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Preparation of AgInS$_2$ quantum dots/In$_2$S$_3$ co-sensitized photoelectrodes by a facile aqueous-phase synthesis route and their photo voltaic performance

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In aqueous-phase system, AgInS$_2$ quantum dots (QDs) sensitized TiO$_2$ photoanodes were in situ prepared by the reaction of β-In$_2$S$_3$ nanocrystals and as-prepared TiO$_2$/Ag$_2$S-QDs electrodes, followed by a covering process with ZnS passivation layer. A facile successive ionic layer adsorption and reaction (SILAR) method was adopted to obtain TiO$_2$/AgInS$_2$ QDs. The best photovoltaic performance of prepared TiO$_2$/AgInS$_2$/In$_2$S$_3$ electrode with short-circuit photocurrent density ($J_{sc}$) of 7.87 mA cm$^{-2}$ and power conversion efficiency ($\eta$) of 0.70% under full one-sun illumination was achieved.

Introduction

Semiconductor quantum dots sensitized solar cells (QDSSCs) have recently drawn significant attention since inorganic quantum dots (QDs) with narrow band gap and appropriate band positions are considered to be next generation alternative sensitizers of costly dyes in dye-sensitized solar cells (DSSCs). In comparison with those binary ones, multicomponent chalcogenide semiconductor nanomaterials, such as CuInS$_2$, AgInS$_2$ and related materials have attracted much attention in recent years for application in solar light energy conversion systems. AgInS$_2$ can crystallize in both the chalcopyrite and orthorhombic phases exhibiting direct band gap of 1.87 and 1.98 eV, respectively, which is suitable for the absorption of visible light. And it can form good matching heterojunction with Ag$_2$S or Cu$_2$ZnSnS$_4$ or CdS or polymer matrix due to its suitable lattice constant, making it a promising alternative for solar cell materials. Importantly, AgInS$_2$ is low-toxic as opposed to the cadmium chalcogenides.

As one of the most important I-III-VI materials, AgInS$_2$ was extensively studied on the electrical and optical properties. So far, most of the studies focus on the synthesis strategies of AgInS$_2$ nanocrystals (NCs) for biological application. And several methods have been adopted to fabricate AgInS$_2$ thin films such as chemical spray pyrolysis, physical vapor deposition and electrochemical deposition. But these traditional preparation routes need harsh reaction conditions and the synthesized AgInS$_2$ films have poor crystal structure. Chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) routes were considered a convenient way to synthesize ternary sulphide thin films. Very recently, the AgInS$_2$ NCs and Cu-doped AgInS$_2$ NCs have been incorporated in organic-inorganic hybried optoelectronic devices. Very poor total energy conversion efficiency is obtained for solar cells made using organic capped AgInS$_2$ NCs because the insulating organic ligands inhibit electron injection to core NCs. It should be noted that ITO/ZnO/ZnS/AgInS$_2$/P3HT/Pt hybrid solar cells showed a
power conversion efficiency (PCE) of 2.11%, which is the relatively highest value ever reported for ZnO-based all-solid-state hybrid solar cells.\textsuperscript{31}

Up to now, there are only few reports about AgInS\textsubscript{2} NCs sensitized solar cells. Nag et al. prepared AgInS\textsubscript{2} NCs by a post-synthesis annealing of NC dispersion that modifies the size and defect density of the NCs, and solution processed AgInS\textsubscript{2} NCs were used to form the photoanode of the QDSSCs post/synthesis annealing of NC dispersion that modifies the size processes at TiO\textsubscript{2} and defect density of the NCs, and solution processed AgInS\textsubscript{2} NCs exhibited a photoresponse in the visible light region.\textsuperscript{31} It has been reported in the literatures that the high conversion efficiency of ternary chalcogenides QDSSCs is generally caused by interfacial charge-transfer processes at TiO\textsubscript{2} film and QDs sensitizer.\textsuperscript{44,45} Approaches such as decreasing the charge recombination within the QDSSCs by modifying the blocking layer,\textsuperscript{36} doping of CdS QDs with Mn? to improve the lifetime of trapped electron,\textsuperscript{37} the deposition of Ru-dyes and QDs as hybrid photosensitizers,\textsuperscript{38} and a buffer layer\textsuperscript{39} has been carried out. Applying a buffer layer such as In\textsubscript{2}S\textsubscript{3} between TiO\textsubscript{2} and Culin\textsubscript{2}S\textsubscript{3} can suppress the interface electron recombination so that improve the cell performance.\textsuperscript{40,41} In\textsubscript{2}S\textsubscript{3}, a typical III-VI group sulphide, exists in three different structure forms: α-In\textsubscript{2}S\textsubscript{3} (defect cubic structure), β-In\textsubscript{2}S\textsubscript{3} (defect spinel structure) and γ-In\textsubscript{2}S\textsubscript{3} (layered hexagonal structure). In fact, β-In\textsubscript{2}S\textsubscript{3} is a well n-type photoactive semiconductor with a direct band gap around 2.0 eV, a relative large exciton Bohr radius approximately 34 nm and a high carrier mobility.\textsuperscript{42,43} To further improve the performance of chalcogenide-based solar cells, an intermediate band gap layer can be incorporated in a CIS solar cell to increase its photoelectric performance.\textsuperscript{35} For this purpose, AgInS\textsubscript{2} QDSSCs embedded β-In\textsubscript{2}S\textsubscript{3} layers should be developed.

