Coordination engineering of Cu-Zn-Sn-S aqueous precursor for efficient kesterite solar cells

Linbao Guo, a, c,1 Jiangjian Shi, a, b,1 Qing Yu, a, c, Biwen Duan, a, c, Xiao Xu, a, c, Jiazheng Zhou, a, c, Jionghua Wu, a, c, Yusheng Li, a, c, Dongmei Li, a, b, d, Huijue Wu, a, Yanhong Luo, a, c, d, e, Qingbo Meng, a, b, d, e

a Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
b Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China
c School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China
d School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China
e School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

Key words: Kesterite solar cell
Aqueous solution
Coordination chemistry
CZTSSe

A B S T R A C T

Aqueous precursors provide an alluring approach for low-cost and environmentally friendly production of earth-abundant Cu2ZnSn(S,Se)4 (CZTSSe) solar cells. The key is to find an appropriate molecular agent to prepare a stable solution and optimize the coordination structure to facilitate the subsequent crystallization process. Herein, we introduce thioglycolic acid (TGA), which possesses strong coordination (SH) and hydrophilic (COOH) groups, as the agent and use deprotonation to regulate the coordination competition within the aqueous solution. Ultimately, metal cations are adequately coordinated with thiolate anions, and carboxylate anions are released to become hydrated to form an ultrastable aqueous solution. These factors have contributed to achieving CZTSSe solar cells with an efficiency as high as 12.3% (a certified efficiency of 12.0%) and providing an extremely wide time window for precursor storage and usage. This work represents significant progress in the non-toxic solution fabrication of CZTSSe solar cells and holds great potential for the development of CZTSSe and other metal sulfide solar cells.

© 2020 Science China Press. Published by Elsevier B.V. and Science China Press. All rights reserved.

1. Introduction

Photovoltaics have made great contributions to the release of global energy and environmental issues. Kesterite Cu2ZnSn(S,Se)4 (CZTSSe) is one of the most environmentally friendly and inexpensive semiconductor light-absorbing materials for photovoltaic applications because of its non-toxic and earth-abundant components [1–3]. CZTSSe exhibits high light absorption of > 104 cm−1, an adjustable bandgap matching the solar spectrum [4–7], high thermodynamic and environmental stability [8,9] and a device manufacturing process compatible with current thin film solar cells [10–13]. Solution processing of the CZTSSe thin film deposition by intermixing of precursor components at the molecular level has advantages of composition uniformity and morphology control over the conventional vacuum technique [14–16]. The hydrazine solution approach, with the advantages of high reduction and coordination ability [17,18], has resulted in the most efficient CZTSSe solar cells [19]. These positive results have encouraged scientists to explore the green solvent technique for CZTSSe fabrication, an ultimate trend toward non-vacuum semiconductor device production [20,21], which has led to the development of a variety of solvent systems [22–24]. Certainly, among these systems, the aqueous system is the most alluring candidate from the perspective of safety, environmental effects and cost.

As early attempts at aqueous precursor systems, metal salt precursor routes such as chemical bath deposition (CBD) [25], successive ionic layer adsorption and reaction (SILAR) [26,27] and electrochemical deposition have been explored [28]. Spin coating using a metal salt-thiourea solution has yielded moderate efficiencies [29,30]. Strategies for synthesizing nanocrystals from aqueous solutions or preparing colloid dispersions have also been developed. Cell performance has been obviously improved through pre-synthesis of the colloid dispersion and detailed adjustment of the element composition [31,32]. However, the resulting device efficiency is still much lower than that of the organic systems used to date [33]. This may arise from residual anions such as chloride ions and long-chain stabilizers, which have a significant impact on CZTSSe crystallization [34–38]. In addition, these aqueous precursor solutions usually suffer from low stability since the formed metal-thiourea complexes and the dispersed colloids easily precipitate due to the lack of strong solute–solvent interactions [29]. Therefore, more judicious engineering of the CZTSSe aqueous precursors is desired to increase the current device performance.
Generally, metal sulfide compounds or complexes are insoluble or easily precipitate within an aqueous solution due to poor hydration [39]. Thus, molecular engineering of organic ligands with hydrophilic groups may help stabilize CZTSSe (or Cu, Zn and Sn) aqueous precursors. Thiols engage in strong coordination interactions with metal cations and have been widely used in the chemical synthesis of metal sulfide films in non-aqueous precursor systems [40,41]. Thiols with hydrophilic groups, such as carboxyl, hydroxyl and amine moieties, should be useful in constructing CZTSSe aqueous precursors [42]. Thioglycolic acid (TGA), which has a lower GHS risk level and low cost, is the most promising water-soluble ligand. Owing to these potential advantages, TGA was once used for aqueous CZTSSe precursor preparation [43,44]. However, the resulting efficiency of 7.38% is still much lower than that of the hydrazine and other organic systems. This mainly arises because (1) the fundamental coordination chemistry of this aqueous system has not been clearly understood and (2) that how to precisely manipulate the complexes structure of TGA-metal to facilitate its application in CZTSSe solar cells has not been studied. Herein, we systematically investigate the coordination engineering in the Cu-Zn-Sn-S aqueous precursor solution. The competition between metal-S and metal-COO coordination interactions has been manipulated by adjusting the deprotonation degree of TGA in solution. In the optimal structure, the metal cation is adequately coordinated with thiolate anions, and the carboxylate anions are released to become fully hydrated, thus facilitating the formation of an ultrastable metal-TGA aqueous solution and improving the nucleation and crystallization of the CZTSSe thin film. Our strategies enable the fabrication of CZTSSe solar cells with a remarkable efficiency of 12.3% and a certified efficiency of 12.0%, which is the best result for CZTSSe solar cells among the aqueous precursor systems investigated to date. This significant progress in the non-toxic solution fabrication of CZTSSe solar cells brings great promise for the future development of CZTSSe solar cells.

