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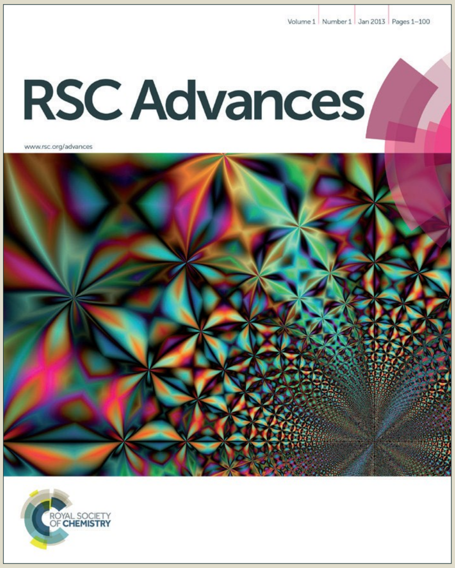

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ARTICLE

Significant Enhancing the Stability of Cu_2ZnSnS_4 Aqueous/ethanol-based Precursor Solution and Its Application in $Cu_2ZnSn(S,Se)_4$ Solar cells

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The stability of CZTS precursor solution play an important role for the potential industrial application, and could provide insight into understanding the solubility mechanism of the raw materials. In this work, we report a systematic investigation on the stability of a metal/thiourea aqueous/ethanol-based precursor solution used for fabricating Cu_2ZnSnS_4 (CZTS) thin films. It is found that the metal/thiourea aqueous/ethanol solution is metastable, and easily produced a mass of precipitation when the solution prepared few hours. This could cause the missing of element and very badly film-processing ability and effect the application of such method. So we detailed studied the crystalline precipitation through SEM, EDS and FTIR, and found that they mainly contains copper ion and thiourea coordination complexes. Furthermore, we demonstrated that the low-toxic 3-mercaptopropionic acid (MPA) can play an important role as auxiliary ligand in the precursor solution. Addition of the MPA into the precursor solution can avoid the precipitation and noticeably improve the stability of the precursor solution from ~3 hours to 1 week. Using the precursor solution added MPA, we fabricated a single phase of CZTS film, and prepared the large-grain and hole-free $Cu_2ZnSn(S,Se)_4$ (CZTSSe) film. More importantly, a CZTSSe film solar cell with a competitive power conversion efficiency of 7.25% has been reported in this work.

Introduction

Kesterite $Cu_2ZnSn(S,Se)_4$ (CZTSSe), as an alternative for $Cu(In,Ga)(S,Se)_2$ (CIGSSe) and CdTe, has attracted much attention over the past several years, due to its direct band gap close to the optimum band gap of 1.0-1.5 eV , high absorption coefficient ($>10^4$ cm^{-1}) and containing earth abundant as well as environmental friendly constituents.[1-3] Up to now, many efficient strategies have been used to fabricate CZTSSe absorber layers, such as thermal co-evaporation,[4-6] sputtering,[7-10] electro-deposition[11, 12] and solution approach,[13-20] etc. Among these deposition methods, the solution approach, as a form of non-vacuum-deposition technology, is considered as the excellent choice for obtaining smooth and high-quality CZTSSe absorber layers, and could offer a potential to significantly lower the manufacturing cost of solar cells compared to the vacuum-deposition technologies. The CZTSSe-based solar cell prepared by the hydrazine-based solution approach has demonstrated the record power conversion efficiency (PCE) of 12.6%.[20] However, since hydrazine is a highly toxic and explosive compound which must be handled in an inert environment such as N_2 filled glove box, the hydrazine-based approach is difficultly used to prepare CZTSSe-based solar cell in practices. Therefore, it is necessary to develop a kind of harmfulless, low cost and environmentally friendly solution approach.

