A thiol-amine mixture for metal oxide towards device quality metal chalcogenides

Tong Zhang, Lijian Zhang, Yiwei Yin, Chenhui Jiang, Shi'ang Li, Changfei Zhu* and Tao Chen*

Metal chalcogenides (MCs) are significant semiconducting materials possessing a variety of applications in catalysts [1,2], thermoelectrics [3,4], rewritable memory [5,6], thin film transistors (TFTs) [7,8], and solar cells [9–16], usually presenting as solid films. Until now, one can deposit the bulk materials on a substrate by either top-down method such as thermal evaporation or bottom-up deposition from molecular precursors. The latter approach, usually described as solution processing, allows low-energy, low-cost, high-speed and high-throughput manufacturing, and is compatible with a variety of substrates [17–19]. A key step for the transformation towards final product is to find suitable solvent for dissolving the precursors and the consequent chemical conversion. A successful approach demonstrated by Mitzi and co-workers [12,20–25] utilized hydrazine-based solution with strong coordination and reduction capability to dissolve bulk MCs, forming molecular inks to generate MC films. However, hydrazine is highly toxic, explosive and hazardous, posing potential challenge regarding the scalable application. To find “greener” approaches, Brutchey's group [26] developed an alkane-thiol-alkylamine solvent mixture to dissolve V_2VI_3 chalcogenides (where $V=As, Sb, Bi$ and $VI=S, Se, Te$). Further studies found that elemental metals [27] and metal oxides [28] with selenium and tellurium could also be dissolved by similar method.

On the other hand, metal oxide/hydroxide precursors are highly desirable because they are the most accessible materials from nature. To dissolve metal oxide for sulfide synthesis, Pan's group [29,30] developed a binary thiol-amine mixed solvent. In this reaction system, metal-organic complex containing thiol is formed, which serves as sulfur source. This method has made great success in the synthesis of metal sulfides, but the dissolution selenium and direct synthesis of selenide or selenosulfide

are rarely observed. For instance, metal selenide (such as $Cu_2ZnSnSe_4$) has to be synthesized by post-selenization [31]. Actually, the direct deposition of selenide is a challenge since selenium is nearly insoluble in common solvent. Therefore, establishing a well-controlled method for the direct deposition of metal selenides is urgent to explore new application with solution processed MCs.

Herein, a new solvent system composed of 2-mercaptoethanol (2-ME) and monoethanolamine (MEA) is used to dissolve ten kinds of metal oxide or hydroxide powders and recover a large number of metal chalcogenides. It can also dissolve thiourea and selenium concurrently or separately. This characteristic allows versatile preparation of metal sulfide, selenide or selenosulfide. By varying thiourea and selenium ratio in precursor solutions, we are able to control S/Se atomic ratios in the final MC films. Importantly, the derived MC film can generate photovoltaic effect in a complete working device.

Specifically, the precursor inks were prepared by dissolving metal oxides and/or hydroxides, including Cu_2O , ZnO , SnO , $In(OH)_3$, GeO_2 , $Cd(OH)_2$, MnO , PbO , Bi_2O_3 , Sb_2O_3 , in a mixture of 2-ME and MEA with a volume ratio of 1:3. For the synthesis of sulfide, selenide or selenosulfide, corresponding thiourea, selenium or thiourea/selenium mixture with stoichiometry are introduced. ZnO , MnO , PbO , Bi_2O_3 , Sb_2O_3 are quickly dissolved in the mixture solvent at room temperature. Nonetheless, a mild heating at 60°C is required for fast dissolution of Cu_2O , SnO , $In(OH)_3$, GeO_2 and $Cd(OH)_2$. The resulting compound inks are all homogenous without visible light scattering (Fig. 1) and remain stable for periods ranging from days to months under ambient conditions, promising in scalable and practical applications.

