1% PbSO$_4$ from Pb 4f spectra, whereas 64.1% PbS, 8.7% PbSO$_3$ and 5.3% PbSO$_4$ from S 2p spectra. The ratio distinction between two spectra is mainly from polythiol product, which does not contain Pb element. But there is no accurate data to prove the effect of polythiol product for reducing the value of band gap. To our best knowledge, PbSO$_3$ and PbSO$_4$ can introduce trap states lying 0.1 and 0.3 eV below the conduction band, respectively$^{33,34}$. The trap states with depth of 0.1 eV introduced by PbSO$_3$ are...
relatively shallow and operate mainly to extend the effective carrier lifetime, which are compatible with the device performance. However, the trap states with depth of 0.3 eV introduced by PbSO_4 are relatively deep and operate mainly as catastrophic recombination centers, which lead to midgap recombination and consequent loss of performance.

Fig. 5 (a) Transient photocurrent responses and (b) time courses of TiO_2 NRs and PbS(n)/TiO_2 photoelectrodes at the potential of -0.6 V vs. SCE under 100 mW cm\(^{-2}\) illumination. (c) Linear sweep voltammograms collected under 100 mW cm\(^{-2}\) illumination with scan rate of 10 mV s\(^{-1}\). (d) EIS Nyquist plots of TiO_2 NRs and PbS(n)/TiO_2...
photoelectrodes measured in the dark and under one sun illumination. (e) Bode plots and (f) electron lifetimes of various photoelectrodes under one sun illumination.

Fig. 5a shows the transient photocurrent responses of the PbS(n)/TiO$_2$ photoelectrodes. When the samples were illuminated under AM 1.5 at full sun intensity of 100 mW cm$^{-2}$, all the PbS(n)/TiO$_2$ photoelectrodes exhibited higher photocurrent properties than pure TiO$_2$ NRs. Moreover, the photocurrent of the PbS/TiO$_2$ photoelectrodes increased along with the SILAR cycle $n \leq 4$. When $n \geq 4$, the photocurrent density decreased, and the photocurrent of PbS(4)/TiO$_2$ photoelectrode was ten times as high as that of pure TiO$_2$ NRs. Hence, it can be deduced that the amount of PbS QDs deposition on the TiO$_2$ NRs plays an important role in affecting their photocurrent properties. Although the increasing quantity of PbS QDs on TiO$_2$ NRs could raise the light absorption, the aggregation of excessive QDs weakens the quantum size effect and increases the recombination of photo electrons and holes, leading to the decrease of photocurrent. Fig. 5b shows the time courses for the photocurrent density of various photoelectrodes. There was no obviously decay of photocurrent under 1 sun illumination, indicating the high structural and chemical stability of the as-prepared photoelectrodes. In addition, a set of linear sweep voltammograms were measured in the dark and under 1 sun illumination to investigate the PEC properties, as shown in Fig. 5c. All photoelectrodes show a low dark current with reference to their respective photocurrent, indicating no fierce electrocatalytic water splitting occurs. Obviously, the photocurrent of PbS(n)/TiO$_2$ photoelectrodes under illumination increases with the SILAR cycle number $n \leq 4$ and decreased when $n \geq 4$, but still apprrently higher than that of bare TiO$_2$ NRs, which is corresponding to the transient photocurrent responses shown in Fig. 5a and 5b. Furthermore, the onset potential of photoelectrodes shows a slight shift from -0.886 V$_{SCE}$ for bare TiO$_2$ NRs to -0.986 V$_{SCE}$ for
PbS(4)/TiO$_2$ NRs. The higher photocurrent and lower onset potential indicate more efficient charge separation and transport in PbS(4)/TiO$_2$ NRs than bare TiO$_2$ NRs$^{35}$.