Aqueous/ethanol-based solution approaches are considered as a green and low-cost preparation method of CZTS due to without containing high-toxic organic solvent. Some research groups have used this approach to prepare kesterite CZTS film.[21-23] Compared with other aqueous/ethanol-based solution approaches, the metal/thiourea aqueous/ethanol-based precursor solution approach is considered superior in simplifying fabrication processing, reducing fabrication costs and environmental damage. Such solution process was first reported by the Li's group and was demonstrated a conversion efficiency of 6.2% under AM1.5G simulated sunlight.[23] However, we found that the metal/thiourea aqueous/ethanol-based precursor solution approach is metastable and precipitation occurs soon after prepared due to the high concentrations of metal salts and thiourea, and leading to an unstable solution.[24] Such metastable solution is hard to

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Electronic Supplementary Information (ESI) available: EDS patterns of as-fabricated and selenized CZTS-A(B) films. See DOI: 10.1039/x0xx00000x fabricate single-phase kesterite CZTS thin film and limit the potential application. Therefore, it is necessary to understand that the mechanism and develop a simple route which could noticeably improve the stability of the metal/thiourea aqueous/ethanol-based solution, and hence fabricate CZTS-based solar cells with high PCEs.

In this work, we systematically investigated the stability of the metal/thiourea aqueous/ethanol-based precursor solution. The solution is easy to crystallize, and then the composition of the precursor solution is become undesired. Furthermore, the film-processing ability will get worse and can't obtain the smooth and hole-free CZTS films. Additionally, we detailed study the crystalline precipitation by SEM, EDS and FTIR. Interestingly, we find the harmfulless 3-mercaptopropionic acid (MPA) can obviously improve the stability of the precursor solution and fabricated high-quality CZTS films. By tuning the composition of the CZTSSe thin film with a selenized processing, a power conversion efficiency of 7.25% has been achieved by this stable aqueous/ethanol-based solution approach, which is comparable to values reported using aqueous/ethanol-based true solution processes.

Experimental

CZTS aqueous/ethanol-based precursor solution preparation

The CZTS aqueous/ethanol-based precursor solution was prepared by dissolving $CuCl_2{\cdot}2H_2O$ (0.4219 g, 2.475 mmol), $ZnCl_2$ (0.2453 g, 1.8 mmol), $SnCl_2{\cdot}2H_2O$ (0.3385 g, 1.5 mmol), and thiourea (0.9134 g, 12 mmol) into a mixture solution containing water (4 mL) and ethanol (2 mL) at room temperature. After stirring for 20 min, a clear CZTS aqueous/ethanol-based precursor solution was obtained.

Precipitation of the CZTS aqueous/ethanol-based precursor solution

When the CZTS aqueous/ethanol-based precursor solution was stored for three hours, some crystalline precipitates were observed clearly. In order to understand the mechanism affecting the stability of the precursor solution, the precipitates were collected by centrifuging method, then were cleaned by deionized water and ethanol for three times, and finally were dried at 60 °C for twelve hours.

Stable CZTS aqueous/ethanol-based precursor solution preparation

0.5 mL 3-mercaptopropionic acid (MPA) was added into the CZTS aqueous/ethanol-based precursor solution. After stirring the solution for a few minutes, a light yellow clean solution formed, it could be stably stored in the air for a week.

Preparation and selenization of the CZTS precursor thin film

Two kinds of CZTS thin films fabricating by the different types CZTS precursor solutions, denoted as CZTS-A and CZTS-B, respectively. The as-prepared CZTS thin films were deposited on Mo-coated soda-lime glass (SLG) substrates by spin-coating the CZTS precursor solutions without and with MPA at 3000 rpm for 30 s, respectively, and then were annealed in the air at 300 °C for 5 minutes. The coating and drying processes were repeated for several times to obtain ~1.5-µm-thick films. The two films were selenized by loading them in a graphite box with a hole in diameter of 1 mm together with some Se powders, then transporting into a rapid thermal processing furnace, and finally annealing for 20 minutes in the furnace which was heated to 540 °C at a heating rate of 5 °C/s with nitrogen gas flow at normal pressure. After annealing, the films were subjected to cooling down to room temperature naturally.