2. Materials and methods

2.1. Materials

Copper (II) oxide (CuO, 99.9%) and selenium particle (Se, 99.999%) were purchased from Zhongnuo Advanced Material Technology Company. Tin(II) oxide (SnO, 99.9%), TGA (HSC(2)COOH, 98%), cadmium sulfate (CdSO4, 99%), thiourea (NH2CSNH2, 99%) and dithiodiglycolic acid (di-TGA) ((CH2COOH)2S2, 96%) were purchased from Sigma-Aldrich. Ammonia solution (NH3.H2O, 28%) was purchased from Beijing Chemical Industry Group Co., Ltd. All chemicals were used as received without any further purification.

2.2. Solution preparation

All solutions were prepared at room temperature in a N2-filled glovebox. The solubility limits were determined after overnight stirring. In all solutions for Raman and nuclear magnetic resonance (NMR) characterization, the concentration of TGA was maintained as 4 mol L−1 and specific amounts of NH3 was added according to the NH3/TGA ratio. The precursor solution for CZTSSe film deposition was obtained by dissolving 0.280 g CuO, 0.195 g ZnO and 0.276 g SnO in a mixture aqueous solutions of 4 mol L−1 TGA and varied NH3.H2O.

2.3. Metal-TGA complex preparation

Metal oxides (1 mmol) were mixed with 2.0 mL of TGA and 1.0 mL of water under magnetic stirring at 60 °C for 2 days. After sufficient reaction, the Metal-TGA complex precipitations were formed. The Metal-TGA complexes were separated by centrifuging and cleaned with water for 3 times. The Metal-TGA complexes were dried in vacuum box for 24 h at room temperature.

2.4. Film deposition

The precursor films of CZTSSe were deposited on Mo-coated soda lime glasses (0.3 2 s−1, DC-magnetron sputtering deposited) by spin-coating the precursor solution at 4000 r min−1 for 20 s in a N2-filled glove box. The as-deposited films were sintered on a hot plate at 400 °C for 2 min to eliminate organic residues. The spin-coating and annealing steps were repeated several times until the thickness of the precursor film reaches 1.0 μm. Finally, these thin films were selenized under Se/N2 atmosphere at 520 °C for 15 min in a semi-enclosed graphite-box containing about 0.3 g selenium particles by using a rapid thermal processing (RTP) furnace (MTI, OTF-1200X-RTP) under nitrogen flow about 80 sccm (the heating rate was about 8.6 °C s−1).

2.5. Solar cell fabrication

The CZTSSe solar cells were prepared with a structure of glass/Mo/CZTSSe/Cds/i-ZnO/ITO/Ni/Al. Firstly, an approximately 40 nm thick CdS buffer layer was deposited onto the selenized CZTSSe film by a CBD method. Then i-ZnO combined with indium tin oxide (ITO) window layers were deposited successively by radio frequency (RF) magnetron sputtering. Finally, the Ni-Al grid electrode was thermally evaporated through a metal shadow mask as a current collector. Notably, a 110 nm MgF2 antireflection layer was evaporated onto the final cell to enhance the photocurrent. A solar cell device with an effective area of 0.18 cm2 was separated by mechanical scribing, yielding 9 standard cells on the same substrate.