As shown in Fig. 5d, electrochemical impedance measurements (EIS) were conducted on various photoelectrodes in the dark and under 1 sun illumination with a frequency interval of $10^5 - 10^7$ Hz. The semicircle corresponds to the electron transfer at the TiO$_2$-QDs/electrolyte interface and transport in the TiO$_2$. The results suggest that the radius of TiO$_2$ NRs electrodes in dark and one sun illumination are larger than PbS(n)/TiO$_2$ electrodes due to large band gap of TiO$_2$, which limit the absorption of light and very small amounts of photo-induced electron can be transferred to FTO film. Moreover, All the composite electrodes of PbS(n)/TiO$_2$ show smaller resistance-circles under illumination than those in dark, which can be attributed to the efficient separation of electron-hole pairs and electron injection between the interfaces of heterojunction and electrolyte for the composite electrodes$^{29}$. The radius of semicircle decreases with increase of SILAR cycle ($n \leq 4$), mainly attribute to the increase of the contact of PbS QDs to electrolyte, which promotes the photo-induced holes collection by S$_2^-$ in the electrolyte, facilitates the electron injection from PbS QDs to TiO$_2$ NRs and drains the electrons transfer in the TiO$_2$ NRs$^{36}$. Fig. 5e shows the bode plots of various photoelectrodes. The plot peak of the spectrum can be accepted to identify the electron lifetime in these photoelectrodes according to the following equation$^{37}$:

$$\tau_n = \frac{1}{2\pi f_{\min}}$$

The electron lifetime ($\tau_n$) calculated according to Fig. 5e are shown in Fig. 5f. Obviously, the frequency peak shifts to higher frequencies, corresponding to a decrease of the electron lifetime. It indicates that $\tau_n$ can remain high value, ~37.7 ms, in the TiO$_2$ NRs photoelectrode, which confirm TiO$_2$ NRs arrays with less crystal defects. The electron lifetime is on the decline with the increase of
PbS QDs. A decrease of the electron lifetime could result from an increase in surface states on the PbS QDs caused by adhering impurities of the electrolyte. Other possibilities are an increase of recombination centers inside the electrolyte, or the formation of a new electrolyte compound during the electrochemical process\textsuperscript{37}. However, in our study, the efficiency obtained for the photoelectrode with \( n = 4 \) is higher than that of other photoelectrodes, which can be explained that the optical absorption is insufficient for photoelectrode with \( n \) less than 3, whereas loss of electrons during transport due to recombination when \( n \) higher than 4.

![Graph](image.png)

Fig. 6 Incident photon to current conversion efficiency (IPCE) spectra of QDSSCs employing TiO\(_2\)/PbS(n) photoelectrodes.

To understand the photogeneration process of the photovoltaic devices, the incident photon to current conversion efficiency (IPCE) spectra of QDSSCs assembled with TiO\(_2\)/PbS(n) photoelectrodes measured from the \( I_{sc} \) monitored at different excitation wavelengths are present in Fig. 6. The value of IPCE enhances sharply after the SILAR deposition of PbS QDs, indicating the strong injection ability of photoexcited electrons. The TiO\(_2\)/PbS(4) photoelectrode achieves the maximum IPCE of 78.9\% in the wavelength range of 350-450 nm, which suggests that the photovoltaic device with TiO\(_2\)/PbS(4) photoelectrode affords more sufficient light absorption without compromising electron transport and collection. While raising the SILAR cycle, the photoelectrode suffers from the losses due to the
increased carrier recombination with holes and/or back-electron transfer to the semiconductor QDs.

Fig. 7 (a) $J-V$ curves of devices employing TiO$_2$ NRs and PbS(n)/TiO$_2$ photoelectrodes. (b) Schematic representation of the energy-level diagram of FTO, TiO$_2$ NRs, PbS QDs and charge transfer pathways between PbS and TiO$_2$ NRs.

Table 2 Parameters obtained from the photocurrent-voltage measurements of the solar cells using various photoelectrodes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (mV)</th>
<th>$FF$</th>
<th>$\eta$</th>
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<tbody>
<tr>
<td>TiO$_2$</td>
<td>1.59</td>
<td>0.261</td>
<td>0.47</td>
<td>0.20%</td>
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<tr>
<td>ZnS/PbS(3)/TiO$_2$</td>
<td>3.72</td>
<td>0.295</td>
<td>0.50</td>
<td>0.55%</td>
</tr>
<tr>
<td>PbS(4)/TiO$_2$</td>
<td>5.12</td>
<td>0.299</td>
<td>0.45</td>
<td>0.69%</td>
</tr>
<tr>
<td>ZnS/PbS(4)/TiO$_2$</td>
<td>5.39</td>
<td>0.295</td>
<td>0.48</td>
<td>0.77%</td>
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<tr>
<td>ZnS/PbS(5)/TiO$_2$</td>
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<td>0.46</td>
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<tr>
<td>ZnS/PbS(6)/TiO$_2$</td>
<td>3.44</td>
<td>0.280</td>
<td>0.59</td>
<td>0.57%</td>
</tr>
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</table>