Device fabrication

Devices were prepared as traditional CZTSSe-based solar cell structure, i.e. SLG/Mo/CZTSSe/CdS/i-ZnO/ITO/Al. Firstly, a CdS buffer layer (~50 nm) was deposited on the CZTSSe film by chemical bath deposition. Then, *i*-ZnO (~70 nm) and ITO (~250 nm) were sputtered on the top of the CdS layer followed by thermal evaporation of Al grid electrode (~2 µm) on the top of ITO layer. The detail can be found elsewhere.[25] Finally, the whole device was mechanically scribed into 4 small cells with an active area of about 0.37 cm^2.

Characterization

The crystal structures of the CZTS and CZTSSe films were characterized by an X-ray diffractmeter (XRD) with Cu Kα radiation (λ = 1.5406 Å). Raman spectra with an excitation wavelength of 532 nm were recorded using a Renishaw system. The scanning electron microscope (SEM) measurement was performed using a Hitachi S-4800 equipped with an energy dispersive X-ray spectroscopy (EDS) system (EDAX Genesis 2000). The Fourier-transform infrared (FTIR) spectrum of the precipitate was measured using Nicolet AVATAR 360 FT-IR system. The PCE of the CZTSSe-based solar cells was determined by measurement of its current density-voltage curves under simulated AM1.5 solar illumination, as calibrated with an official certified crystalline Si reference cell. External quantum efficiency (EQE) was measured by a Zolix SCS 100 QE system.

Results and discussion

The stability of CZTS precursor solution and the CZTS thin films fabrication process

Fig. 1 shows the flow diagram of the CZTS thin films fabrication process using the two kinds of CZTS aqueous/ethanol-based precursor solution. It indicates that some precipitates can be clearly observed at the bottom of the precursor solution without MPA when the solution is stored in the air for 3 hours, and the CZTS thin film prepared by the solution without MPA has some big cavities with diameter in ~2 µm, as shown in the Fig.1. However, for the CZTS precursor solution with MPA, no precipitate is observed in it even though the solution is put in the air for one week, revealing good stability in the air. In the previous reported works, thioglycolic acid showed a strong coordinating ability with the Cu^+, Zn^{2+} and Sn^{4+}. We speculate

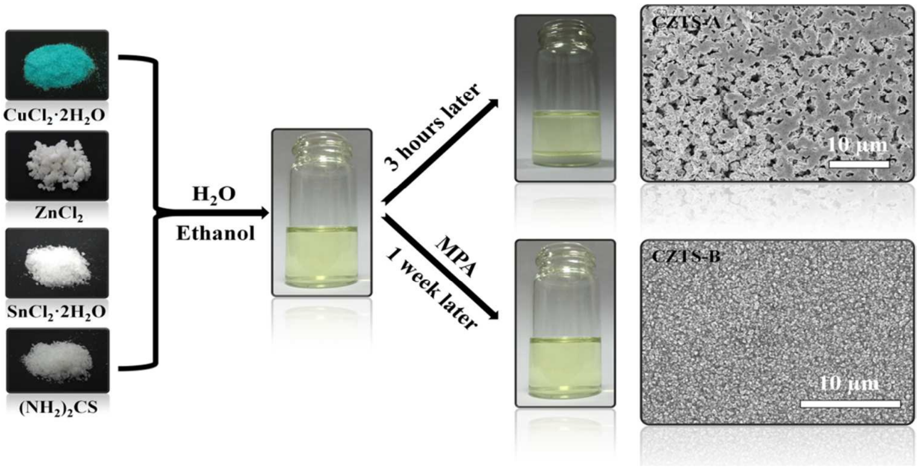

Fig. 1 Flow diagram of two kinds of CZTS thin films fabrication process. The right SEM images show the surface morphologies of the films (CZTS-A and CZTS-B) fabricated using aqueous/ethanol-based precursor solution without and with MPA.

the MPA play a parallel role for the similar structures of MPA and thioglycolic acid. Furthermore, the CZTS thin film obtained by using the solution with MPA (CZTS-B) shows compact and hole-free, as shown in SEM image of Fig. 1. The SEM results indicate that the CZTS-B has better crystal quality than CZTS-A, and hence can be used to fabricate high-efficiency CZTS-based solar cells compared to CZTS-A thin film. Above reslts indicate that addition of the MPA not only can obviously improve the stability of the CZTS precursor solution, but also can enhance the crystals quality of the CZTS thin films due to the homogeneous composition.