2.6. Characterization

Raman spectra were collected by a Raman spectrometer (LabRAM HR Evolution, HORIBA), using a 633 nm excitation laser with a power of 6 mW. The FT-IR spectra were collected by a Fourier Transform Infrared (FTIR) Spectrophotometer (TENSOR27, Bruker) and the KBr disk method. Solution 13C and 119Sn NMR spectra were recorded on a Bruker Avance III 400HD or Avance III 500 MHz spectrometer at 100.6 or 186.5 MHz. Spectra were obtained at room temperature with 10% of deuter oxide adding for locking of the main magnetic field. Each experiment of 119Sn, 13C used a 12.5 and 10 μs pulse width and a 1.0 and 2.0 s relaxation delay and collected 256 scans, respectively. A spectral window from 350 to −650 and 225 to −25 ppm was used to search for the signals of 119Sn and 13C, respectively. The morphologies of the films and devices were obtained by a scanning electron microscope (S4800-SEM, Hitachi). X-ray diffraction (XRD) patterns of selenized CZTSSe films were collected by an X-ray diffractometer with Cu Kα line as the source (Empyrean, PANaltcal). Current density–voltage (J-V) characteristics of the solar cells were collected on Keithley 2601B Source Meter under AM 1.5G illumination (1000 W m−2) from Zolix SS150A solar simulator. The light intensity of the solar simulator was calibrated by a standard monocrystalline silicon reference solar cell. The external quantum efficiency (EQE) curve was measured using an Enlitech QE-R test system, where a xenon lamp and a bromine tungsten lamp were used as the light sources and a certified Si and InGaAs diode was used as the reference detector. The C-V data was performed at 100 kHz and 14 mV alternating current (AC) excitation source with direct current (DC) bias ranging from 0.6 to −1.0 V. Transient photovoltage spectra of the cell were obtained by a tunable nanosecond laser (Optotek, RADIANT 532 LD)
with an ultralow light intensity of about 10 nJ cm$^{-2}$ and recorded by a sub-nanosecond resolved digital oscilloscope (Tektronix DPO7104) with input impedances of 1 MΩ.

3. Results and discussion

3.1. Coordination competition between metal-S and metal-O

As a preliminary attempt, metal oxides, such as CuO, ZnO and SnO, were added to an aqueous TGA solution, and the mixture was continuously stirred for several days. Unfortunately, these metal oxides have limited solubility in the TGA solution (Fig. S1 online) and the obtained mixtures cannot be used as precursors for CTSSe film deposition. Nonetheless, we found chemical reactions had occurred within these solid–liquid mixtures, and new complexes formed, as evidenced by the apparent colour change of the added solids. For instance, the colour of the CuO powder changed from black to white, that of SnO changed from black to light brown, and the precipitate in the ZnO system remained white but fluffy (Fig. 1a). These results are positive because chemical or coordination reactions are usually the first step in the dissolution of metal oxides, sulfides or elementary substances.

Chemical reactions between these metal oxides and TGA in an aqueous solution were investigated by FTIR spectroscopy of the precipitation products (Fig. 1b). Notably, Cu(II) was reduced to Cu(I) in the presence of excess TGA, resulting in the formation of di-TGA as a byproduct [45]. The presence of di-TGA was confirmed according to $^{13}$C NMR spectra of the supernatant (Fig. S2 online). We further found that Sn(II) can be oxidized to Sn(IV) by the di-TGA while generating TGA as coordinating ligand. When both Cu(II) and Sn(II) were present in the system, a redox reaction occurred between them to form Cu(I) and Sn(IV) [22]. Thus to imitate the actual reaction within the Cu-Zn-Sn-S precursor in the spectra study of individual metal oxide-TGA systems, stoichiometric di-TGA was added to oxidize Sn(II) to Sn(IV). In the spectra of pure TGA, characteristic absorption bands for both the SH and COOH groups are clearly observed at ~1570 and ~1714 cm$^{-1}$, respectively [46,47]. Changes in the absorption bands are observed after the reaction. First, the disappearance of the SH stretching vibration in the spectra of the ZnO-TGA and SnO-TGA products implies that the SH group was deprotonated, allowing S to coordinate to the metal atom [48]. This change was realized through a metal oxide-thiol reaction, releasing H$_2$O as another product. Second, a new peak at ~1570 cm$^{-1}$ is observed for all three solid products, which mainly arises from the asymmetric stretching of COO$^-$ and is accompanied by a symmetric stretching peak in the low-frequency region [46,47], as depicted by arrows in Fig. 1b. This FTIR spectral change indicates that the COOH group was also deprotonated through the metal oxide–acid reaction, resulting in coordination between the oxygen (COO$^-$) group and the metal atoms. Unlike the reaction products of ZnO and SnO with TGA, the products of the reaction with CuO still gave rise to an SH absorption band, most likely because Cu coordinated only with COO$^-$ to form HSCH$_2$COOCu at low pH [49]. On the basis of these spectral signatures, possible reactions between TGA and these metal oxides were proposed (Scheme S1 online), and possible structures of the produced metal-TGA complexes are presented in Fig. 1c. It is clear that both deprotonated thiol and carboxyl groups coordinated to Sn and Zn, while only the carboxylate group coordinated to Cu. In these structures, the polarity of the carboxylate group is significantly weakened, and its hydrophilic characteristics cannot be fully expected. Therefore, to enhance the solubility of the metal-TGA complexes, the carboxylate group must be adequately released to be hydrated by the surrounding water molecules by substituting the metal-catecholate coordination with metal-thiolate coordination.