Fig. 7a shows the characteristics of the experimental photocurrent density-voltage ($J-V$) for the TiO$_2$ NRs, PbS(n)/TiO$_2$ and ZnS/PbS(n)/TiO$_2$ photoelectrodes with various SILAR cycles under illumination at one sun light intensity of 100 mW cm$^{-2}$. As shown in Table 1, the photovoltaic parameters, including the short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor ($FF$) and power conversion efficiency ($\eta$) are listed. Apart from the recombination loss of photogenerated carriers, the recombination of electrons from TiO$_2$ into the electrolyte also reduces the energy...
conversion efficiency for QDSSCs. An effective way to retard the back transfer of photoelectrons and protect the QDs from photocorrosion is preparing a ZnS passivation layer according to the literature. Interestingly, we noticed that the introduction of ZnS leads to the increase of \( \eta \). Consequently, an overall energy conversion efficiency of 0.77% was achieved, resulting a 11.6% increment compared with the value of 0.69% treated without ZnS. The benefit effect of ZnS coating is attributed to the suppression of electron leakage to electrolyte due to efficient passivation of TiO\(_2\) and PbS QDs. In addition, the results demonstrate that the performance of ZnS/PbS(n)/TiO\(_2\) devices depends on the value of n. It can be found that the \( J_{sc} \) gradually increases from 1.59 to 5.39 mA cm\(^{-2}\) when \( n \leq 4 \) and the solar cell yields the maximum \( J_{sc} \) and a \( \eta \) of 0.77% at the forth cycle. With further increase of SILAR cycles, the \( J_{sc} \), \( V_{oc} \), and \( \eta \) values begin to decrease after reaching the maximum value, corresponding to the results observed in Fig. 5(a-c). The thicker semiconductor layers may increase internal recombination of charge carriers in the absorber before the carriers are injected into electron conductors\(^1\), resulting in the decrease of photocurrent density. Furthermore, we can find the \( V_{oc} \) exhibits almost the same value at the third and forth cycle, while a tendency of decreasing with the increasing deposition cycles of PbS QDs, which can be ascribe to decrease of the electron lifetime in QDSSCs\(^3\). This fact is an additional indicator of the presence of internal recombination losses in closely packed QDs.

The energy diagram of the involved components and charge transfer pathways between PbS and TiO\(_2\) NRs are shown in Fig. 7b. When the solar cell is illuminated through the FTO substrate, the PbS QDs and TiO\(_2\) NRs absorb photons and generate electron-hole pairs. The photogenerated excitons divide into electrons and holes on account of the presence of the built-in electric field developed at the interface of PbS QDs and TiO\(_2\) NRs. The photo-induced electrons from PbS can be quickly injected
into TiO$_2$ NRs, arriving at the FTO substrate through the well-aligned crystalline TiO$_2$ NRs. Meanwhile, the photo-induced holes are trapped by S$^2$ in the electrolyte to produce S$_x$$^2$. However, the cell performance in this study is still inferior due to the weak driving force of electron injection for PbS QDs although they have the wider absorption compared to other QDs. Thus, further improvement should be made, such as optimizing the quality of PbS QDs and co-sensitizing with other semiconductor QDs. All these investigations are ongoing in our laboratory.

4. Conclusions

In this work, PbS quantum dot-sensitized TiO$_2$ nanorod arrays have been prepared by SILAR method. The details of SILAR cycles for deposition of PbS QDs are discussed and it is found that the performance of PbS QDSSCs depends on the value of $n$ dominantly. The PbS QDs sensitized TiO$_2$ NRs exhibit a significant enhancement in $J_{sc}$ when $n = 4$, which is attributed to more quantum dots were harvested. Furthermore, the long electron lifetime in the TiO$_2$ make it possible to transfer the photo-induced electrons to FTO substrate. On the other hand, the enlarge absorption edges to the visible region and the effective separation of photogenerated electron-hole pairs at the PbS-TiO$_2$ NRs interface also promote the value of power conversion efficiency. The results confirm that PbS QDs can be used as effective sensitizers for quantum dot-sensitized solar cells.

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References


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Cross-sectional view FESEM images of (a) TiO$_2$ NRs, (b) PbS(4)/TiO$_2$ NRs (The insets show the top-view of the corresponding Cross-sectional view FESEM images). 3D schematic diagrams of (c) TiO$_2$ NRs, (d) PbS(4)/TiO$_2$ NRs.