Herein, for the first time, we fabricate AgInS\textsubscript{2}-QDs/In\textsubscript{2}S\textsubscript{3} co-sensitized solar cells by a facile aqueous-phase synthesis route. The growth process of AgInS\textsubscript{2}-QDs/In\textsubscript{2}S\textsubscript{3} on TiO\textsubscript{2} film was demonstrated in detail. By using the Pt counter electrode (CE) and polysulfide electrolyte to assemble a QDSC, the AgInS\textsubscript{2}-QDs/In\textsubscript{2}S\textsubscript{3} co-sensitizers provide the PCE of 0.70% and the short-circuit current density of 7.87 mA cm\textsuperscript{-2} under one-sun illumination.

**Experimental section**

**Materials**

Silver(I) acetate (Ag(OAc), 99+%), sodium sulfide (Na\textsubscript{2}S·9H\textsubscript{2}O, 98+%), indium chloride (InCl\textsubscript{3}·4H\textsubscript{2}O, 98+%), thioacetamide (CH\textsubscript{3}CSNH\textsubscript{2}, 98+%), citric acid (C\textsubscript{6}H\textsubscript{8}O\textsubscript{7}, 98+%), ethanol (99.5%), zinc acetate (Zn(OAc)\textsubscript{2}, 99+%), sulfur (S, 99.5%), potassium chloride (KCl, 99+) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). TiO\textsubscript{2} powder (P25, a mixed phase of 70% anatase and 30% rutile; average size 25nm) was purchased from Degussa (Japan) and was used to prepare TiO\textsubscript{2} anatase nanoparticles for photoelectrodes. Ethylene cellulose and terpineol from Fluka (Germany) were used to suspend TiO\textsubscript{2} particles in viscous solutions. All the materials were used without further purification. Fluorine-doped tin oxide (FTO) conducting glass substrate (2.3 mm thick, 14 Ω·cm) was purchased from Nippon Sheet Glass.

**Preparation of TiO\textsubscript{2}/Ag\textsubscript{2}S-QDs electrodes**

Mesoporous TiO\textsubscript{2} electrodes were prepared by following a method reported earlier.\textsuperscript{44,45} In brief, FTO glass was cleaned in a detergent solution using an ultrasonic bath for 15 min, and then rinsed with water and ethanol. Two layers of TiO\textsubscript{2} were deposited on FTO, a blocking layer and active layer. The blocking layer was deposited by treating the glass in a 40 mM TiCl\textsubscript{4} aqueous solution at 70 °C for 30 min followed by annealing at 500°C for 30 min. The active TiO\textsubscript{2} layer (P25 paste) was coated on top of the blocking layer by the doctor blade technique. The film was dried at 125 °C for 6 min followed by annealing 500 °C for another 30 min. A post treatment process of the calcined film was similar with that of blocking layer. The thickness of the TiO\textsubscript{2} mesoporous electrode was approximately 9 µm, measured by an optical profiler (Wyko NT9100, Veeco Co., USA). TiO\textsubscript{2}/Ag\textsubscript{2}S-QDs electrodes were subsequently prepared by SILAR method.\textsuperscript{46} The electrode was dipped into 0.02 M Ag(OAc) aqueous solution for 30 s, rinsing with water, subsequent 30 s immersion in 0.05 M Na\textsubscript{2}S aqueous solution followed by further rinsing with water. Each series of two immersions was considered as one SILAR cycle.