3.2. Engineering of coordination structures

However, within the acidic or neutral TGA/water environment, metal-thiolate coordination cannot easily be fully realized because thiol groups are usually difficult to deprotonate to form R-S$^-$ (R: HOOCCH$_2$) with strong metal complexing ability [50–52]. Thus, the above desired substitution process can be achieved only when ionization (i.e., deprotonation) of the thiol group of the TGA is enhanced [40]. Fig. 2 schematically presents the O donor and S donor coordination substitution processes that may occur with increasing TGA deprotonation in the aqueous metal oxide-TGA solution, where Sn compounds are used as an example. For the initial state (Sn-TGA-1), a double decomposition reaction occurs between SnO and TGA to form salt and water, and both oxygen atoms of the carboxylate group are coordinated to the Sn atom, forming a bidentate carboxylate structure. When the deprotonation degree of TGA in solution is increased, the highly concentrated

---

Fig. 1. (Color online) Chemical reactions between metal oxides and TGA. (a) Photographs of the metal oxide-TGA reaction products in water. (b) FTIR spectra of the collected products and pure TGA. Characteristic peaks and their corresponding vibration modes that can reflect the reaction processes are marked by dashed lines and arrows. The change in the atomic valence of Cu or Sn arose from redox reactions with TGA or di-TGA. (c) Proposed structures of the metal oxide-TGA insoluble products. Within these structures, almost all the carboxylate groups are coordinated to metal atoms rather than exposed to the surrounding water molecules to facilitate dissolution.
and activated R-S\(^-\) can substitute for one of the Sn-O coordination bonds of the bidentate carboxylate (Sn-TGA-2). This will introduce an additional Sn-S bond and a free carboxylate terminal group and thus help enhance the hydrophilicity of the Sn-TGA complex. Upon further deprotonation of the thiol group, more Sn-O coordination of the bidentate carboxylate can be substituted by Sn-S bonds, forming the Sn-TGA-3 structure and ultimately the Sn-TGA-4 structure. Within Sn-TGA-4, the Sn atom is completely coordinated by R-S\(^-\), and all the carboxylate groups are exposed to water molecule surroundings. This coordination structure should be able to form a more stable (or the most stable) Sn-TGA aqueous solution. For the Cu-TGA and Zn-TGA complexes, similar coordination substitution processes should also be realized (Fig. S3 online), thus helping to prepare stable and effective CZTSSe precursors.

The above coordination substitution processes depend highly on deprotonation of the SH group. Increasing the pH of the solution is the simplest, most reliable and most widely used method to facilitate this process [53,54]. Ammonia is the best candidate for this purpose because it does not introduce any metal or carbon impurities and can be easily removed at relatively low temperatures. These advantages prompted us to use ammonia to regulate the aqueous system, and positive results were obtained. The molar ratio between ammonia and TGA was the main variable, while the concentrations of both TGA (4 mol L\(^-1\)) and the metal (0.4 mol L\(^-1\)) were held constant for simplicity. Distinct variations in the Cu-Zn-Sn-TGA system were observed when the amount of ammonia increased (Tables S1, S2 and Fig. S4, online). Specifically, the metal oxides were completely dissolved when the NH\(_3\)/TGA ratio approached 1.0, and the solution colour changed from dark amber to light yellow when the ratio approached 2.0 (Fig. S5 online). These phenomena indicate changes in the metal-TGA complexing structures within the aqueous solution. Solution Raman scattering and NMR spectroscopies, which are sensitive to coordination structure and chemical environment, were used to trace the coordination chemistry of this solution system [41,55]. To obtain comprehensive information, Cu-Zn-Sn-TGA, Cu-TGA, Zn-TGA and Sn-TGA were all studied in our measurements.

