A straightforward chemical approach for excellent In$_2$S$_3$ electron transport layer for high-efficiency perovskite solar cells†

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Perovskite solar cells (PSCs) have attracted significant attention in recent years owing to some of their advantages: high-efficiency, low cost and ease of fabrication. In perovskite photovoltaic devices, charge transport layers play a vital role for selectively extracting and transporting photo-generated electrons and holes to opposite electrodes. Therefore, it is very important to prepare high-quality charge transport layers using simple processes at low cost. As reported, In$_2$S$_3$-based electron selective layers display excellent performance including high solar-cell efficiency and negligible hysteresis. In this study, a simple chemical method was developed to prepare In$_2$S$_3$ thin films as the electron selective layers in organic–inorganic hybrid perovskite photovoltaic devices to shorten the fabrication time and simplify the technology, which can provide a new avenue for a low-cost and solution-processed method. By optimizing the preparation conditions, it was demonstrated that In$_2$S$_3$ thin film prepared using our straightforward chemical approach have higher electron extraction efficiency and comparable efficiency compared with archetypical TiO$_2$ as the electron transport layer (ETL) in perovskite photovoltaic device.

Introduction

Halide perovskites undoubtedly represent one of the most prospective photovoltaic semiconductors for light-absorbing materials due to some of their appealing optoelectronic attributes; this has contributed to unbelievable achievements in power-conversion efficiency (PCE) beyond 20% just in a few years,1–7 matching with and even surpassing those of the state-of-the-art CdTe and monocrystalline silicon solar cells. Up to now, PCE of PSCs has been as high as about 23.3%,8 and the value keeps persistently improving. Generally, the classic PSC photovoltaic devices are designed using a “sandwich” architecture, in which the light-harvesting layer lies between electron transport layer (ETL) and the absorption layer, electron transport layer,9–11 hole transport layer,12–14 and the interfaces between the adjacent layers.15,16 Until now, compact TiO$_2$ layers are the most widely utilized inorganic ETLs. However, the application of TiO$_2$ ETL in PSCs is limited due to its high-temperature fabrication and intrinsic low carrier mobility.17–19 Hence, some research communities have been investigating alternative ETL materials, including some organics (PCBM (6,6)-phenyl-C$_6$$_1$-butyric acid methyl ester,20–22 C$_{60}$,23–26 and N,N'-bis[3-(dimethylamino)propyl]-5,11-dioctylcoronene-2,3,8,9-tetracarboxdiimide (CDIN)),27 and widely employed inorganic semiconductor materials such as ZnO,28–30 SnO$_2$,31–36 WO$_3$,37,38 In$_2$O$_3$,39 CdS,40,41 Fe$_2$O$_3$,42,43 Zn$_2$SnO$_4$,44–46 and Nb$_2$O$_5$.47,48 Recently, Yang’s group found that well-organized In$_x$S$_{1-x}$ nanoflake arrays can be applied in perovskite solar cells as the ETL with better performance (higher efficiency and less hysteresis) compared to commonly used TiO$_2$-based solar cells.49 The In$_x$S$_{1-x}$ thin film exhibited superior performance compared to TiO$_2$ owing to its higher carrier mobility (17.6 cm$^2$ V$^{-1}$ s$^{-1}$ vs. 10$^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$). However, the In$_x$S$_{1-x}$ thin film deposition is a complicated chemical bath process that requires several hours, which is time-consuming and energy-intensive.