**Fabrication of the AgInS\textsubscript{2}-QDs/In\textsubscript{2}S\textsubscript{3}/ZnS QDSSCs**

QDs-sensitized solar cells consisting of AgInS\textsubscript{2} QDs sensitizer with In\textsubscript{2}S\textsubscript{3} buffer layer were prepared by CBD of In\textsubscript{2}S\textsubscript{3} and in situ reaction with TiO\textsubscript{2}/Ag\textsubscript{2}S-QDs films with one-step method. A precursor aqueous solution of In\textsubscript{2}S\textsubscript{3} was prepared from a mixture of InCl\textsubscript{3} (0.01 M), CH\textsubscript{3}CSNH\textsubscript{2} (0.04 M). During the mixing procedure, C\textsubscript{6}H\textsubscript{5}O\textsubscript{2} (0.06 M) was added with the chemical solution for the formation of indium complexe. The resulting clear mixture was transferred into a 70 mL Teflon-lined stainless steel autoclave, holding a vertically oriented FTO glass substrate (with a Ag/S/TiO\textsubscript{2} film), which was then sealed and maintained at 150 °C for 3 h. The substrate was then rinsed with water and ethanol and dried at room temperature. The electrode was marked as TiO\textsubscript{2}/AgInS\textsubscript{2}(n)/QDs/In\textsubscript{2}S\textsubscript{3} according to the different Ag\textsubscript{2}S SILAR cycle (where n is Ag\textsubscript{2}S SILAR cycle). All the electrodes analyzed in this study have been coated with ZnS, carried out by two SILAR cycle consisting of twice dipping alternatively in the 0.1 M Zn(OAc)\textsubscript{2} and 0.1 M Na\textsubscript{2}S aqueous solution for 1 min per dip. The QDSC was sealed in a sandwich structure with a spacer film (50 µm thick polyester film, DuPont) by using Pt-coated FTO glass. The space between the electrodes was filled with the polysulfide electrolyte which consisted of Na\textsubscript{2}S (2 M), S (2 M), and KCl (0.2 M), using pure water as solvent. A mask with a window of 0.25 cm\textsuperscript{2} was clipped on the photoanode side to define the active area of the cell.

**Characterization**

High-resolution transmission electron microscopy (HRTEM) images were obtained using a JEM 2100 F (JEOL Co., Japan) operating at 200 kV. The surface morphology and structure of the resulting films was studied using a field emission scanning electron microscope (FESEM, S-4800, Hitachi, Japan). The crystal structure was investigated by an X-ray diffraction technique (XRD, D/Max 2550 V, Rigaku, Japan) with Cu Kα (λ = 0.154 nm) radiation at 40 kV and 200 mA in 20 ranging from 20° to 80°. X-ray photoelectron spectra (XPS) were recorded on an ESCALab MKII X-ray photoelectron spectrometer. UV-visible absorption spectra were recorded using a spectrophotometer (Lambda 950, Perkin-Elmer Co., USA). Photocurrent-voltage characteristics (J–V curves) of QDSSCs were measured using a Keithley 2400 Source Meter under
illumination of simulated sunlight (100 mW cm\(^{-2}\)) provided by a Newport solar simulator (Model 96160) with an AM 1.5G filter. Incident photon-to-current conversion efficiency (IPCE) spectra were measured as a function of wavelength from 350 to 800 nm using a specially designed IPCE system (Newport, USA) for the QDSSCs.

Results and discussion

In aqueous-phase system, AgInS\(_2\)-QDs sensitized TiO\(_2\) photoanodes were in situ prepared by the reaction of AgInS\(_2\) nanocrystals and as-prepared TiO\(_2\)/Ag\(_2\)S-QDs electrodes. TiO\(_2\)/Ag\(_2\)S-QDs electrodes were obtained by a facile successive ionic layer adsorption and reaction (SILAR) method. β-In\(_2\)S\(_3\) nanocrystals synthesized by chemical bath deposition (CBD) process serve as the reactant of AgInS\(_2\) as well as buffer layer between the interfaces of TiO\(_2\) and AgInS\(_2\) QDs. The overall reactions are presented as the follow:

\[
\begin{align*}
\text{Ag}^+ + \text{S}^2- &\rightarrow \text{Ag}_2\text{S} \\
(\text{The reaction was processed on TiO}_2 \text{ films}) \\
L &\rightleftharpoons L^+ + \text{H}^+ (L \text{ is citric acid}) \\
\text{In}^{3+} + \text{L}^{-} &\rightarrow \text{InL} \\
\text{CH}\(_2\)\text{CSNH}_2 + \text{H}^+ &\rightarrow \text{CH}_2\text{CNH}^+ + \text{H}_2\text{S} \\
\text{H}_2\text{S} &\rightleftharpoons \text{HS}^- + \text{H}^+ \\
\text{In}^{3+} + \text{S}^2- &\rightarrow \text{In}_2\text{S}_3 \\
\text{Ag}_2\text{S} + \text{In}_2\text{S}_3 &\rightarrow 2\text{AgInS}_2
\end{align*}
\]