Characterization of the precipitate and its effect on film quality

For investigating the morphology and composition of the precipitate, we analysed the precipitate using SEM, EDS and FTIR in detail. Fig. 2(a) shows the EDS spectrum of the precipitate. The SEM image and the composition of the precipitate are shown in the insets of Fig. 2(a). The results of Fig. 2 indicate that the elements in the precipitate are N, C, S, Cu and Cl. Among these elements, C, N and S come from thiourea, while Cu and Cl come from $CuCl_2$. To confirm the chemical composition of the precipitate, FTIR measurement was performed, as shown in Fig. 2(b). In the previous reported works, the Hillhouse's group has demonstrated that the Cu^{2+} and Sn^{2+} could produce the oxidation-reduction reaction and then formed Cu^{+} and Sn^{4+}. The FTIR absorbance bands at 3463, 3263 and 3162 cm^{-1} correspond to $-NH_2$ functional groups, 1604 cm^{-1} band is attributed to Cu (I) complexes and also attributed to NH_2 deformation.[26] The peaks at 1388 and 563 cm^{-1} are due to asymmetric N-C-N stretching and N-C-N bending vibrational modes in the molecule， respectively. Two peaks at 1095 and 709 cm^{-1} are attributed to C=S stretching.[26] Based on the EDX and FTIR results, it is concluded that the precipitate is composed of Cu^{+} and thiourea coordination compound. These results indicate that the coordination compound of Cu^{+} and thiourea solution is easy to crystallize. Therefore, we proposed that the crystgcrystallizing mechanism of copper salt and thiourea in aqueous/ethanol solution was formed coordination complexes (R = H_2O or ethanol) through the following reactions:

$$2Cu^{2+} + Sn^{2+} \rightarrow 2Cu^{+} + Sn^{4+} \qquad (1)$$

$$Cu^{+} + Cl^{-} + x\,(NH_2)_2CS + y\,R \rightarrow Cu(Cl^{-})[(NH_2)_2CS]x\,Ry\downarrow \qquad (2)$$

The precipitation of Cu from the precursor solution without MPA will cause serious lack of Cu in CZTS-A film, as shown in Fig. S1 of supplementary information, which indicates that the Cu content in the CZTS-A and selenized CZTS-A is only about 7.24 and 4.36 at%, respectively, much smaller than Cu contents in stoichiometric kesterite CZTS and CZTSSe. To check the structures of the as-fabricated and selenized CZTS-A films, XRD and Raman spectra measurements were performed for the two films. Fig. 3(a) and (b) show the XRD pattern and Raman spectrum of the as-fabricated CZTS-A film, respectively, indicating that the film is not composed by a single phase. Besides kesterite CZTS phase, there also are SnS_2 and ZnS phases in the film[27-31], and the CZTS and SnS_2 phases are dominant. Fig. 3(c) and (d) shows the XRD pattern and Raman spectrum of the selenized CZTS-A film, respectively, indicating that the film consists of kesterite CZTSSe, $Sn(S,Se)_2$ and Zn(S,Se) phases,[27-31] however, the $Sn(S,Se)_2$ phase is dominant. The results of Fig. 3 demonstrate that a single kesterite phase of CZTS or CZTSSe films cannot be fabricated by using the unstable CZTS aqueous/ethanol-based precursor solution.

In order to avoid the precipitation and improve the stability of the CZTS aqueous/ethanol-based precursor solution, we added MPA into the aqueous/ethanol-based precursor solution. It was found that the precipitate dissolved completely, moreover, no additional precipitate was observed after one week, indicating that a stable CZTS aqueous/ethanol-based precursor solution was obtained.