Within the wide-region Raman spectra (Fig. 3a and Fig. S6 online), the characteristic scattering signals attributable to SH and CH\(_2\) stretching at ~2580 and ~2935 cm\(^{-1}\), respectively, can be seen for all aqueous solutions [53,54]. The C=O stretching frequency in the pure TGA aqueous solution is 1714 cm\(^{-1}\). The apparently depolarized CH\(_2\) bending frequency at 1395–1400 cm\(^{-1}\), clearly visible in the un-ionized acid, is present in all states of deprotonation (Fig. S7 online). Upon ionization of the carboxyl group, the Raman peak at 1395–1400 cm\(^{-1}\) is partially masked by the very intense symmetrical stretching frequency of the ionized carboxyl, and the asymmetrical stretching frequency of the latter (1550–1575 cm\(^{-1}\)) also appears (Fig. 3a). The \(\nu(CH_2)\) intensity at ~2935 cm\(^{-1}\) is almost independent of the amount of ammonia, which is in good agreement with the unchanged TGA concentration and thus confirms that other optical properties within the Raman process, such as the light penetration depth and other scattering processes (e.g., Mie scattering and Rayleigh scattering), have not been influenced by the solution conditions (Figs. S7, S8 online). In the pure TGA solution, under a low NH\(_3\)/TGA ratio, the \(\nu(SH)\) intensity remained nearly unchanged, and the \(\nu(COO^-)\) intensity increased gradually. At higher NH\(_3\)/TGA ratios, the \(\nu(SH)\) intensity was significantly reduced. After addition of the metal oxide, the \(\nu(SH)\) intensity decreased by a constant value compared with that of the TGA solution, indicating that deprotonation of the SH group occurred and that R-S coordinated with the metal (Fig. S7 online). In addition, more abundant spectroscopic signatures arising from Sn atom-associated vibrations were observed in the low wavenumber region, amplified in Fig. 3b. At NH\(_3\)/TGA ratios lower than 1.0, strong scattering signals appeared at ~380 cm\(^{-1}\). These signals abruptly vanished and a slightly lower-frequency vibration mode appeared at 365 cm\(^{-1}\) when the NH\(_3\)/TGA ratio exceeded 1.2. At a ratio of 1.1, these two scattering signals coexisted within the spectrum. Both of these Raman signals can be attributed to the stretching vibration of the Sn-O bond, while the frequency difference implies modified coordination geometries [56], as depicted in the inset of Fig. 3b. An O–Sn-O bidentate structure is expected to possess a tighter Sn-O Coulomb interaction and thus a higher bond stretching frequency. Accompanying the vanishing of this bidentate structure, new Raman scattering peaks were observed at 240 and 330 cm\(^{-1}\). These two peaks were confirmed to arise from the stretching vibration of the Sn-S bond [57–59] by obtaining Raman spectra of the Sn-mercaptopropanol solution, which possesses only Sn-S coordination (Fig. S9 online). Therefore, based on the changes in the low-frequency Raman scattering signals, we can confirm that the coordination substitution reaction from Sn-O to Sn-S indeed occurred when the NH\(_3\)/TGA ratio exceeded 1.0. This finding agrees well with the substitution processes schematically presented in Fig. 2. For the coordination of other metal atoms, we believe similar processes can also occur, although they cannot be directly probed by Raman scattering.

This replacement of one of the bidentate carboxylate O atoms by S\(^-\) consumes more R-S\(^-\) groups and thus results in a reduction in the SH concentration (Scheme S2 online), which can be quantitatively reflected by the \(\nu(SH)\) intensity in the Raman spectra [54]. The CH\(_2\) band at 2935 cm\(^{-1}\) was chosen as an internal standard since all the evidence indicated that the intensity of this band was not substantially affected by the change in the NH\(_3\)/TGA ratio (Fig. S8 online). For clarity, the initial \(\nu(SH)\) intensity relative to the
The intensity of $I_{(CH_2)}$ for these samples is set to be the same by adding certain values (Fig. 3c). It is apparent that in the pure TGA solution, the $I_{(SH)}/I_{(CH_2)}$ value remains unchanged when the ratio is lower than 1.2 and then exhibits an obvious decline, indicating significant deprotonation of the SH group. When the metal oxides are dissolved, a certain proportion of SH is consumed in the initial stage to react with metal oxides and coordinate to the metal atoms. At low NH$_3$/TGA ratios of <0.9, this initial $I_{(SH)}/I_{(CH_2)}$ value remains constant, implying an unchanged metal-TGA coordination structure. Compared to the solvent itself, this $I_{(SH)}/I_{(CH_2)}$ value begins to decrease at an obviously lower NH$_3$/TGA ratio of ~0.9, implying that the coordination substitution (from metal-S to metal-O) accelerated the pH-induced deprotonation of the SH group. This result is strong support for the observed coordination substitution process. From these intensities, we can further estimate the coordination number of the metal-S (Note S1 online) and trace the variations. Clearly, the coordination number of all the metal atoms has increased at higher NH$_3$/TGA ratios (Fig. 3d), further confirming the coordination substitution process that we have proposed.