(1) (2) (3) (4) (5) (6) (7)

The high-resolution TEM (HRTEM) image of the TiO\(_2\)/AgInS\(_2\)-QDs/In\(_2\)S\(_3\) composite in Fig. 1 clearly depicts the crystalline lattice fringes of the involved species. The lattice spacing distance of 0.352 nm, illustrated in the right zone of the image, corresponds to the (101) plane of anatase TiO\(_2\). The lattices with spacing distances of 0.334 and 0.325 nm round TiO\(_2\) particle encompassed by red lines correspond to the (112) plane of the tetragonal AgInS\(_2\) (JCPDS file no. 75-0117) and (311) plane of the In\(_2\)S\(_3\) (JCPDS file no. 84-1385), respectively. The In\(_2\)S\(_3\) coating with CBD method is in close contact with both the AgInS\(_2\) QDs and TiO\(_2\) particles.

Fig. 1 HRTEM image of TiO\(_2\)/AgInS\(_2\)(6)-QDs/In\(_2\)S\(_3\) electrode.

Fig. 2 shows a series of color changes for the TiO\(_2\) electrodes after sensitization in the reaction process. TiO\(_2\)/In\(_2\)S\(_3\) electrode was prepared as a reference. The TiO\(_2\) film was originally white and semi-transparent, becoming black-brown when it was coated with Ag\(_2\)S QDs and red-brown when it coated with AgInS\(_2\)-QDs/In\(_2\)S\(_3\). Due to the quantum confinement effect in the optics, the color for the TiO\(_2\)/AgInS\(_2\)-QDs/In\(_2\)S\(_3\) electrode is distinct with black bulk AgInS\(_2\). It was also found that the color of TiO\(_2\)/AgInS\(_2\)-QDs/In\(_2\)S\(_3\) electrode changes from pale red-brown to dark reddish brown, indicating the increase of AgInS\(_2\)-QDs layer thickness (see Fig. 1S†). The present claybank color on TiO\(_2\)/AgInS\(_2\)-QDs/In\(_2\)S\(_3\) electrodes indicates the deposition of In\(_2\)S\(_3\) films on the bare FTO glass.

FESEM images in Fig. 3 demonstrate the surface topography of the electrodes at different reaction stages. SILAR method was used to deposit Ag\(_2\)S on TiO\(_2\) films as the basic electrode, and the growth mechanism of the Ag\(_2\)S-QDs on the TiO\(_2\) films was monitored with FESEM image (see Fig. 3a, b). It is clear that the entire surface of the FTO substrate is covered uniformly and densely with TiO\(_2\) nanoparticles from Fig. 3a. The average particle diameter is approximately 30 nm and the average pore size among TiO\(_2\) nanoparticles is less than 10 nm. After assembled with Ag\(_2\)S for 6 cycles, the TiO\(_2\) nanoparticles structure is retained, and the Ag\(_2\)S particles could be generated in the pores as well as on the surface of porous TiO\(_2\) films as shown in Fig. 3b. In addition, the small diameter of pores of the TiO\(_2\) films restricts further growth of the Ag\(_2\)S particles. Thus, Ag\(_2\)S particles were smaller in the porous TiO\(_2\) films, meaning that the size of Ag\(_2\)S is in the scope of quantum dot. Fig. 3c shows the surface topography of TiO\(_2\)/In\(_2\)S\(_3\) film prepared by CBD method as comparison. The surface of the as-deposited film shows a smooth granular structure with very-well-defined grain boundaries and with some larger grains dispersed on the film surface. The grains have an irregular round shape. Fig. 3d shows the surface morphology of AgInS\(_2\)(6)-QDs/In\(_2\)S\(_3\) co-sensitized TiO\(_2\) electrode. It was found that AgInS\(_2\) nanoparticles with pyramid-like shape appear on the surface of the film. The surface morphology of TiO\(_2\)/AgInS\(_2\)-QDs/In\(_2\)S\(_3\) films prepared with different Ag\(_2\)S SILAR cycle seem to be slightly affected by the Ag\(_2\)S SILAR cycles (see Fig. 2S†). All the samples show the similar surface morphology, however, as
the Ag$_2$S SILAR cycle increases, the pyramid-like structure becomes denser and the size of AgIn$_2$S$_3$ particles become larger on the surface of electrode.