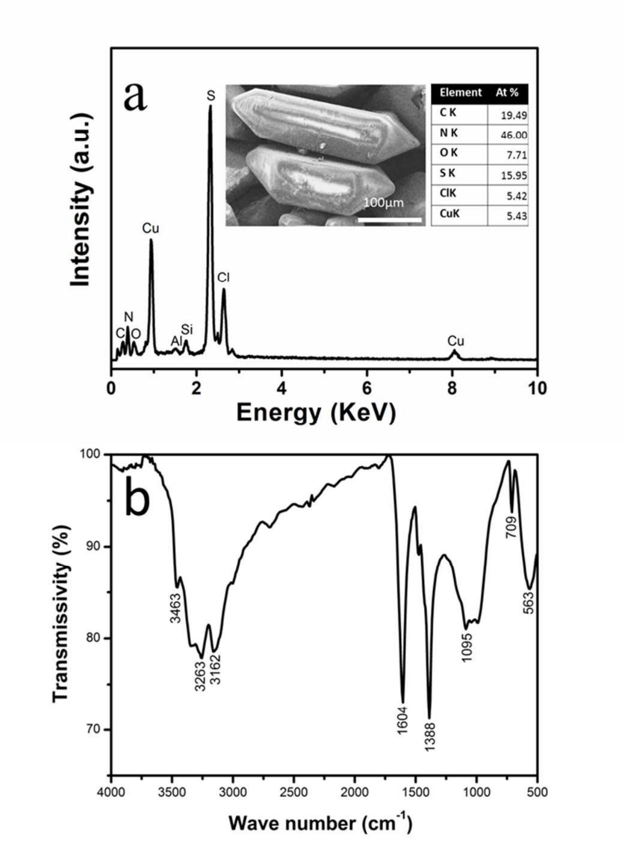

Fig. 2 EDS spectrum (a) and FTIR (b) of the precipitate from the CZTS precursor solution without MPA. The inset shows the SEM image and the components of the precipitate.

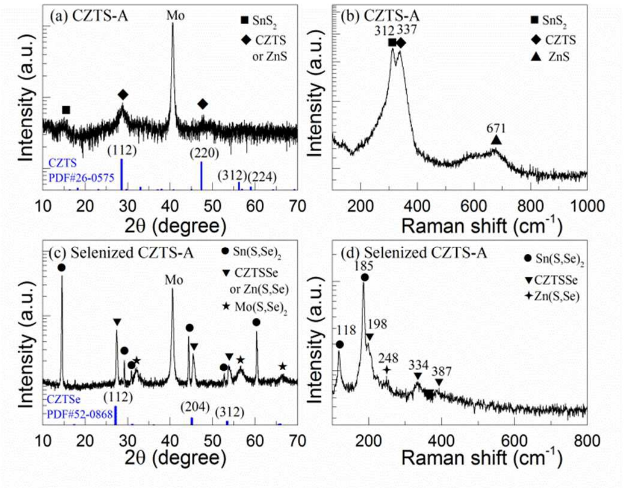

Fig. 3 XRD patterns and Raman spectra for the CZTS-A (a,b) and the selenized CZTS-A (c,d) thin films. The reference diffraction data of CZTS and CZTSSe are also presented at the bottom of (a) and (c), respectively.

Characterization of the CZTS and CZTSSe thin films

With the stable aqueous/ethanol-based precursor solution, a CZTS film (CZTS-B) was fabricated by spin-coating, while a CZTSSe film was obtained by selenizing the CZTS-B film. The XRD patterns of the CZTS-B and CZTSSe thin films are shown in Fig. 4(a), where only the (112), (220), and (312) diffraction peaks of CZTS with kesterite structure are observed, suggesting that the CZTS-B film consists of a single kesterite CZTS phase. These diffraction peaks are very broad，implying that the CZTS-B thin film is composed of small-size grains.[27-31] However, for the CZTSSe film (selenized CZTS-B), only XRD diffraction peaks of kesterite CZTSSe are observed in the XRD pattern of the CZTSSe film, as shown in Fig. 4(a), and the diffraction peaks become very sharp, indicating that the CZTSSe film consists of a single kesterite CZTSSe phase with large-size grains, which is highly desirable for high-efficiency CZTSSe solar cells.[27-31] It is also found that the diffraction peaks of the CZTSSe shift toward lower angles compared to the CZTS-B, which is attributed to the expansion of the unit cell volume induced by the partial replacement of S with Se. In addition, some minor peaks, such as (011) (110), (103), (211), and (040)/(008), become observable, indicating that the CZTSSe thin film has good crystallinity.[27-31] The EDS measurements indicate that the chemical compositions of the both films are closed to the stoichiometric ratio of CZTS and CZTSSe, as shown in Fig. S2 of supplementary information. The chemical composition of the CZTSSe film has a Cu/(Zn +Sn) ratio of 0.85 and a Zn/Sn ratio of 1.18, which are slightly different from those of the non-selenized CZTS thin film and are consistent with those reported previously for high-efficiency CZTSSe devices.[32, 33]