More evidence was gathered from independent NMR characterizations (Fig. 3e). Within the Sn-TGA solution, two types of carboxyl $^{13}$C chemical shifts were observed at a low NH$_3$/TGA ratio. The chemical shift at $\delta = 177$ ppm (marked by dashed lines) was attributed to the free COOH or COO$^-$ within the solvent, while another downfield chemical shift at $\delta = 178$ ppm (triangles) was attributed to the carboxyl carbon of the Sn-OOC because the donor coordination weakened the shielding effect. Free carboxyl groups existed in all studied NH$_3$/TGA ratios, while the Sn-OOC NMR signal disappeared when the ratio exceeded 1.0. A new weak signal appeared at $\delta = 178.6$ ppm (# marks) at a ratio of 1.1 but disappeared at ratios higher than 1.2. This signal was also ascribed to the Sn-OOC but with a modified coordination geometry [60]. The complete disappearance of the Sn-OOC coordination signal indicates that the proportion of Sn-O bonds among the Sn-TGA coordination was too low to be detected when the ratio was higher than 1.3. The $^{13}$C NMR signal from the bidentate carboxylate Sn-O bonding was initially observed at $\delta = –344$ ppm (asterisks) and shifted upfield as the NH$_3$/TGA ratio increased. When the ratio exceeded 1.1, this signal completely disappeared, and a new NMR signal appeared at a chemical shift of $\delta = –339.5$ ppm. This large downfield shift also implies a new Sn-TGA coordination structure, which strongly supports the appearance of the added Sn-S bonds. The Sn-S coordination possesses a long bond length and thus has a weak shielding effect on the Sn nucleus. Accompanying the Sn-S bond signal, a shoulder signal also appeared on the downfield side and disappeared at high NH$_3$/TGA ratios. Finally, broadened and upfield-shifted Sn-S signals dominated the NMR spectra, demonstrating that the Sn-TGA had a stable coordination structure with a high density of covalent electrons in the Sn-S bond and fast molecule exchange with the free TGA in the solution. This fast exchange behaviour indicates that the metal-TGA coordination...
system was adequately assimilated into the water molecule surroundings, which should be helpful for solution stability. Overall, we have realized the dissolution of the Cu-Zn-Sn-TGA system into an aqueous solution through thiol deprotonation, and the coordination structure can be adjusted by the NH$_3$/TGA ratio.

### 3.3. Thin film deposition and solar cell performance

These fully soluble solutions with an NH$_3$/TGA ratio of $\geq 1.0$ were used as precursors for thin film deposition (spin coating), selenization and final fabrication of CZTSSe solar cells. XRD patterns in Fig. S10 (online) confirmed that all selenized films had the kesterite structure and no obvious difference was found. However, the NH$_3$/TGA ratio (i.e., Cu-Zn-Sn-TGA coordination structure) significantly affected the morphology of the CZTSSe film after selenization at 520 °C for 15 min. As in the top-view SEM images of Fig. 4a, large voids were observed for the samples derived from the precursors with NH$_3$/TGA molar ratios of 1.0:1 and 1.3:1. A dense and void-free film surface was realized only when the NH$_3$/TGA molar ratio exceeded 1.7. These differences are further reflected by the cross-sectional SEM images. For the 1.0-ratio sample, an interlayer boundary due to the multiple spin coating and severe interlayer separation were clearly seen in the fine grain layer in Fig. 4b. This means that mass transport and exchange during the selenization process were not sufficient for this sample. Comparatively, the 2.0-ratio sample exhibited a dense-packed fine grain layer as well as a relatively smooth and large top grain layer. As shown in Fig. 4c, these morphological differences arise from the distinct nucleation properties between these two samples. The 2.0-ratio sample possessed a much higher nucleation velocity and density than the other samples, serving as an important foundation for subsequent crystallization and ripening processes.

Essentially, these nucleation and mass transport properties are closely correlated with the activity of the metal elements within the CZTSSe precursor film. For the sample with a low NH$_3$/TGA ratio, carboxylate groups occupied a significant proportion of coordination sites around the metal atoms. The strong binding between the bidentate oxygen and the metal atoms that remained in the precursor limited the interdiffusion ability of the metal atoms and thus suppressed the nucleation and mass transport processes [25]. Comparatively, metal sulfides exhibited much higher reactivity within the selenization process, thus affording better crystallization morphology.

CZTSSe solar cells were fabricated with a device configuration of glass/Mo/CZTSSe/CdS/ZnO/ITO/Ni/Al (Fig. S11 online), as previously reported [61,62]. The optimal cell exhibited a high efficiency of 12.3% in our laboratory measurement (Fig. 5a), which is the highest among the aqueous precursor systems studied to date and is comparable to that of the DMSO system [33]. Certification of a CZTSSe cell yielded high efficiency of 12.0% (Fig. S12 online) with an effective area of 0.1633 cm$^2$. Integration of the EQE of the cell resulted in a short-circuit current density ($J_{SC}$) of ~37 mA cm$^{-2}$ (Fig. 5b), agreeing well with the current–voltage curve. The EQE spectrum indicates that the CZTSSe film possessed a bandgap of ~1.1 eV (Fig. S13 online). Compared with the record cell [19], our champion device exhibited a smaller open-circuit voltage deficit of ~0.613 V and a similar ideal factor (1.62) (Table S3 online). The correlation between the cell efficiency and the NH$_3$/TGA ratio is presented in Fig. 5c and other parameters are presented in Fig. S14 (online). High efficiency can be achieved only when metal-S bonds dominate the coordination (NH$_3$/TGA ratio $\geq 1.7$). This on the one hand arises from a better CZTSSe film morphology and, on the other hand, benefits from a lower material defect density and slower charge recombination velocity (Fig. S15 online). Owing to the stable metal-TGA coordination structure and its adequate hydration through the exposed carboxyl groups, the aqueous precursor solution exhibited ultrahigh stability for several months without the appearance of any solid precipitation or opaque suspensions. These stored precursors can still be used to fabricate efficient solar cells without any decline in efficiency, as presented in Fig. 5d. This result highlights another advantage of our system, that is, precursor stability, which should be considerably higher than those of previous systems based on nanocrystal or colloid dispersions. Such high precursor stability provides an
extremely wide time window for the industrial production of CZTSSe solar cells.

4. Conclusion

The coordination structure of the metal-TGA has been systematically engineered by promoting deprotonation of the thiol group. Through engineering, the metal-S bond dominates the coordination, and the terminal carboxyl group is adequately exposed to hydration by the surrounding water to form an ultrastable precursor at the molecular level. This coordination structure affords better CZTSSe nucleation and crystallization and contributes to reduced electronic defects. These advantages contribute to achieving a remarkable efficiency up to 12.3% and a certified efficiency of 12.0%. In addition, this ultrastable precursor provides an extremely wide time window for CZTSSe solar cell fabrication. These results represent significant progress in the non-toxic solution fabrication of CZTSSe solar cells and provide great promise for the future development of CZTSSe and other metal sulfide solar cells.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (51961165108, 51421002, 51972332 and 51627803).

Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/10.1016/j.scib.2020.01.005.

Author contributions

Linbao Guo, Jiangjian Shi, Yanhong Luo and Qingbo Meng conceived the idea, designed the experiments and did the data analysis. Linbao Guo and Yanhong Luo did the experiments and the data acquisition. Qing Yu, Xiao Xu and Jiazheng Zhou contributed to CZTSSe solar cell fabrications. Biwen Duan, Jionghua Wu and Yusheng Li performed SEM, CV and TPV measurements. Dongmei Li and Huijue Wu supported the CZTSSe fabricating, characterizations and discussions. Linbao Guo, Jiangjian Shi, Yanhong Luo and Qingbo Meng participated in writing the manuscript. All authors were involved in the discussions and approved the manuscript.

References

[1] Mitzi DB, Gunawan O, Todorov TK, et al. The path towards a high-performance solution-processed kesterite solar cell. Solar Energy Mater Solar Cells 2011;95:1421–36.
[2] Wadia C, Alivisatos AP, Kammen DM. Materials availability expands the opportunity for large-scale photovoltaics deployment. Environ Sci Technol 2009;43:2072–7.
[3] Zhang X, Han Y, Chai SZ, et al. Advances in Cu2ZnSn(S, Se)4 thin film solar cells. Acta Phys Chim Sin 2016;32:1330–46.
[4] Seol JS, Lee SY, Lee JC, et al. Electrical and optical properties of Cu2ZnSnS4 thin films prepared by rf magnetron sputtering process. Solar Energy Mater Solar Cells 2003;75:155–62.
A non-toxic, solution-processed, earth abundant semiconductor approach to deposit earth abundant Cu(In, Zn)Se2 thin film solar cells. RSC Adv 2015;5:20178–85.

Guo Q, Ford GM, Yang WC, et al. Fabrication of 7.2% efficient CZTSSe solar cells using CuInSe2 precursor solution. Inorg Chem 2012;51:20023–4.

Lee YS, Gershon T, Gunawan O, et al. Cu2ZnSnSe4 thin-film solar cells by thermal co-evaporation with 11.6% efficiency and improved minority carrier diffusion length. Adv Energy Mater 2015;5:1400137.

Guo Q, Ford GM, Yang WC, et al. Fabrication of 7.2% efficient CZTSe thin solar cells using CTZS nanocrystals. J Am Chem Soc 2010;132:17384–6.

Yang WB, Duans HS, Cha KC, et al. Molecular solution approach to synthesize electronic quality Cu2ZnSnS4 thin films. J Am Chem Soc 2013;135:6915–20.

Habibi Y, Platt HJ, Hetz HMAT, et al. Softest inorganic: solar cells from ink to printed device. Chem Rev 2010;110:6571–94.

Uhl AR, Katahara JK, Hillhouse HW. Molecular-ink-process to 13.0% efficient broadband-gap CuInS2 (S0.37Se0.63) and 14.7% efficient CuIn(Ga, S)0.37Se0.63 solar cells. Energy Environ Sci 2012;5:8564–71.

Mitzi DB. Solution processing of chalcogenide semiconductors via dimensional advection. Adv Mater 2009;21:3141–58.

Hsu WC, Bob B, Yang WC, et al. Reaction pathways for the formation of Cu2ZnSnSe3, Cu2ZnSnS3, and Cu2SnS3 in liquid-phase hydrazine-based precursor inks. Energy Environ Sci 2012;5:8564–71.

Wang G, Winkler MT, Gunawan O, et al. Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency. Adv Energy Mater 2014;4:1301465.

Luo G, Wu H. Going green. Nat Energy 2016;1:16001.

Lesnyak V, Gaponik N, Eychmueller A. Colloidal semiconductor nanocrystals: the aqueous approach. Chem Soc Rev 2013;42:2905–29.

Xiao Y, Katahara JK, Braly IL, et al. Efficient Cu2ZnSn(S, Se)4 thin-film solar cells from redox equilibrium driven simple precursors in DMSO. Adv Energy Mater 2014;4:1301823.

Qi YF, Kou DX, Zhou WH, et al. Engineering of interface band bending and material composition in Cu2ZnSn(S, Se)4 thin-film solar cells. Energy Environ Sci 2012;5:8564–71.

Suryawanshi MP, Ghorade VP, Suryawanshi UP, et al. Aqueous-solution-processed Cu2ZnSn(S, Se)4 thin-film solar cells via an improved successive ion-layer-adsorption-reaction sequence. ACS Omega 2017;2:9211–20.

Toura H, Khattak YH, Baig F, et al. Effect of complexing agent on the morphology and annealing temperature of CZTS kesterite thin films by electrochemical deposition. Curr Appl Phys 2019;19:606–13.

Xiao ZY, Lu YF, Yao B, et al. Significantly enhancing the stability of a Cu2ZnSnS4/aqueous-ethanol-based precursor solution and its application in Cu2ZnSnS4 solar cells. RSC Adv 2015;5:103341–7.

Jiang ML, Lan F, Yan XZ, et al. Cu2ZnSn(S, Se)4 thin film solar cells prepared by water-based solution process. Phys Status Solidi B 2014;8:223–7.

Wei SY, Liao YC, Hsu CH, et al. Achieving high efficiency Cu2ZnSnS4, Se4 solar cells by non-aqueous toxic ink: defect analysis and electrical modeling. Nanoscale 2013;5:1624–7.

Larsson MG, Levenko S, Bourdais S, et al. Fine-tuning the Sn content in CZTSSe thin films to achieve 10.8% solar cell efficiency from spray-deposited water-ethanol-based colloidal inks. Adv Energy Mater 2015;5:1501404.

Cabras-Vidani A, Haass SG, Andres C, et al. High-efficiency [Li,Cu2]2ZnSnS4, Se4 kesterite solar cells with lithium alloying. Adv Energy Mater 2018;8:1801191.

Williams BA, Smeaton MA, Trejo ND, et al. Effect of nanocrystal size and carbon on grain growth during annealing of copper zinc tin sulﬁde nanocrystalline thin ﬁlms. Chem Mater 2017;29:86–98.
Linbao Guo got his B.S. degree from School of Science, Hebei University of Technology in 2015. Now he is a Ph.D. candidate at Institute of Physics, Chinese Academy of Sciences (CAS) under the supervision of Prof. Qingbo Meng and Prof. Yanhong Luo. His research work focuses on kesterite solar cells.

Jiangjian Shi obtained his Ph.D. degree from Institute of Physics, CAS in 2017. Now, he is an associate professor at Institute of Physics, CAS. His research interest includes investigation on charge carrier dynamics, interfacial charge transfer and surface modification in new generation solar cells.

Yanhong Luo is now a professor at Institute of Physics, CAS. She obtained her Ph.D. degree from Institute of Chemistry, CAS in 2003 followed by working as a post-doctoral fellow at National Institute for Materials Science. Her research interest includes kesterite solar cells and perovskite solar cells.

Qingbo Meng is now a professor at Institute of Physics, CAS. He received his Ph.D. degree from Changchun Institute of Applied Chemistry, CAS (1997). His current research interest focuses on solar energy materials and technologies as well as research of the dynamics of electron injection, diffusion, recombination in solar cells.