The valence states and composition of the surface of TiO$_2$/AgIn$_2$S$_3$(6)/QDs/In$_2$S$_3$ electrode were further investigated by XPS (see Fig. 4).

Table 1 The elementary composition of calculated from XPS spectrum of the surface of TiO$_2$/AgIn$_2$S$_3$(6)/QDs/In$_2$S$_3$ electrode.

<table>
<thead>
<tr>
<th>Name</th>
<th>Peak Binding Energy (eV)</th>
<th>FWHM (eV)</th>
<th>Atomic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag 3d</td>
<td>367.4</td>
<td>0.94</td>
<td>2.3</td>
</tr>
<tr>
<td>In 3d</td>
<td>444.4</td>
<td>1.1</td>
<td>22.41</td>
</tr>
<tr>
<td>S 2p</td>
<td>161.2</td>
<td>1.12</td>
<td>27.81</td>
</tr>
<tr>
<td>Ti 2p</td>
<td>458.5</td>
<td>1.09</td>
<td>29.48</td>
</tr>
<tr>
<td>O 1s</td>
<td>529.9</td>
<td>1.31</td>
<td>17.99</td>
</tr>
</tbody>
</table>

![Fig. 4 XPS survey, Ag 3d, In 3d, S 2p, Ti 2p and O 1s of the surface of TiO$_2$/AgIn$_2$S$_3$(6)/QDs/In$_2$S$_3$ electrode.](image)

The Ag 3d, In 3d, S 2p, Ti 2p and O 1s were examined, respectively, which confirm the presence of these elements in the typical sample. The binding energies of Ag 3d$_{3/2}$ and Ag 3d$_{5/2}$ for AgIn$_2$S$_3$ were located at 373.5 eV and 367.4 eV with a peak splitting of 6 eV, which is consistent with the standard reference XPS of Ag$^+$. The In 3d peaks were located at 444.4 eV and 451.9 eV with a peak splitting of 7.5 eV, matching well with In$^{3+}$. The S 2p peaks splitting of 161.2 eV and 162.3 eV with a peak splitting of 1.1 eV, which corresponds to a binding energy of S$^{2-}$. The Ti 2p spectra exhibits two peaks corresponding to the binding energies of 458.5 eV (Ti 2p$_{3/2}$) and 464.2 eV (Ti 2p$_{1/2}$), resulting from the Ti of TiO$_2$. The binding energies of O 1s were located into two peaks, the peak at 529.9 eV, resulting from the crystal lattice oxygen of TiO$_2$ and the peak at 532 eV, corresponding to the hydroxyl oxygen. It can be seen in Table 1 through the quantification of peaks, there are excess In, S elements according to the stoichiometric coefficient of AgIn$_2$S$_3$, showing the sensitizers consist of AgIn$_2$S$_3$ and In$_2$S$_3$ over the electrode. And there are excess O elements according to the stoichiometric coefficient of TiO$_2$ attributing to the hydroxyl oxygen on the surface of the sample.

To explore the formation process of AgIn$_2$S$_3$-QDs/In$_2$S$_3$ co-sensitized electrodes, the TiO$_2$ electrodes after sensitization at different reaction stages were monitored by XRD analyses in Fig. 5. There are un conspicuous Ag$_2$S diffraction peaks according to the similar XRD patterns of TiO$_2$/Ag$_2$S(6) electrode and TiO$_2$ electrode, showing the size of Ag$_2$S is in quantum dot range. In addition, it is also not easy to determine AgIn$_2$S$_3$ phase (JCPDS file no. 75-0117) over AgIn$_2$S$_3$(6)-QDs/In$_2$S$_3$ electrode due to smaller size of AgIn$_2$S$_3$ QDs and the higher intensity of the TiO$_2$ (P25) diffraction peak. However, the main diffraction peaks such as (111), (400) and (511) diffraction peaks of $\beta$-In$_2$S$_3$ (JCPDS file no. 84-1385) appear on the XRD pattern of AgIn$_2$S$_3$-QDs(6)/In$_2$S$_3$ co-sensitized electrode, indicating that there are excess $\beta$-In$_2$S$_3$ over the electrode.