It is well known that some binary and ternary sulfides and selenides, such as ZnS, ZnSe, Cu2SnS$_3$, or Cu$_2$SnSe$_3$, have similar XRD patterns with kesterite CZTS or CZTSSe.[27-31] Therefore, only XRD is insufficient to determine if there are other phases in the CZTS (or CZTSSe) thin films besides the kesterite CZTS (or CZTSSe). Since Raman spectroscopy is able to identify difference between CZT(S,Se) and the secondary phases, such as Cu$_x$(S,Se), Zn(S,Se), Sn(S,Se)$_2$, and Cu$_2$Sn(S,Se)$_3$, etc, we examined the CZTS-B and CZTSSe thin films using Raman spectroscopy, as shown in Fig. 4b. For the CZTS-B thin film, the major peak appears at 333 cm^{-1}, consistent with literature reported previously,[28-30] indicating that a single phase of kesterite CZTS thin film was obtained. For the CZTSSe thin film, the main peaks are located at 173, 195 and 235 cm^{-1}, which are in good agreement with the results of CZTSSe with S/(S+Se)$\approx$0.08 reported previously.[32] No Raman peak of the impurity phases, such as Cu$_x$(S,Se)$_y$, Zn(S,Se), Sn(S,Se)$_2$, and Cu$_2$Sn(S,Se)$_3$, are found in the Raman spectrum of the CZTSSe thin film，indicating that the CZTSSe film consists of a single phase of kesterite CZTSSe.[28-31]

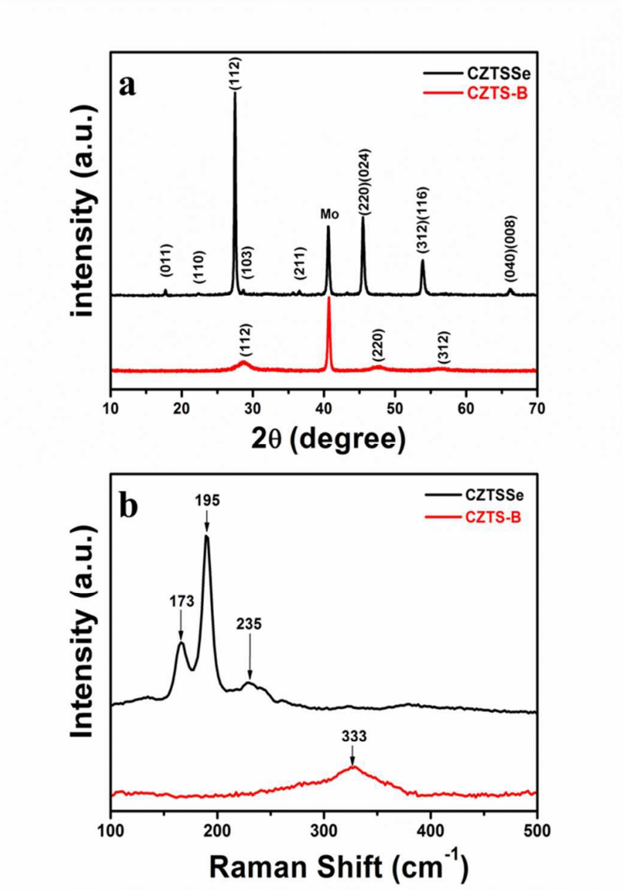

Fig.4 XRD patterns (a) and Raman spectra (b) for the CZTS-B and the CZTSSe thin films (selenized CZTS-B).