In this scenario, we fabricated In$_x$S$_{1-x}$ thin films using a simple method that shortened the process time to several minutes. By optimizing the concentration of the metal precursors and deposition parameters, a smooth In$_x$S$_{1-x}$ film was obtained. In fact, In$_x$S$_{1-x}$ ETL performed better than the most commonly used TiO$_2$ in extracting and transporting electrons. Moreover, the
perovskite was used as the absorbing material. Spiro-OMeTAD as the hole transport layer; also, Au and FTO with 3:2, corresponding to the stoichiometric ratio. Subsequently, EDS (energy dispersive spectroscopy) analysis was also conducted to check the ratios of In and S in the prepared thin films. The acquired solid In-complex precursor was studied in the temperature range of 100–500 °C in nitrogen atmosphere. From the TG curve, it is clear that there is no further loss when the temperature increased up to 225 °C, suggesting the annealing temperature to prepare In2S3 thin films. Therefore, we determined that the In2S3 thin film could be sintered at 200 °C for 1 min to remove organic ligands and solvents and subsequently at 300 °C for 2 min to further burn off the leftovers to obtain the In2S3 thin film. For identifying the In2S3 thin film, the valence states of In and S ions in the annealed thin film were researched, as shown in Fig. S2.† It can be seen that In 3d peaks are located at 444.4 eV and 452 eV with a splitting value of 7.6 eV, and S 2p peaks are located at 160.8 eV and 162.4 eV with a splitting value of 1.6 eV, which are associated with In3+ and S2− ions, respectively. In addition, EDS (energy dispersive spectroscopy) analysis was also conducted to check the ratios of In and S in the prepared thin film (Fig. S3†). The results revealed that the thin film exhibited the ratio of S:In = 11.6:7.8, which is accurately consistent with 3:2, corresponding to the stoichiometric ratio. Subsequently, the device was assembled in a typical structure with Spiro-OMeTAD as the hole transport layer; also, Au and FTO were employed as the electrodes, and organic–inorganic hybrid perovskite was used as the absorbing material.

The relative valence band and conductive band positions of ETL, absorbing layer and HTL affect the routes for the electron and hole transport, which is the core for designing the battery architecture. Thus, the valence band maximum (VBM) and Fermi energy of the In2S3 thin film were investigated by UPS (ultraviolet photoelectron spectroscopy) (Fig. S4†). The Fermi energy was first obtained as −3.86 eV by subtracting the spectrum onset of 17.36 eV from the ultraviolet photoelectron energy of 21.22 eV. By linear extrapolation in the low binding energy region, the distance between Fermi energy and VBM was calculated as 2.23 eV. Thus, the value of VBM is −6.09 eV. The optical band gap of In2S3 was calculated from ultraviolet-visible absorption spectra and Tauc formula to be 2.29 eV. Thus, the conduction band energy (Ec) was calculated to be −3.8 eV, according to the equation Ec = VBM + Eg. The valence band and conduction band values of other layers were obtained from the literature. The relative energy-level diagram of the PSC device is shown in Fig. 2(a). We found that In2S3 has a suitable energy level to promote the extraction of electrons. The conduction band minimum (CBM) of CH3NH3PbI3 is closer to that of In2S3 than to that of TiO2, which leads to lower energy barrier for electron injection from the perovskite layer into In2S3 ETL. Fig. 2(b) shows the transmittance spectra for In2S3 coated on FTO/glass substrates with different In precursor concentrations. The transmittance of In2S3 thin film decreased with increase in the precursor concentration. Especially, the transmittance of In2S3 film sharply decreased in the 300–500 nm range, which was due to its narrow band gap. The thicker the In2S3 thin film, the stronger the absorbance. The absorbance of In2S3 thin film can result in decrease in light for the perovskite absorber layer, which was presented by Jsc of the solar cell. The image of In2S3 thin film deposited on different concentrations is displayed in Fig. 2(c), in which it can be clearly seen that the In2S3 thin film gradually turned more yellow with increase in the precursor concentration, illustrating that a thicker In2S3 thin film was deposited.

Atomic force microscopy (AFM) measurements were obtained to characterize the surface properties of In2S3 thin films (Fig. S5†). The flatness of the In2S3 film was approximate to that

Fig. 1 The schematic of the synthesis of In2S3 film and device assembly.
of TiO₂, and it was even more smoother. Smooth substrates are beneficial for the formation of even perovskite layers. The top-view SEM images of the prepared In₂S₃ films on FTO substrates with different precursor concentrations are shown in Fig. 3(a)–(d), which demonstrate a great change in the film morphology. With decrease in the concentration of In precursor, the amount of pinholes in the films decreased except for 50 mmol L⁻¹ concentration due to possible incomplete coverage. It can be explained that more small organic ligands escape from the film during the heating process when the concentration of the precursor is high. Therefore, seeking In₅S₃ with suitable In concentration and thickness is important for application in PSCs.