The formation of MCs was conducted by thermal

CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China

* Corresponding authors (emails: cfzhu@ustc.edu.cn (Zhu C); tchenmse@ustc.edu.cn (Chen T))

Figure 1 Photographs of metal oxides (hydroxides) dissolving in 2-ME and MEA. (a) Photographs of Cu₂O, ZnO, SnO, In(OH)₃, GeO₂, Cd(OH)₂, MnO, PbO, Bi₂O₃, Sb₂O₃, binary Cu₂O and Sb₂O₃, ternary Cu₂O, ZnO and SnO in the mixed solution with thiourea (a) and Se (b), respectively.

decomposition of the precursor inks under N₂ atmosphere. Upon annealing at 280–400°C, binary metal sulfides ZnS, SnS, CdS, MnS, PbS, Bi₂S₃, Sb₂S₃ are obtained from the corresponding metal oxide precursor inks. X-ray diffraction (XRD) patterns indicate phase pure metal sulfides (Fig. 2a, Fig. S1), and the detailed peak

assignment for each of the compounds is in Supplementary information. It is worth noting that the synthesis in absence of thiourea would not produce sulfide, indicating that the thiourea provides sulfur source [32]. The synthesis of metal selenide was conducted in a similar way to sulfide by substituting thiourea with selenium

Figure 2 XRD characterizations of the as-generated metal chalcogenides films from the solution. (a) XRD patterns of Sb₂S₃, Sb₂Se₃, MnS, MnSe, PbS, PbSe, Cu₂ZnSnS₄, Cu₂ZnSnSe₄. (b) XRD patterns of CuSbSe_{2-x}S_x alloys, where $x=2.0, 1.5, 1.0, 0.5$ and 0 .

power. Phase-pure crystalline selenides including Cu_2Se , ZnSe , In_2Se_3 , CdSe , MnSe , PbSe , Sb_2Se_3 are generated from the corresponding precursor inks after thermal decomposition at 300–400°C (Fig. 2a, Fig. S2).

This method is capable to synthesize ternary CuSbSe_2 , $\text{CuSbSe}_{0.4}\text{S}_{1.6}$, Cu_2SnS_3 and quaternary $\text{Cu}_2\text{ZnSnS}_4$, $\text{Cu}_2\text{ZnSnSe}_4$ (Fig. S3). Moreover, by tuning selenium ratio in the reaction precursors, the band gap of the metal chalcogenide can be conveniently tuned. Recently, it has been discovered that $\text{CuSbSe}_{2-x}\text{S}_x$ is a promising light absorbing material with direct band gap energy $E_g = 0.91\text{--}1.89\text{ eV}$ and high absorption coefficient [33–35], while there has been no report on the solution processed $\text{CuSbSe}_{2-x}\text{S}_x$ with tunable band gap. Herein, we synthesize the composition/band gap tunable $\text{CuSbSe}_{2-x}\text{S}_x$ with the aforementioned method. Cu_2O and Sb_2O_3 were applied as copper and antimony sources which were dissolved in the mixed solvent. The composition was tuned by varying metal/Se stoichiometric ratios (EXPERIMENTAL SECTION in SI). The spin coated precursor solution was then annealed at 390°C for 3 min. Fig. 2b shows the XRD patterns of the as-generated $\text{CuSbSe}_{2-x}\text{S}_x$ alloys (nominal $x=2, 1.5, 1, 0.5, 0$) are crystalline. With the increase of Se content in $\text{CuSbSe}_{2-x}\text{S}_x$, the XRD patterns display gradual shift to lower diffraction angle, which is attributed to the larger anionic radius of Se^{2-} than S^{2-} (Shannon–Prewitt anionic radii of S^{2-} and Se^{2-} are 1.84 and 1.98 Å, [36] respectively). Raman spectroscopy (Fig. S4) of CuSbSe_2 and CuSbSe_2 show distinctive peaks located at 333 cm^{-1} for CuSbSe_2 and at 114, 152, 197, 226 cm^{-1} for CuSbSe_2 , exhibiting phase pure $\text{CuSb}(\text{S,Se})_2$ [34,37]. The final composition of $\text{CuSbSe}_{2-x}\text{S}_x$ is determined by energy-dispersive X-ray spectroscopy (EDS) analysis (Table S1), and they are thus described as CuSbSe_2 , $\text{CuSbSe}_{0.4}\text{S}_{1.6}$, $\text{CuSbSe}_{0.88}\text{S}_{1.12}$, $\text{CuSbSe}_{1.32}\text{S}_{0.68}$ and $\text{CuSbSe}_{1.92}\text{S}_{0.08}$ with nominal $x=2, 1.5, 1, 0.5, 0$. The actual elemental composition of each compound generally matches the nominal element ratio in the precursors. According to the UV-vis spectra and Tauc plots, the corresponding band gap energies of them are determined to be 1.31, 1.29, 1.24, 1.17, 1.08 eV (Fig. 3a). The dependence of E_g on composition (Fig. 3b) was found to slightly deviate from Vegard's law. This result indicates that it is convenient to manipulate the composition and then the band gap of MCs by the current method.

Synthesis of quaternary metal chalcogenide with controllable phase and stoichiometry remains a challenge. Our method is also applicable for the direct synthesis of phase pure $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ (CZTSSe). CZTSSe has emerged as an ideal light-absorbing material for new

Figure 3 (a) Tauc plots showing band gap tunability of CuSbSe_2 (I), $\text{CuSbSe}_{0.4}\text{S}_{1.6}$ (II), $\text{CuSbSe}_{0.88}\text{S}_{1.12}$ (III), $\text{CuSbSe}_{1.32}\text{S}_{0.68}$ (IV) and $\text{CuSbSe}_{1.92}\text{S}_{0.08}$ (V) measured by UV-vis spectroscopy, exhibiting direct band gaps of 1.31, 1.29, 1.24, 1.17, 1.08 eV for CuSbSe_2 , $\text{CuSbSe}_{0.4}\text{S}_{1.6}$, $\text{CuSbSe}_{0.88}\text{S}_{1.12}$, $\text{CuSbSe}_{1.32}\text{S}_{0.68}$ and $\text{CuSbSe}_{1.92}\text{S}_{0.08}$, respectively. (b) The relationship between x and band gap (E_g) of $\text{CuSbSe}_{2-x}\text{S}_x$ alloys.

generation thin film solar cells due to its suitable band gap and high absorption coefficient [38–40]. Here we fabricated high quality pure selenide CZTSe thin film by dissolving stoichiometric amounts of Cu_2O , ZnO , SnO and Se (EXPERIMENTAL SECTION in SI). In Fig. 2a, the XRD pattern of the as-realized CZTSe thin film shows the strong diffraction at 27.16°, 45.12° and 53.39° assigned to (112), (220) and (312) crystal planes of kesterite structure (JCPDS No. 52-0868). Raman spectroscopy identifies whether there is potential binary and ternary secondary phases, such as Cu_xSe , ZnSe and Cu_2SnSe_3 , since they exhibit indistinguishable XRD patterns compared with CZTSe. Three peaks located at 174, 196, and 234 cm^{-1} (Fig. S5) are typical Raman scattering of CZTSe kesterite phase [41]. There are no peaks at 260, 253 and 180 cm^{-1} for Cu_xSe , ZnSe and Cu_2SnSe_3 [42], indicating that our method is able to directly synthesize phase purity CZTSe film. Furthermore, X-ray photoelectron spectroscopy (Fig. S6) indicates that Cu 2p peaks located at 932.1 and 951.9 eV with a splitting value of 19.8 eV (Fig. S7a), corresponding to Cu^+ rather than Cu^{2+} [43]. EDS was employed to determine the chemical composition (Table S2). The ratio of $\text{Cu}/(\text{Zn}+\text{Sn})$ is 0.83 and Zn/Sn is 1.10, which falls into the optimum compositional ratio region (i.e., $\text{Cu}/(\text{Zn}+\text{Sn})$ and Zn/Sn are 0.75–0.95 and 1.1–1.4) [44], conforming to the criteria of Cu-poor and Zn-rich for high performance kesterite solar cell. The morphological characterizations of the as-synthesized film are provided in Fig. S7.

Finally, we investigated the dissolution process and applied Sb_2S_3 in solar cell. 2-ME and MEA solvent mixture with volume ratio of 1:3.2 was applied to dissolve Sb_2O_3 (EXPERIMENTAL DETAILS in SI). The solution was stirred for 30 min at ambient condition to obtain a

homogenous solution. The dissolution reaction was firstly analyzed by Fourier transform infrared spectroscopy (FTIR) and the Raman spectroscopy (Fig. S8). After Sb_2O_3 was introduced into the solvent mixture of 2-ME ($\text{C}_2\text{H}_6\text{OS}$) and MEA ($\text{C}_2\text{H}_7\text{NO}$), $\nu_{\text{S-H}}$ stretch at $2,550\text{ cm}^{-1}$ disappeared (Fig. S8a), indicating the deprotonation of S-H, which is evidenced by Raman spectra (Fig. S8b). The peak located at 284 cm^{-1} is typical Raman scattering of Sb-S bonding. Moreover, the peak at 332 cm^{-1} can be ascribed to C_{3v} symmetric modes of SbS_3 pyramid structure [45,46], with no peaks at $360\text{--}390\text{ cm}^{-1}$ for Sb-N stretching vibration [47]. Therefore, the total dissolution reaction can be described as follow:

Different from many reports in literature [48,49], we need introduce another sulfur source to fabricate metal sulfides in this particular solvent mixture, herein, the thiourea. Ultimately, the reaction between this Sb-complex and thiourea can lead to Sb_2S_3 . In addition, the dissolution of selenium was studied by Raman spectroscopy. After selenium dissolved in 2-ME and MEA, two bands at 272 and 394 cm^{-1} are ascribed to selenium rings and S-Se stretching vibration (Fig. S9) [50,51]. Regardless

the formation of molecular selenium or S-Se in the solution, the final transformation towards metal selenide or selenosulfide becomes feasible.

Thermogravimetric analysis (TGA) was used to guide the preparation of Sb_2S_3 light absorbing film. The precursor solution displays a weight loss of 89 wt.% with an ending temperature at 280°C (Fig. S10), indicating the formation of Sb_2S_3 when temperature is raised to 280°C . For device fabrication, the precursor solution was spin-coated on the TiO_2 compact layer (abbreviated as c- TiO_2) at 3,000 rpm for 30 s. SEM images show that the as-prepared Sb_2S_3 thin film displays compact surface morphology (Fig. 4a). The solar cell was completed by coating a layer of 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) as hole transporting material, followed by thermal deposition of Au metal film as back contact according to the reported method [52,53]. The device configuration is thus described as FTO/c- TiO_2 / Sb_2S_3 /Spiro-OMeTAD/Au (Fig. 4b). A cross sectional SEM image shows that the thicknesses of Sb_2S_3 , Spiro-OMeTAD, Au are 134, 150 and 80 nm, respectively. The photocurrent density-voltage (*J*-*V*) spectra were measured under one Sun AM 1.5G irradiation (Fig. 4c). The solar cell delivers a power conversion efficiency (PCE) of 4.39% with a short-circuit

Figure 4 (a) SEM image of as-prepared Sb_2S_3 thin film deposited on FTO/c- TiO_2 and (b) cross-sectional SEM image of the solar cell device. (c) *J*-*V* curve of Sb_2S_3 planar heterojunction solar cell measured under one Sun AM 1.5G illumination. (d) EQE spectrum of the Sb_2S_3 planar heterojunction solar cell.

Figure 5 Ultraviolet photoelectron spectroscopy of VBM (a) and secondary electron cut-off (b) of Sb_2S_3 . (c) Band gap determined by the $[h\nu \times \ln(1 - \text{EQE})]^2$ versus $h\nu$ curve. (d) Energy level diagram of FTO/ TiO_2 / Sb_2S_3 /spiro-OMeTAD/Au.

current density (J_{sc}) of 15.39 mA cm^{-2} , open-circuit voltage (V_{oc}) of 0.599 V , and fill factor (FF) of 47.62% , respectively. In fact, during our investigations we tried other amine such as *n*-butylamine, *n*-propylamine, and 1, 2-ethylenediamine to substitute for monoethanolamine. However, the device efficiency becomes quite poor. The relatively high and similar boiling point of monoethanolamine with 2-ME enables the solvent dissociation at a temperature close to their boiling points. In this manner, the electric property of the film could be improved and thus the device efficiency is enhanced. Fig. 4d presents the external quantum efficiency (EQE) spectrum of the corresponding solar cell, which shows a strong response of above 80% in the wavelength range from 360 to 500 nm , indicating a high photocurrent conversion collection efficiency. The integrated current density of device is 13.68 mA cm^{-2} , which is quite close to the value obtained from J - V measurement (15.39 mA cm^{-2}). The energy level of as-synthesized Sb_2S_3 film is characterized by synchrotron-based high resolution ultraviolet photoelectron spectroscopy (Fig. 5), which shows both valence band maximum (VBM, Fig. 5a) and secondary electron cut-off (Fig. 5b) of Sb_2S_3 . The VBM is 1.42 eV below the

Fermi level, and the work function (ϕ), defined as the difference between vacuum level and Fermi level, is 4.09 eV for Sb_2S_3 . We can calculate the conduction band minimum by considering the band gap of as-fabricated Sb_2S_3 of 1.79 eV determined by plotting $[h\nu \times \ln(1 - \text{EQE})]^2$ versus $h\nu$ (Fig. 5c), which is consistent with the value acquired from UV-vis absorption (Fig. S13) and the reported E_{g} value in literature [54–56]. Finally, the band alignment of the solar cell in Fig. 5d shows that the electron can transfer from the conduction band of Sb_2S_3 to c- TiO_2 and hole is able to transfer from the valence band of Sb_2S_3 to spiro-OMeTAD. In addition, the device based on as-obtained Sb_2S_3 film was also prepared. With a rough optimization, it generates a PCE of 1.77% , with J_{sc} of 11.37 mA cm^{-2} , V_{oc} of 0.364 V and FF of 42.97% (Fig. S14). The active area of the device was defined at 0.12 cm^2 . This performance is slightly lower than the hydrazine derived Sb_2S_3 film for planar heterojunction solar cells [57].

In summary, a low-toxic, versatile binary solution of 2-ME and MEA was used to fabricate metal chalcogenides. Mechanistic investigations shows that the deprotonation of $-\text{SH}$ is responsible for the dissolution of metal

oxide or hydroxide. The successful dissolution of thiourea and selenium allows convenient tuning of the S/Se ratio in the final products. With that, binary crystalline metal chalcogenides including ZnS, SnS, CdS, MnS, PbS, Bi₂S₃, Sb₂S₃, Cu₂Se, ZnSe, In₂Se₃, CdSe, MnSe, PbSe, Sb₂Se₃, ternary CuSbS₂, CuSbSe₂, Cu₂SnS₃ and quaternary Cu₂ZnSnS₄, Cu₂ZnSnSe₄ have been successfully prepared. Band gap tunable CuSbSe_{2-x}S_x was illustrated by varying precursor ratios. The implement in solar cell application is also demonstrated by using the as-prepared Sb₂S₃ film, indicating this approach is able to generate device grade films.

Received 12 October 2018; accepted 20 November 2018;
published online 30 November 2018

- Wang H, Liang Y, Li Y, *et al.* Co_{1-x}S-graphene hybrid: a high-performance metal chalcogenide electrocatalyst for oxygen reduction. *Angew Chem Int Ed*, 2011, 50: 10969–10972
- Zhang R, Cho S, Lim DG, *et al.* Metal-metal chalcogenide molecular precursors to binary, ternary, and quaternary metal chalcogenide thin films for electronic devices. *Chem Commun*, 2016, 52: 5007–5010
- Wang RY, Feser JP, Gu X, *et al.* Universal and solution-processable precursor to bismuth chalcogenide thermoelectrics. *Chem Mater*, 2010, 22: 1943–1945
- Bottner H, Nurnus J, Gavrikov A, *et al.* New thermoelectric components using microsystem technologies. *J Microelectromech Syst*, 2004, 13: 414–420
- Milliron DJ, Raoux S, Shelby RM, *et al.* Solution-phase deposition and nanopatterning of GeSbSe phase-change materials. *Nat Mater*, 2007, 6: 352–356
- Ohta T. Phase-change optical memory promotes the dvd optical disk. *J Optoelectron Adv Mater*, 2001, 3: 609–626
- Ohta T. Quick-set thin films. *Nature*, 2004, 428: 269–271
- Milliron DJ, Mitzi DB, Copel M, *et al.* Solution-processed metal chalcogenide films for p-type transistors. *Chem Mater*, 2006, 18: 587–590
- Choi YC, Lee YH, Im SH, *et al.* Efficient inorganic-organic heterojunction solar cells employing Sb₂(S_x/Se_{1-x})₃ graded-composition sensitizers. *Adv Energy Mater*, 2014, 4: 1301680
- Bag S, Gunawan O, Gokmen T, *et al.* Low band gap liquid-processed CZTSe solar cell with 10.1% efficiency. *Energy Environ Sci*, 2012, 5: 7060–7065
- Mitzi DB, Gunawan O, Todorov TK, *et al.* The path towards a high-performance solution-processed kesterite solar cell. *Sol Energy Mater Sol Cells*, 2011, 95: 1421–1436
- Todorov TK, Reuter KB, Mitzi DB. high-efficiency solar cell with earth-abundant liquid-processed absorber. *Adv Mater*, 2010, 22: E156–E159
- Kronik L, Cahen D, Schock HW. Effects of sodium on polycrystalline Cu(In,Ga)Se₂ and its solar cell performance. *Adv Mater*, 1998, 10: 31–36
- Zhang R, Szczepaniak SM, Carter NJ, *et al.* A versatile solution route to efficient Cu₂ZnSn(S,Se)₄ thin-film solar cells. *Chem Mater*, 2015, 27: 2114–2120
- Zhao D, Tian Q, Zhou Z, *et al.* Solution-deposited pure selenide CIGSe solar cells from elemental Cu, In, Ga, and Se. *J Mater Chem A*, 2015, 3: 19263–19267
- Zhao X, Lu M, Koeper MJ, *et al.* Solution-processed sulfur depleted Cu(In, Ga)Se₂ solar cells synthesized from a monoamine-dithiol solvent mixture. *J Mater Chem A*, 2016, 4: 7390–7397
- Graetzel M, Janssen RAJ, Mitzi DB, *et al.* Materials interface engineering for solution-processed photovoltaics. *Nature*, 2012, 488: 304–312
- Sun Y, Welch GC, Leong WL, *et al.* Solution-processed small-molecule solar cells with 6.7% efficiency. *Nat Mater*, 2012, 11: 44–48
- Xiao Z, Bi C, Shao Y, *et al.* Efficient, high yield perovskite photovoltaic devices grown by interdiffusion of solution-processed precursor stacking layers. *Energy Environ Sci*, 2014, 7: 2619–2623
- Mitzi DB, Kosbar LL, Murray CE, *et al.* High-mobility ultrathin semiconducting films prepared by spin coating. *Nature*, 2004, 428: 299–303
- Mitzi DB. Solution processing of chalcogenide semiconductors via dimensional reduction. *Adv Mater*, 2009, 21: 3141–3158
- Yuan M, Mitzi DB. Solvent properties of hydrazine in the preparation of metal chalcogenide bulk materials and films. *Dalton Trans*, 2009, 13: 6078
- Mitzi DB. Solution-processed inorganic semiconductors. *J Mater Chem*, 2004, 14: 2355–2365
- Mitzi DB, Yuan M, Liu W, *et al.* A high-efficiency solution-deposited thin-film photovoltaic device. *Adv Mater*, 2008, 20: 3657–3662
- Todorov TK, Gunawan O, Gokmen T, *et al.* Solution-processed Cu(In,Ga)(S,Se)₂ absorber yielding a 15.2% efficient solar cell. *Prog Photovolt-Res Appl*, 2013, 21: 82–87
- Webber DH, Brutchey RL. Alkahest for V₂VI₃ chalcogenides: dissolution of nine bulk semiconductors in a diamine-dithiol solvent mixture. *J Am Chem Soc*, 2013, 135: 15722–15725
- Webber DH, Buckley JJ, Antunez PD, *et al.* Facile dissolution of selenium and tellurium in a thiol-amine solvent mixture under ambient conditions. *Chem Sci*, 2014, 5: 2498–2502
- McCarthy CL, Webber DH, Schueller EC, *et al.* Solution-phase conversion of bulk metal oxides to metal chalcogenides using a simple thiol-amine solvent mixture. *Angew Chem Int Ed*, 2015, 54: 8378–8381
- Tian Q, Wang G, Zhao W, *et al.* Versatile and low-toxic solution approach to binary, ternary, and quaternary metal sulfide thin films and its application in Cu₂ZnSn(S,Se)₄ solar cells. *Chem Mater*, 2014, 26: 3098–3103
- Wang G, Wang S, Cui Y, *et al.* A novel and versatile strategy to prepare metal-organic molecular precursor solutions and its application in Cu(In,Ga)(S,Se)₂ solar cells. *Chem Mater*, 2012, 24: 3993–3997
- Yang Y, Wang G, Zhao W, *et al.* Solution-processed highly efficient Cu₂ZnSnSe₄ thin film solar cells by dissolution of elemental Cu, Zn, Sn, and Se powders. *ACS Appl Mater Interfaces*, 2015, 7: 460–464
- Choi YC, Seok SI. Efficient Sb₂S₃-sensitized solar cells via single-step deposition of Sb₂S₃ using S/Sb-ratio-controlled SbCl₃-thiourea complex solution. *Adv Funct Mater*, 2015, 25: 2892–2898
- Kumar M, Persson C. CuSbS₂ and CuBiS₂ as potential absorber materials for thin-film solar cells. *J Renew Sustain Energy*, 2013, 5: 031616
- Xue DJ, Yang B, Yuan ZK, *et al.* CuSbSe₂ as a potential photovoltaic absorber material: studies from theory to experiment.

- Adv Energy Mater*, 2015, 5: 1501203
- 35 Choi YC, Yeom EJ, Ahn TK, *et al.* CuSbS₂-sensitized inorganic-organic heterojunction solar cells fabricated using a metal-thiourea complex solution. *Angew Chem Int Ed*, 2015, 54: 4005–4009
 - 36 Ladd MFC. Symmetry of crystals and molecules. Oxford: Oxford University Press, 2014
 - 37 McCarthy CL, Cottingham P, Abuyen K, *et al.* Earth abundant CuSbS₂ thin films solution processed from thiol-amine mixtures. *J Mater Chem C*, 2016, 4: 6230–6233
 - 38 Azimi H, Hou Y, Brabec CJ. Towards low-cost, environmentally friendly printed chalcopyrite and kesterite solar cells. *Energy Environ Sci*, 2014, 7: 1829–1849
 - 39 Polizzotti A, Repins IL, Noufi R, *et al.* The state and future prospects of kesterite photovoltaics. *Energy Environ Sci*, 2013, 6: 3171–3182
 - 40 Zhou H, Hsu WC, Duan HS, *et al.* CZTS nanocrystals: A promising approach for next generation thin film photovoltaics. *Energy Environ Sci*, 2013, 6: 2822–2838
 - 41 Redinger A, Hönes K, Fontané X, *et al.* Detection of a ZnSe secondary phase in coevaporated Cu₂ZnSnSe₄ thin films. *Appl Phys Lett*, 2011, 98: 101907
 - 42 Altosaar M, Raudoja J, Timmo K, *et al.* Cu₂Zn_{1-x}Cd_xSn(Se_{1-y}S_y)₄ solid solutions as absorber materials for solar cells. *Phys Stat Sol (a)*, 2008, 205: 167–170
 - 43 Shavel A, Arbiol J, Cabot A. Synthesis of quaternary chalcogenide nanocrystals: stannite Cu₂Zn_xSn_ySe_{1+x+2y}. *J Am Chem Soc*, 2010, 132: 4514–4515
 - 44 Wang G, Zhao W, Cui Y, *et al.* Fabrication of a Cu₂ZnSn(S,Se)₄ photovoltaic device by a low-toxicity ethanol solution process. *ACS Appl Mater Interfaces*, 2013, 5: 10042–10047
 - 45 Shaji S, Garcia LV, Loredó SL, *et al.* Antimony sulfide thin films prepared by laser assisted chemical bath deposition. *Appl Surf Sci*, 2017, 393: 369–376
 - 46 Medles M, Benramdane N, Bouzidi A, *et al.* Raman and optical studies of spray pyrolysed Sb₂S₃ thin films. *J Optoelectron Adv Mater*, 2014, 16: 726–731
 - 47 Haiges R, Vij A, Boatz JA, *et al.* First structural characterization of binary As(III) and Sb(III) azides. *Chem Eur J*, 2004, 10: 508–517
 - 48 Buckley JJ, McCarthy CL, Del Pilar-Albaladejo J, *et al.* Dissolution of Sn, SnO, and SnS in a thiol-amine solvent mixture: insights into the identity of the molecular solutes for solution-processed SnS. *Inorg Chem*, 2016, 55: 3175–3180
 - 49 Tian Q, Cui Y, Wang G, *et al.* A robust and low-cost strategy to prepare Cu₂ZnSnS₄ precursor solution and its application in Cu₂ZnSn(S,Se)₄ solar cells. *RSC Adv*, 2015, 5: 4184–4190
 - 50 Poborchii VV, Kolobov AV, Caro J, *et al.* Polarized Raman spectra of selenium species confined in nanochannels of AlPO₄ single crystals. *Chem Phys Lett*, 1997, 280: 17–23
 - 51 Eysel HH, Sunder S. Homonuclear bonds in sulfur-selenium mixed crystals: A Raman spectroscopic study. *Inorg Chem*, 1979, 18: 2626–2627
 - 52 Zhang Y, Li J, Jiang G, *et al.* Selenium-graded Sb₂(S_{1-x}Se_x)₃ for planar heterojunction solar cell delivering a certified power conversion efficiency of 5.71%. *Sol RRL*, 2017, 1: 1700017
 - 53 Wang X, Li J, Liu W, *et al.* A fast chemical approach towards Sb₂S₃ film with a large grain size for high-performance planar heterojunction solar cells. *Nanoscale*, 2017, 9: 3386–3390
 - 54 Kondrotas R, Chen C, Tang J. Sb₂S₃ solar cells. *Joule*, 2018, 2: 857–878
 - 55 Choi YC, Lee DU, Noh JH, *et al.* Highly improved Sb₂S₃ sensitized-inorganic-organic heterojunction solar cells and quantification of traps by deep-level transient spectroscopy. *Adv Funct Mater*, 2014, 24: 3587–3592
 - 56 Wang X, Tang R, Wu C, *et al.* Development of antimony sulfide-selenide Sb₂(S, Se)₃-based solar cells. *J Energy Chem*, 2018, 27: 713–721
 - 57 Zhou Y, Leng M, Xia Z, *et al.* Solution-processed antimony selenide heterojunction solar cells. *Adv Energy Mater*, 2014, 4: 1301846
- Acknowledgements** This work was supported by the Fundamental Research Funds for the Central Universities (WK2060140023, WK2060140022, CX3430000001 and WK2060140024), the Major/Innovative Program of Development Foundation of Hefei Center for Physical Science and Technology (2016FXZY003), and the National Natural Science Foundation of China (GG2060140085 and CX2310000097).
- Author contributions** Zhang T and Zhang L performed the experiments; Zhang T, Zhang L, Yin Y, Jiang C and Li S analyzed the data; Zhang T wrote the paper with support from Zhu C and Chen T; all authors contributed to the general discussion.
- Conflict of interest** The authors declare no conflict of interest.
- Supplementary information** Supporting data are available in the online version of the paper.

Zhang Tong was born in Hefei, Anhui province (China) in 1993. He received his Bachelor degree from Hefei University of Technology (HFUT) in new energy materials and devices (2015), and now he is pursuing his Master degree in the University of Science and Technology of China (USTC), working on new solar energy materials and solar cells.

Changfei Zhu received his BS and PhD degrees both from USTC in 1984 and 1990, respectively. He has been working in the Department of Materials Science and Engineering of USTC since 1990 and was promoted to full professor in 2000. His research interests include the fundamental study and application of transitional metal oxides, wide band gap semiconductors and thin film solar cells.

Tao Chen received his PhD degree in chemistry from Nanyang Technological University (Singapore) in 2010. From 2011 to 2015, he was working in the Chinese University of Hong Kong as a research assistant professor. He is now a professor at the Department of Materials Science and Engineering, USTC. His research interests include the fabrication and engineering of antimony sulfide-selenide ($\text{Sb}_2(\text{S,Se})_3$) solar cells.

一种硫醇/胺方法将金属氧化物转换为器件级金属硫属化物

张童, 张立建, 尹奕炜, 江晨辉, 李诗昂, 朱长飞*, 陈涛*

摘要 利用分子前驱体溶液制备金属硫属化物薄膜在器件领域具有广泛的应用前景. 本文利用巯基乙醇和乙醇胺这种新型硫醇/胺溶剂, 溶解很多价格便宜的金属氧化物和氢氧化物, 如 Cu_2O , ZnO , SnO , $\text{In}(\text{OH})_3$, GeO_2 , $\text{Cd}(\text{OH})_2$, MnO , PbO , Bi_2O_3 , Sb_2O_3 . 通过添加硫脲和硒粉作为硫源和硒源后可以制得相应的二元金属硫化物、硒化物. 此方法还可用来制备纯物相的带隙可调的三元 $\text{CuSbSe}_{2-x}\text{S}_x$ 和四元 $\text{Cu}_2\text{ZnSnSe}_4$. 我们用这种方法合成的 Sb_2S_3 平面异质结太阳能电池光电转化效率可高达4.39%. 这项研究提供了一种制备二元、三元、四元器件级金属硫属化物薄膜的普适性方法.