UV-vis absorption spectroscopy was used to track the formation of AgIn$_2$S$_3$-QDs/In$_2$S$_3$ co-sensitized electrodes and investigate the suitability for photovoltaic application. Fig. 6 shows the absorption spectra of the correlative electrodes during the preparation process of TiO$_2$/AgIn$_2$S$_3$-QDs/In$_2$S$_3$ photoanode that from the plain TiO$_2$, TiO$_2$/Ag$_2$S-QDs to TiO$_2$/AgIn$_2$S$_3$-QDs/In$_2$S$_3$ electrode. TiO$_2$/In$_2$S$_3$ electrode was chosen as a comparision. The spectrum shows that the plain TiO$_2$ can mainly absorb UV light with wavelength smaller than 420 nm. The TiO$_2$/Ag$_2$S-QDs electrode can absorb UV to near-infrared light, but its optical absorption ability is rather weak, probably being bad for solar cell performance. The TiO$_2$ film with In$_2$S$_3$ CBD deposition, the light absorbance of the electrode was enhanced in the visible region, and its absorption band edge is about 530 nm. The prepared TiO$_2$/AgIn$_2$S$_3$-QDs/In$_2$S$_3$ electrode has excellent optical absorption performance not only UV region, but also in the visible region. A shoulder appears between 530 and 600 nm with a long tail.
extending to longer wavelengths, which is mainly due to the formation of the AgInS$_2$ layer coated on the TiO$_2$ electrode. These results confirm that AgInS$_2$ layer can effectively improve the light absorption property of TiO$_2$ film. It was also found that the absorption spectra of the TiO$_2$/AgInS$_2$-QDs/In$_2$S$_3$ electrodes obtained by CBD of In$_2$S$_3$ and in situ reaction with different cycles of Ag$_2$S SILAR deposition on TiO$_2$ film are similar (see Fig. 3S†). The absorption spectra of the prepared TiO$_2$/AgInS$_2$-QDs/In$_2$S$_3$ electrodes were red-shifted with the increase of the Ag$_2$S SILAR cycles probably because of the increase of AgInS$_2$-QDs size or the increase of AgInS$_2$-QDs layer thickness. The enhanced absorption in the longer wavelength region is probably due to the remission of quantum confinement effect on the AgInS$_2$ QDs.

We fabricated QDSSCs using the FTO/TiO$_2$/AgInS$_2$-QDs/In$_2$S$_3$/ZnS as the photoanode and a Pt electrode as the cathode along with a polysulfide electrolyte between the electrodes. Fig. 7 shows schematic descriptions of the working principle of a QDSSC and its charge transfer mechanism, respectively. β-In$_2$S$_3$ QDs obtained by CBD method react with as-prepared Ag$_2$S QDs in the holes of TiO$_2$ films to form AgInS$_2$@In$_2$S$_3$ QDs and there are also excess AgInS$_2$ and In$_2$S$_3$ particles on the surface of the electrodes. AgInS$_2$ QDs absorb photons and generate electron-hole pairs. These photo-generated electrons can be efficiently transferred from AgInS$_2$ QDs to the mesoporous TiO$_2$ layer, finally collected by the FTO glass substrate. Moreover, there are non-radial recombination electron and hole via the defect state as marked in Fig. 7(b) with a green dotted arrow.$^{12}$ At the same time, the photo-generated holes are scavenged by the polysulfide based redox electrolyte. AgInS$_2$-QDS/In$_2$S$_3$ surface was passivated with a wider band gap semiconductor (ZnS, 3.6 eV)$^{48}$ to prevent the leakage of current from AgInS$_2$-QDS/In$_2$S$_3$ to the electrolyte.

Fig. 6 Optical absorption spectra of the plain TiO$_2$ film, TiO$_2$/Ag$_2$S-QDs electrode prepared by 6 cycles of Ag$_2$S SILAR deposition, TiO$_2$/AgInS$_2$-(6)-QDs/In$_2$S$_3$ electrode and TiO$_2$/In$_2$S$_3$ electrode prepared by CBD of In$_2$S$_3$ for 3 h on the plain TiO$_2$ film.

Fig. 7 Schematic diagrams representing the working principle and charge transfer mechanism of TiO$_2$/AgInS$_2$-QDs/In$_2$S$_3$ QDSSC.

Fig. 8 presents the photocurrent-voltage characteristics (J-V curves) of the TiO$_2$/AgInS$_2$-QDs(6)/In$_2$S$_3$ co-sensitized photonaode with Pt counter electrode and polysulfide electrolyte. TiO$_2$/In$_2$S$_3$ electrode prepared by CBD of In$_2$S$_3$ on TiO$_2$ film for 3 h and TiO$_2$/Ag$_2$S(6)-QDs electrode prepared by SILAR method were used as comparison. The intermediate values for the main resultant photovoltaic parameters based on five parallel cell devices and the error intervals of PCE ($\eta$) are summarized in Table 2. For the cell based on just Ag$_2$S(6)-QDs or In$_2$S$_3$ sensitized TiO$_2$ photo-electrode, a short-circuit photocurrent density ($J_{sc}$) of 0.49 or 1.19, an open-circuit photovoltage ($V_{oc}$) of 0.19 or 0.23 V, a fill factor (FF) of 0.34 or 0.31 and a PCE ($\eta$) of 0.03 or 0.08 were revealed respectively. The poor photovoltaic performance may be attributed to the poor light absorption ability or the unmatched energy level. For AgInS$_2$(6)-QDs/In$_2$S$_3$ co-sensitized QDSSC, the J-V curve reveals that $J_{sc}$=7.87 mA cm$^{-2}$, $V_{oc}$=0.32 V, and $\eta$=0.70%, which are higher than those of TiO$_2$/Ag$_2$S(6)-QDs and TiO$_2$/In$_2$S$_3$ electrodes. The higher photocurrent density and efficiency is probably because of the broader light absorption spectrum and the better charge carriers generation ability of AgInS$_2$ QDs for AgInS$_2$(6)-QDs/In$_2$S$_3$ co-sensitized TiO$_2$ photo-electrode. In general, the current density for QDSSCs are determined by the initial number of photo-generated charge carriers, the electron injection efficiency from QD-sensitizers to photo-electrodes, and the recombination rate between the injected electrons and holes of excited QDs or redox species in the electrolyte. The IPCE is defined as the number of photo/electrons and holes of excited QDs or redox species in the electrolyte. In general, the current density for QDSSCs are determined by the initial number of photo-generated charge carriers, the electron injection efficiency from QD-sensitizers to photo-electrodes, and the recombination rate between the injected electrons and holes of excited QDs or redox species in the electrolyte. The IPCE spectra of the QDSSCs were basically consistent with the corresponding UV-Vis spectra shown in Fig. 6. TiO$_2$/AgInS$_2$-QDs(6)/In$_2$S$_3$ QDSSC shows a maximum IPCE of about 37% from 500 to 625 nm, which is much higher than that of TiO$_2$/In$_2$S$_3$ and TiO$_2$/Ag$_2$S(6)-QDs electrodes.
Therefore, we believe that AgInS$_2$-QDs are the main photo-sensitizers. On the other hand, the lower FF indicates the increasing of carrier recombination on the interfaces between TiO$_2$ and QDs sensitizer or electrolyte and CE. It is well known that Pt is not a good catalyst for polysulfide regeneration, which leads to poor fill factors for QDSSCs because their surface activity and conductivity are suppressed as result of adsorption of the sulfur atom.  

The lower open-circuit photovoltage of TiO$_2$/AgInS$_2$-QDs(6)/In$_2$S$_3$ QDSSC may be due to the surface defects of the synthesized AgInS$_2$ QDs. β-In$_2$S$_3$ serves not only as the reactant of AgInS$_2$ but also intermediate band gap layer that may change the unmatched band alignments in the heterostructure between TiO$_2$ and AgInS$_2$ QDs. However, the excess β-In$_2$S$_3$ particles on the surface of TiO$_2$/AgInS$_2$-QDs/In$_2$S$_3$ may increase of carrier recombination on the interfaces between TiO$_2$ and AgInS$_2$ QDs. Therefore, we believe that AgInS$_2$ QDs/In$_2$S$_3$ co-sensitized photoanodes lead to unhomogeneous In$_2$S$_3$ deposition, which may affect the surface state of the AgInS$_2$ QDs.

In addition, based on the same construction for the given TiO$_2$/AgInS$_2$-QDs/In$_2$S$_3$ QDSSCs system, it is reasonable that the photocurrent density and energy conversion efficiency are directly affected by the initial Ag$_2$S SILAR cycles (See Fig. 4S† and Table 1S†). With increasing the Ag$_2$S SILAR deposition from 2 cycles to 6 cycles, the $J_{sc}$ of TiO$_2$/AgInS$_2$-QDs/In$_2$S$_3$ photoanodes increases substantially from 3.39 to 7.87 mA cm$^{-2}$. The increase of $J_{sc}$ is attributed to extending the light absorption range and the increase in absorption ability with red-shift of the absorption onset of AgInS$_2$-QDs/In$_2$S$_3$ sensitizer. The increase of incorporated amount of AgInS$_2$-QDs can not only contribute to absorb more photons to generate more photoexcited electrons, but also form a uniform and dense shell to reduce direct contact areas between the bare TiO$_2$ surface and polysulfide electrolyte. However, the $J_{sc}$ and η were found to decrease when the Ag$_2$S coating increased to 8 cycles. The possible reason for the reduced cell performance may be attributed to the aggregations and growth of the Ag$_2$S QDs (See Fig. 2S†), which will result in the presence of subsequently synthesized AgInS$_2$ QDs with no direct contact with the TiO$_2$, leading to block the infiltration of the electrolyte into the photoelectrode, thereby decreasing the regeneration efficiency of the solar cell.  

![Fig. 8 Photocurrent voltage characteristics of QDSSCs based on TiO$_2$/Ag$_2$S (SILAR for 6 cycles), TiO$_2$/In$_2$S$_3$ (CBD for 3h), TiO$_2$/AgInS$_2$-QDs/In$_2$S$_3$ electrodes.](image)

<table>
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<tr>
<th>Photoanode</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>η (%)</th>
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</thead>
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<tr>
<td>TiO$_2$/Ag$_2$S-QDs(6)</td>
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<td>0.19</td>
<td>0.34</td>
<td>0.03±0.01</td>
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<tr>
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<td>0.23</td>
<td>0.31</td>
<td>0.08±0.01</td>
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<tr>
<td>TiO$_2$/AgInS$_2$(6)-QDs/In$_2$S$_3$</td>
<td>7.87</td>
<td>0.32</td>
<td>0.28</td>
<td>0.70 ± 0.02</td>
</tr>
</tbody>
</table>

**Table 2 Photovoltaic parameters of QDSSCs based on TiO$_2$/Ag$_2$S (SILAR for 6 cycles), TiO$_2$/In$_2$S$_3$ (CBD for 3h), TiO$_2$/AgInS$_2$(6)-QDs/In$_2$S$_3$ electrodes.**

**Fig. 9 IPCE spectra of QDSSCs based on TiO$_2$/Ag$_2$S (SILAR for 6 cycles), TiO$_2$/In$_2$S$_3$ (CBD for 3h), TiO$_2$/AgInS$_2$(6)-QDs/In$_2$S$_3$ electrodes.**

**Conclusions**

As one of the most important I-III-VI materials, AgInS$_2$ was extensively studied on the electrical and optical properties, and the reports about AgInS$_2$ QDs sensitized solar cells are quite few. In this study, for the first time, we have presented a facile aqueous-phase synthesis route to prepared QDs-sensitized photoelectrodes consisting of AgInS$_2$-QD/In$_2$S$_3$ co-sensitizers based on CBD of In$_2$S$_3$ and in situ reaction with TiO$_2$/Ag$_2$S-QDs films obtained by SILAR method. AgInS$_2$-QDs are the main photo-sensitizers. AgInS$_2$ nanoparticles with pyramid-like shape and excess In$_2$S$_3$ layer were found on the surface of the TiO$_2$/AgInS$_2$-QDs/In$_2$S$_3$ electrodes. The TiO$_2$/AgInS$_2$(6)-QDs/In$_2$S$_3$ QDSSC shows the better photovoltaic performance with $J_{sc}$ of 7.87 mA cm$^{-2}$, η of 0.70% and maximum IPCE of about 37% than those of the TiO$_2$/Ag$_2$S(6)-QDs and TiO$_2$/In$_2$S$_3$ QDSSCs attributing to the broader light absorption spectrum and the better charge carriers generation ability of AgInS$_2$ QDs for AgInS$_2$(6)-QDs/In$_2$S$_3$ co-sensitized TiO$_2$ photo-electrode. The absorption spectra of the prepared TiO$_2$/AgInS$_2$-QDs/In$_2$S$_3$ electrodes were red-shifted with the increase of the Ag$_2$S SILAR cycles probably because of the increase of AgInS$_2$-QDs size or the increase of AgInS$_2$-QDs layer thickness. Based on the same construction for the given TiO$_2$/AgInS$_2$-QDs/In$_2$S$_3$ QDSSCs system, the photocurrent density and energy conversion efficiency are directly affected by the initial Ag$_2$S SILAR cycles. We expect that this facile synthesis method should provide an insight into the fabrication of heterojunction thin film solar cells based on multicomponent chalcogenide.
Acknowledgements
We gratefully acknowledge the financial support by Natural Science Foundation of China (No.51172042), Specialized Research Fund for the Doctoral Program of Higher Education (2011075130001), Science and Technology Commission of Shanghai Municipality (12nm053900, 13JC1400200, 15ZR1401200), Innovative Research Team in University (IRT1221) and the Program of Introducing Talents of Discipline to Universities (No.111-2-04).

Notes and references