CH₃NH₃PbI₃ absorption layers were coated on In₂S₃ ETLs using a typical one-step solution process; the corresponding SEM images are exhibited in Fig. 3(e)–(h). The quality of the perovskite films was influenced by In₂S₃ substrates. All the perovskite films were compact and uniform except for the perovskite layer coated on In₂S₃ thin film with 220 mmol L⁻¹ precursor, which exhibited some small granules on the perovskite surface. The appearance of the small granules may be due to incomplete decomposition of the In₂S₃ film. A high concentration resulted in thick thin film, which needed longer time to decompose In-complex. Thus, small organic molecules escaped from the In₂S₃ film during the subsequent annealing process to prepare the perovskite layer. It can be seen that the pinholes in the In₂S₃ films have different sizes and depths, where deeper/larger pinholes have more serious impact on the quality of the films. Fig. S6f shows the AFM height images of the CH₃NH₃PbI₃ films based on different In₂S₃ films. It is clear that all the films are flat, and the RMS values of all the perovskite films are less than 10 nm. Smooth absorption layers provide high-quality surfaces for electron transport, which are necessary for high-efficiency devices.

In addition, the ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectra, room-temperature photoluminescence (PL) spectra and external quantum efficiency (EQE) for the perovskite films or solar cells based on different In precursor concentrations were measured. As demonstrated in Fig. 4(a), the absorbance intensity of perovskite films coated on In₂S₃ ETLs enhanced with the increase of In₂S₃ film thickness, especially in the 300–500 nm range, which is in agreement with the transmittance of In₂S₃ films due to the absorbance of In₂S₃ thin film. The PL spectra shown in Fig. 4(b) reveal the presence of weak photoluminescence of CH₃NH₃PbI₃ samples based on different In₂S₃ thin films, which indicates the low level of recombination of electron–hole pairs because the photogenerated electrons are transferred quickly to ETL. In particular, the sample with 75 mmol L⁻¹ precursor concentration exhibited the lowest intensity, indicating that 75 mmol L⁻¹ is the suitable concentration for fabricating perovskite solar cells. The current density–voltage (J–V) characteristics for PSCs with In₂S₃ ETLs with different concentrations were measured under simulated AM 1.5 G solar irradiation, as shown in Fig. 4(c). The values of short-circuit current density (Jₛ𝑐), open-circuit voltage (Vₒ𝑐), fill factor (FF) and power-conversion efficiency (η) were obtained from the J–V curves, as summarized in Table S1.† Evidently, PSCs with In₂S₃ ETL prepared with the concentration of 75 mmol L⁻¹ exhibited Jₛ𝑐, Vₒ𝑐 and FF of 21.00 mA cm⁻², 1060.2 mV and 0.69, respectively, yielding PCE of 15.48%. The PCEs for the PSCs with In₂S₃ ETLs of different precursor concentrations are summarized in Fig. S7.† Jₒ𝑐 of the solar cells increased with decrease in In-complex concentration of In₂S₃ ETL, which indicated that very thick In₂S₃ ETL can hinder the absorption of the perovskite layer. Similarly, EQE measurement (Fig. 4(d)) indicated that the integrated current densities for the PSCs based on In₂S₃ ETL with the In precursor concentrations of 220, 110, 75 and 50 mmol L⁻¹ were 18.22 mA cm⁻², 19.42 mA cm⁻², 20.01 mA cm⁻² and 18.58 mA cm⁻², respectively, which agreed well with the measured Jₒ𝑐 values.

To study the performance of PSCs based on In₂S₃ ETL in this straightforward precursor solution process, we made a comparison with the commonly used TiO₂-based PSCs. First, the quality of MAPbI₃ films was evaluated by crystallinity measurements. Fig. 5(a) displays the XRD patterns of the MAPbI₃ films coated on In₂S₃ or TiO₂. Both of them showed the
In2S3 was also demonstrated by the photoluminescence (PL) to a band gap of about 1.60 eV. Besides these, the superiority of samples show a sharp band edge at 780 nm, which corresponds measured with excitation at 325 nm (Fig. 5(d)). In2S3 exhibited that of TiO2. The time-resolved photoluminescence (TR-PL) interface, the PL intensity decreased significantly compared to that of TiO2, especially for the (110) peak, which revealed that the perovskite film deposited on In2S3 substrate has better crystallinity and orientation. The light absorbance spectra of the MAPbI3 films are coated on In2S3 and TiO2 ETLs.

The little efficiency gap between In2S3 and TiO2 exists in $J_{sc}$, whereas $V_{oc}$ and FF remain almost consistent. The specific parameters are listed in Table 1. On comparing the relevant parameters, it was found that the In2S3-based photovoltaic device exhibited lower shunt resistance, which illustrated that there were more shunt paths in the In2S3-based device, explaining the cause for low $J_{sc}$. Thus, we can enhance the photovoltaic efficiency by further optimizing the In2S3 thin film.

The In2S3 ETL-based device showed a faster response to photocurrent compared to the TiO2 ETL-based device. This can be ascribed to the fast trap filling process or the low density of charge traps in the CH3NH3PbI3 layer coated on In2S3 ETL. In addition, the In2S3 ETL-based device exhibited better stability compared to the TiO2-based device (Fig. 7(b)). For In2S3 ETL-based PSC, slight decrease was observed at the first few seconds and then, it remained constant, whereas the TiO2-based device exhibited a continuous descent.

**Experimental**

**Preparation of In2S3 and TiO2 layer**

In(OH)3 was used as the In source and was dissolved in carbon disulphide (CS2) and n-butyamine mixed solution, forming an In-complex precursor solution. In this system, the reaction between CS2 and n-butyamine generated butyldithiocarbamic acid (BDCAl) (Fig. 1). This kind of thiol-amine acid is highly active and thus, it can react with a series of metal oxides and metal hydroxides to form an organometallic complex. First, 1 mmol In(OH)3 (99.99%, Aladdin reagent) powder was dispersed in 1 mL ethanol with magnetic stirring at room temperature. Then, 0.3 mL n-butyamine (99.5%, Aladdin...
Table 1  Some key parameters of the perovskite device with TiO2 and In2S3 as the ETL

<table>
<thead>
<tr>
<th>ETL type</th>
<th>Jsc (mA cm-2)</th>
<th>Voc (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Rsh (Ω)</th>
<th>Rsc (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2</td>
<td>21.58</td>
<td>1.05</td>
<td>66.73</td>
<td>15.13</td>
<td>82.32</td>
<td>465.43</td>
</tr>
<tr>
<td>In2S3</td>
<td>20.08</td>
<td>1.04</td>
<td>67.09</td>
<td>14.02</td>
<td>76.40</td>
<td>9920.95</td>
</tr>
</tbody>
</table>

reagent) was added to it. Later, 225 μL carbon disulphide (CS2) (99.9%, Aladdin reagent) was introduced into the mixed solution in a dropwise manner. The solution was further stirred for another 2 h to obtain a clear solution (Fig. 1). Here, In-complex formed is indium butyldithiocarbamates (In(S2CNHC4H9)3). The above solution was then filtered with 0.22 μm filtrator, and 1 mL filtered solution was diluted with 0.5 mL, 2 mL, 3.5 mL and 5.75 mL ethanol to form 220 mmol L−1, 110 mmol L−1, 75 mmol L−1 and 50 mmol L−1 In-complex precursors, respectively. For In2S3 thin films, different concentrations of In-complex precursor were spin-coated at a speed of 5000 rpm for 40 s on cleaned fluorine-doped tin oxide (FTO). The FTO/glass substrates were treated by UV-ozone treatment for 15 min before deposition of the In2S3 films. This was followed by annealing on a hot plate in an N2-purged glove box at 200 °C for only 1 min and at 300 °C for 2 min.

TiO2 layers were grown by chemical bath deposition on cleaned FTO substrates. The deposition was made by putting the FTO/glass substrates in a glass container filled with titanium chloride solution in a 70 °C lab oven for 1 h. The deposited substrates were rinsed with deionized water for 2 min to remove any loosely bound materials, dried in a stream of N2, and annealed for 30 min at 200 °C on a hot plate.

Device assembly

The PSC adopted the structure of FTO/TiO2 or In2S3/CH3NH3PbI3/Spiro-OMeTAD/Au. All TiO2/FTO/glass substrates were treated by UV-ozone treatment for 15 min before deposition of the perovskite films. PbI2 was purchased from Alfar Aesar (99.99%), and CH3NH3I was purchased from Xi’an Polymer Light Technology Corp (99.5%). First, 1.1064 g PbI2 and 0.3816 g CH3NH3I were dissolved in 1.4 mL γ-butylrolactone (GBL, 99.9%, Aldrich) and 0.6 mL dimethyl sulfoxide (DMSO, 99.9%, Aldrich) in a glovebox with constant stirring at room temperature to form the perovskite solution. Then, the perovskite solution was spin-coated on top of the ETLs (TiO2 or In2S3) at 1000 rpm for 10 s and at 4000 rpm for 40 s while dripping chlorobenzene (as the antisolvent) onto the substrate during the second spinning step. All the samples were then heated at 100 °C for 10 min, resulting in the formation of dark perovskite films. Also, 900 mg Spiro-OMeTAD (90 mg was dissolved in 1 mL chlorobenzene doped with 36 μL 4-tert-butylpyridine (TBP, Sigma-Aldrich) and 22 μL (520 mg mL−1) lithium bis inside acetonitrile solution) was deposited by spin-coating (5000 rpm for 30 s) as the hole transport layer on top of perovskite film. Finally, a 100 nm-thick gold electrode was deposited by thermal evaporation using a shadow mask to form an active area of 9 mm2.

Characterizations

X-ray diffraction was used to monitor perovskite film formation (XRD; DX-2700) via Cu-Kz radiation (λ = 1.5416 Å). The absorption spectra of the In2S3 film coated on FTO were measured by using an UV-Vis spectrometer (Lambda 950, PerkinElmer). A field emission scanning electron microscope (FESEM; SU-8020, Hitachi) was used to investigate the morphology of the perovskite films. An atomic force microscope (AFM; MULTIMODE 8, Bruker) was used to image the topography and measure the surface roughness in peak force mode. The photovoltaic performances were characterized in air without encapsulation under simulated sunlight illumination generated by a solar simulator (XES-4082-CE, San-Ei Electric, AM 1.5 G filter at 100 mW cm−2), which was calibrated by using a certified silicon photodiode. J-V characteristics were obtained by using a source meter (2400, Keithley) at a sweep rate of 0.1 V s−1 in forward and backward scan mode.

Conclusion

In conclusion, we have demonstrated a convenient, simple solution processable approach for the fabrication of In2S3 film as the ETL for high-performance planar perovskite solar cells. In2S3 ETL facilitates the injection and transport of photogenerated electrons from the perovskite absorber with reduction in charge recombination. In addition, the photoresponse rate is enhanced using In2S3 ETL compared to that obtained using TiO2. Meanwhile, In2S3 thin film used in the simplified method exhibited efficiency comparable to that of traditional TiO2 ETL in PSCs. The optimization of electron and hole transport materials and interfacial engineering are expected to further boost the conversion efficiency.

Conflicts of interest

There are no conflicts to declare.

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Notes and references