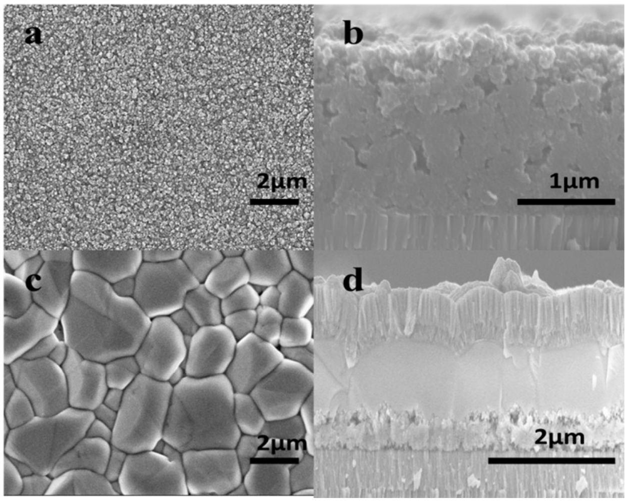

Fig.5 Plane-views (a) and cross-sectional (b) SEM images of the as-fabricated CZTS thin film (CZTS-B). Plane-views (c) and cross-sectional (d) SEM images of the completed CZTSSe solar cell (selenized CZTS-B).

The typical SEM images of the surface and cross-section of the CZTS-B thin film are shown in Fig. 5(a) and 5(b), indicating that a uniform CZTS nanocrystalline thin film with a thickness of ~1.5 μm was formed by a consecutive spin-coating process. Fig. 5(c) shows the SEM image of surface of the CZTSSe thin film, indicating that the surface is smoothing and its grain size is in the range between 1 and 3 μm, moreover, most of the grain sizes are larger than 1.5 μm, which is desired for high-efficiency CZTSSe solar cells.[6, 33, 34] A cross-sectional SEM image of a completed CZTSSe solar cell is shown in Fig. 5(d). The selenized CZTSSe thin film exhibits an obvious bi-layer morphology consisting of a dense large-grained top layer of about 1.1 μm and a fine-grain layer of about 400 nm near the Mo interface as well as a $MoSe_2$ layer of about 400 nm in thickness. The similar fine-grain layer has been observed by various groups for CZTSSe solar cells fabricated by nanocrystals-based ink process and molecular precursor solution approach.[34, 35]

Characterization of device performance

The CZTSSe-based solar-cell was fabricated with the conventional structure of SLG/Mo/CZTSSe/CdS/*i*-ZnO/ITO/Al. The current density-voltage (J-V) curves for a CZTSSe-based solar cell measured in the dark and under AM1.5 illumination are shown in Fig. 6(a). The as-fabricated device exhibits a PCE of 7.25% on the basis of the active area of 0.37 cm^2, open circuit voltage of V_{oc}= 0.412 V, short circuit current density of J_{sc}= 31.86 mA/cm^2, and filling factor of FF = 55.2%. Fig. 6(b) shows the EQE spectrum of the CZTSSe-based solar-cell, indicating that the highest quantum efficiency in the visible-light range reaches ~80% in the wavelength range of 600-1050 nm. The band gap of CZTSSe absorber layer is calculated to be 1.1 eV, as shown in the inset of Fig. 6(b). Compared to the record CZTSSe solar cells with similar structure reported previously,[20] our PCE of 7.25% is smaller than that of the record CZTSSe (12.6%), that is mainly attributed to that our V_{oc}, J_{sc}, FF and EQE are much lower than those of the record CZTSSe solar cell (V_{oc} = 0.513 V, J_{sc} = 35.2 mA/cm^2, FF =69.8% and EQE above 90%). The low J_{sc} and FF is due to that high serial resistance of our cell (1.03 $\Omega \bullet cm^2$) is much higher than that of the record cell (0.2 $\Omega \bullet cm^2$), while low V_{oc} to that the shunt resistance of our cell (G = 0.8 $mS \bullet cm^{-2}$) is low. It is well known that the serial resistance is related to bulk resistance of the layers in solar cell, such as CZTS absorber, and CdS layers etc, and contact resistance of electrodes, while the shunt resistance is related to leakage current of p-n joint. The serial resistance can be decreased by improving crystal quality of these layers, and the decrease in the contact resistance and increase in the shunt resistance can be realized by optimizing manufacturing techniques of contact electrode and *p-n* joint. As we known, EQE is related to structure of solar cell, including antireflection layer, thickness and crystal quality of emitting and absorb layers and recombination rate at former and back surfaces. Compared to the structure of the record CZTSSe solar cell, our solar cell lacks an antireflection layer.[20] So, the low EQE may be due to no antireflection layer in our solar cell structure. Based on above discussion, it can be expected that the PCE of the solar cell prepared by aqueous/ethanol-based approach can be further enhanced by increasing crystal quality of the layers, optimizing structure of solar cell and preparation technologies of contact electrodes and *p-n* joint and depositing an MgF_2 antireflection film.[36] Therefore, we believe that the aqueous/ethanol-based approach can become a promising preparation method of CZTS-based solar cell with low-cost and friendly environment, though the PCE in the present is still low compared to the record PCE.

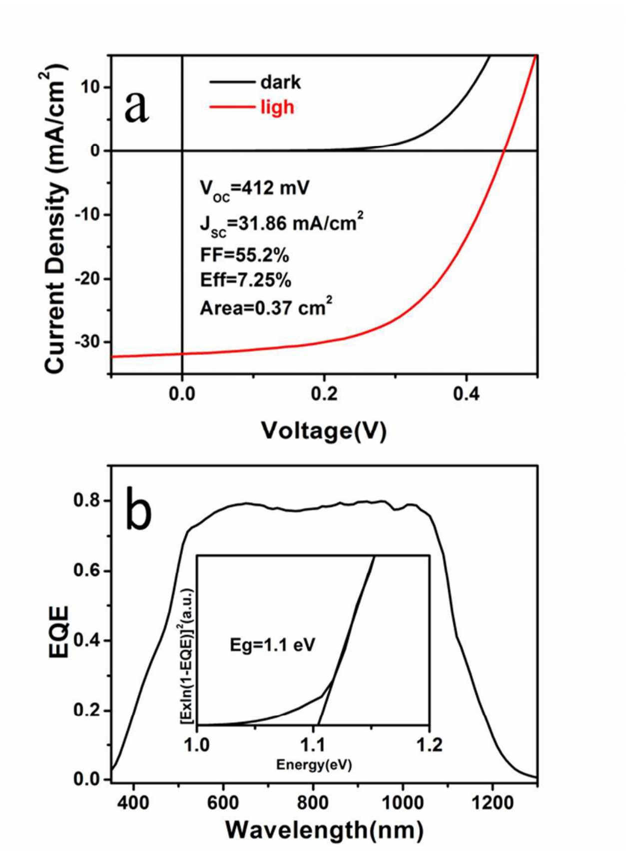

Fig. 6 (a) J-V curves of the CZTSSe thin film solar cell measured in the dark (black line) and under AM 1.5 illumination (red line). (b) EQE spectrum of the CZTSSe thin film solar cell. The inset in (b) shows the plot of $[E\times\ln(1-EQE)]^2$ as a function of photon energy.

Conclusions

In summary, we systematically studied the stability of the CZTS aqueous/ethanol-based precursor solution, and found that the precursor solution is metastable and precipitation occurs easily when it is stored some hours. The precipitate is identified to contain a large amount of Cu^+ ions, which leads to that the solution miss a large amount of Cu, and hence cannot be used for preparation of a single phase of kesterite CZTS. However, addition of the harmfulless MPA into the precursor solution can avoid the precipitation and obviously improve the stability of the precursor solution. By adding the MPA into the precursor solution, we fabricated a single phase of CZTS film, and then obtained a large-grain and hole-free CZTSSe film by selenizing the as-prepared CZTS film. The CZTSSe thin film solar cell with a competitive power conversion efficiency of 7.25% has been received, which is obviously higher than the previously reported metal/thiourea aqueous/ethanol-based solution approach.

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Graphical abstract: