

# PAPER

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# A straightforward chemical approach for excellent In<sub>2</sub>S<sub>3</sub> electron transport layer for high-efficiency perovskite solar cells†

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<sub>2</sub>S-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<sub>2</sub>S<sub>3</sub> 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<sub>2</sub>S<sub>3</sub> thin film prepared using our straightforward chemical approach have higher electron extraction efficiency and comparable efficiency compared with archetypical TiO<sub>2</sub> as the electron transport layer (ETL) in perovskite photovoltaic device.

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## 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 stateof-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 efficient ETL and hole transporting layer (HTL). Regular n-i-p and inverted p-i-n are the two types of planar structures on account of the sequence of the charge transport layers.9-15 Therefore, in the pursuit of advancement or improvement in the performance or fabrication cost, many attempts have been made to optimize

In this scenario, we fabricated  $In_2S_3$  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  $In_2S_3$  film was obtained. In fact,  $In_2S_3$  ETL performed better than the most commonly used  $TiO_2$  in extracting and transporting electrons. Moreover, the

the absorption layer, electron transport layer, 16-19 hole transport layer, 20-28 and the interfaces between the adjacent layers. 29,30 Until now, compact TiO2 layers are the most widely utilized inorganic ETLs. However, the application of TiO<sub>2</sub> ETL in PSCs is limited due to its high-temperature fabrication and intrinsic low carrier mobility.31-33 Hence, some research communities have been investigating alternative ETL materials, including some organics (PCBM (6,6)-phenyl-C<sub>61</sub>-butyric acid methyl ester,34-36 C60,37,38 and N,N'-bis(3-(dimethylamino)propyl)-5,11dioctylcoronene-2,3,8,9-tetracarboxdiimide (CDIN))39 widely employed inorganic semiconductor materials such as  $ZnO_{1}^{18,40}$   $SnO_{2}^{41-44}$   $WO_{x}^{45}$   $In_{2}O_{3}^{46}$   $CdS_{3}^{32,47,48}$   $Fe_{2}O_{3}^{49}$ Zn<sub>2</sub>SnO<sub>4</sub>,<sup>50-52</sup> and Nb<sub>2</sub>O<sub>5</sub>.<sup>53</sup> Recently, Yang's group found that well-organized In<sub>2</sub>S<sub>3</sub> nanoflake arrays can be applied in perovskite solar cells as the ETL with better performance (higher efficiency and less hysteresis) compared to commonly used TiO2-based solar cells.54 The In2S3 thin film exhibited superior performance compared to TiO2 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<sub>2</sub>S<sub>3</sub> thin film deposition is a complicated chemical bath process that requires several hours, which is time-consuming and energy-intensive.

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 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available: TG curves, XPS, SEM-EDX UPS, and AFM height image of  $In_2S_3$  thin film, AFM height images of perovskite thin films, the best PSC device parameters table, PCE distribution image and cross-sectional SEM image of the perovskite solar cells are exhibited. See DOI: 10.1039/c8ra08940j

photovoltaic devices utilizing the  $In_2S_3$  thin films as the ETL exhibited PCE of 15.48%.

#### Results and discussion

Fig. 1 shows a schematic for the preparation of In<sub>2</sub>S<sub>3</sub> thin film and the PSC device assembly. The In<sub>2</sub>S<sub>3</sub> thin film was prepared by dissolving In(OH)<sub>3</sub> in butyldithiocarbamic acid, which was formed via a reaction between carbon disulfide and butylamine in situ in ethanol at room temperature, followed by annealing. To decide a suitable sintering temperature for depositing the compact In<sub>2</sub>S<sub>3</sub> thin film, the thermal decomposition behaviour of In-complex was studied by thermogravimetric (TG) analysis exhibited in Fig. S1.† Before the TG measurement, In-complex solution with high concentration was dried at 40 °C for a couple of days to remove the solvents and excess ligands. 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 In<sub>2</sub>S<sub>3</sub> thin films. Therefore, we determined that the In<sub>2</sub>S<sub>3</sub> 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 In<sub>2</sub>S<sub>3</sub> thin film.

For identifying the  $\rm In_2S_3$  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  $\rm In^{3+}$  and  $\rm S^{2-}$  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.

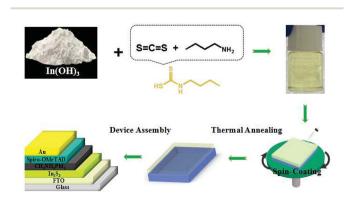


Fig. 1 The schematic of the synthesis of  $\mbox{In}_2\mbox{S}_3$  film and device assembly.

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 In<sub>2</sub>S<sub>3</sub> 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.32 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  $(E_c)$  was calculated to be -3.8 eV, according to the equation  $E_c = VBM + E_g$ . The valence band and conduction band values of other layers were obtained from the literature.46 The relative energy-level diagram of the PSC device is shown in Fig. 2(a). We found that In<sub>2</sub>S<sub>3</sub> has a suitable energy level to promote the extraction of electrons. The conduction band minimum (CBM) of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> is closer to that of In<sub>2</sub>S<sub>3</sub> than to that of TiO2, which leads to lower energy barrier for electron injection from the perovskite layer into In<sub>2</sub>S<sub>3</sub> ETL. Fig. 2(b) shows the transmittance spectra for In<sub>2</sub>S<sub>3</sub> coated on FTO/glass substrates with different In precursor concentrations. The transmittance of In<sub>2</sub>S<sub>3</sub> thin film decreased with increase in the precursor concentration. Especially, the transmittance of In<sub>2</sub>S<sub>3</sub> film sharply decreased in the 300-500 nm range, which was due to its narrow band gap. The thicker the In<sub>2</sub>S<sub>3</sub> thin film, the stronger the absorbance. The absorbance of In<sub>2</sub>S<sub>3</sub> thin film can result in decrease in light for the perovskite absorber layer, which was presented by  $J_{sc}$  of the solar cell. The image of  $In_2S_3$ thin film deposited on different concentrations is displayed in Fig. 2(c), in which it can be clearly seen that the  $In_2S_3$  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  $In_2S_3$  thin films (Fig. S5†). The flatness of the  $In_2S_3$  film was approximate to that

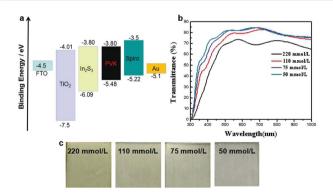


Fig. 2 (a) The energy-level diagram of the PSC device and (b) the transmittance spectra of  $ln_2S_3$  thin films with different In concentrations; (c) the photograph of  $ln_2S_3$  thin film deposited on different concentrations.

application in PSCs.

of  $TiO_2$ , and it was even more smoother. Smooth substrates are beneficial for the formation of even perovskite layers. The topview SEM images of the prepared  $In_2S_3$  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  $In_2S_3$  with suitable In concentration and thickness is important for

CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> absorption layers were coated on In<sub>2</sub>S<sub>3</sub> 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 In<sub>2</sub>S<sub>3</sub> substrates. All the perovskite films were compact and uniform except for the perovskite layer coated on In<sub>2</sub>S<sub>3</sub> thin film with 220 mmol L<sup>-1</sup> precursor, which exhibited some small granules on the perovskite surface. The appearance of the small granules may be due to incomplete decomposition of the In<sub>2</sub>S<sub>3</sub> film. A high concentration resulted in thick thin film, which needed longer time to decompose In-complex. Thus, small organic molecules escaped from the In<sub>2</sub>S<sub>3</sub> film during the subsequent annealing process to prepare the perovskite layer. It can be seen that the pinholes in the In<sub>2</sub>S<sub>3</sub> films have different sizes and depths, where deeper/ larger pinholes have more serious impact on the quality of the films. Fig. S6† shows the AFM height images of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> films based on different In<sub>2</sub>S<sub>3</sub> 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 highefficiency 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  $In_2S_3$  ETLs enhanced with the increase of  $In_2S_3$  film thickness, especially in the 300–500 nm range, which is in agreement with

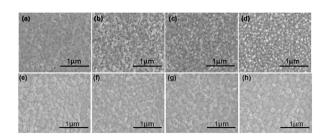


Fig. 3 Top-view SEM (scanning electron microscopy) images of  $\rm In_2S_3$  films on FTO substrates and perovskite films coated on relative  $\rm In_2S_3$  ETLs with different precursor concentrations of (a) and (e) 220 mmol  $\rm L^{-1}$ , (b) and (f) 110 mmol  $\rm L^{-1}$ , (c) and (g) 75 mmol  $\rm L^{-1}$ , (d) and (h) 50 mmol  $\rm L^{-1}$ .

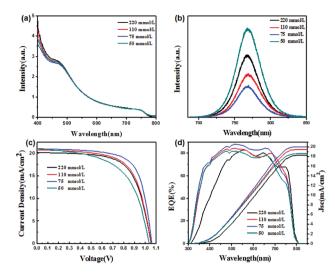


Fig. 4 (a) Absorption spectra, (b) room-temperature photo-luminescence (PL) spectra of the perovskite films based on  $In_2S_3$  films with different precursor concentrations (excitation at 532 nm) and relative (c) current density–voltage curves and (d) EQE curves for perovskite solar cells based on  $In_2S_3$  ETLs.

the transmittance of In<sub>2</sub>S<sub>3</sub> films due to the absorbance of In<sub>2</sub>S<sub>3</sub> 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 In<sub>2</sub>S<sub>3</sub> 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  $(J_{sc})$ , open-circuit voltage  $(V_{\rm oc})$ , fill factor (FF) and power-conversion efficiency  $(\eta)$  were obtained from the J-V curves, as summarized in Table S1.† Evidently, PSCs with In<sub>2</sub>S<sub>3</sub> ETL prepared with the concentration of 75 mmol  $L^{-1}$  exhibited  $J_{sc}$ ,  $V_{oc}$  and FF of 21.00 mA cm<sup>-2</sup>, 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.†  $J_{sc}$  of the solar cell increased with decrease in In-complex concentration of In<sub>2</sub>S<sub>3</sub> ETL, which indicated that very thick In<sub>2</sub>S<sub>3</sub> 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 In<sub>2</sub>S<sub>3</sub> ETL with the In precursor concentrations of 220, 110, 75 and 50 mmol  $L^{-1}$  were 18.22 mA cm<sup>-2</sup>, 19.42 mA cm<sup>-2</sup>, 20.01 mA cm<sup>-2</sup> and 18.58 mA cm<sup>-2</sup>, respectively, which agreed well with the measured  $J_{sc}$  values.

To study the performance of PSCs based on  $In_2S_3$  ETL in this straightforward precursor solution process, we made a comparison with the commonly used  $TiO_2$ -based PSCs. First, the quality of MAPbI<sub>3</sub> films was evaluated by crystallinity measurements. Fig. 5(a) displays the XRD patterns of the MAPbI<sub>3</sub> films coated on  $In_2S_3$  or  $TiO_2$ . Both of them showed the

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Fig. 5 (a) XRD patterns, (b) absorption spectra, (c) room-temperature steady-state photoluminescence (PL) spectra, and (d) time-resolved photoluminescence (TR-PL) spectra of the  $CH_3NH_3PbI_3$  films (excitation at 325 nm and emission at 765 nm). Note: all the  $CH_3NH_3PbI_3$  films are coated on  $In_2S_3$  and  $TiO_2$  films.

same diffraction peaks at 14.02, 19.94, 23.36, 24.32, 28.26, 31.74, 40.56, and 43.08°, corresponding to the (110), (112), (211), (202), (220), (310), (224), and (314) crystal planes, without other impurity phases. On the other hand, the film based on In<sub>2</sub>S<sub>3</sub> showed stronger (110), (220), and (310) diffraction peaks than TiO<sub>2</sub>, especially for the (110) peak, which revealed that the perovskite film deposited on In<sub>2</sub>S<sub>3</sub> substrate has better crystallinity and orientation. The light absorbance spectra of the MAPbI<sub>3</sub> films prepared based on In<sub>2</sub>S<sub>3</sub> or TiO<sub>2</sub> were investigated. As exhibited in Fig. 5(b), the absorbance spectra for both samples show a sharp band edge at 780 nm, which corresponds to a band gap of about 1.60 eV. Besides these, the superiority of In<sub>2</sub>S<sub>3</sub> was also demonstrated by the photoluminescence (PL) emission results, which are shown in Fig. 5(c). Due to the enhanced electron quenching rate at the In<sub>2</sub>S<sub>3</sub>/perovskite interface, the PL intensity decreased significantly compared to that of TiO<sub>2</sub>. The time-resolved photoluminescence (TR-PL) decays of perovskite films based on In2S3 and TiO2 were measured with excitation at 325 nm (Fig. 5(d)). In<sub>2</sub>S<sub>3</sub> exhibited time constants of  $\tau_1 = 20.860$  ns and  $\tau_2 = 5.665$  ns, whereas TiO<sub>2</sub>

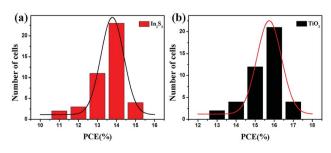


Fig. 6 Statistical PCE distribution of perovskite solar cells based on (a)  $In_2S_3$  and (b)  $TiO_2$  ETLs.

exhibited time constants of  $\tau_1 = 64.507$  ns and  $\tau_2 = 10.585$  ns, which verified the faster electron injection rate from perovskite into  $\text{In}_2\text{S}_3$  than into  $\text{TiO}_2$ , resulting in higher electron injection quantum efficiency after electron-hole separation.

Statistics analysis confirmed that PSCs based on  $In_2S_3$  achieved average PCE of 13.8% on the basis of 43 devices in Fig. 6, whereas  $TiO_2$ -based PSCs exhibited average efficiency of 15.1%. The little efficiency gap of  $In_2S_3$ -based PSCs compared to that of  $TiO_2$ -based PSCs resulted from the shunt paths in the  $In_2S_3$ -based PSCs. Fig. 7(a) shows the J-V curves of perovskite solar cells with  $In_2S_3$  and  $TiO_2$  as the ETL around the average efficiency. It can be seen that the efficiency gap between  $In_2S_3$  and  $TiO_2$  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  $In_2S_3$ -based photovoltaic device exhibited lower shunt resistance, which illustrated that there were more shunt paths in the  $In_2S_3$ -based device, explaining the cause for low  $J_{sc}$ . Thus, we can enhance the photovoltaic efficiency by further optimizing the  $In_2S_3$  thin film.

The In<sub>2</sub>S<sub>3</sub> ETL-based device showed a faster response to photocurrent compared to the TiO<sub>2</sub> ETL-based device. This can be ascribed to the fast trap filling process or the low density of charge traps in the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> layer coated on In<sub>2</sub>S<sub>3</sub> ETL. In addition, the In<sub>2</sub>S<sub>3</sub> ETL-based device exhibited better stability compared to the TiO<sub>2</sub>-based device (Fig. 7(b)). For In<sub>2</sub>S<sub>3</sub> ETL-based PSC, slight decrease was observed at the first few seconds and then, it remained constant, whereas the TiO<sub>2</sub>-based device exhibited a continuous descent.

# Experimental

#### Preparation of In<sub>2</sub>S<sub>3</sub> and TiO<sub>2</sub> layer

 $In(OH)_3$  was used as the In source and was dissolved in carbon disulphide (CS<sub>2</sub>) and *n*-butylamine mixed solution, forming an In-complex precursor solution. <sup>55–57</sup> In this system, the reaction between CS<sub>2</sub> and *n*-butylamine generated butyldithiocarbamic acid (BDCA) (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*-butylamine (99.5%, Aladdin

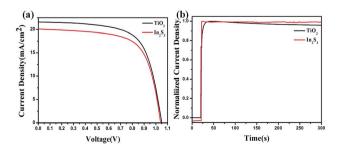


Fig. 7 (a) The J-V characterization and (b) stability of perovskite solar cells with  $\rm In_2S_3$  and  $\rm TiO_2$  as the ETL.

Table 1 Some key parameters of the perovskite device with TiO<sub>2</sub> and In<sub>2</sub>S<sub>3</sub> as the ETL

ETL type	$J_{ m sc}~({ m mA~cm}^{-2})$	$V_{\rm oc}$ (V)	FF (%)	PCE (%)	$R_{\mathrm{s}}\left(\Omega\right)$	$R_{\mathrm{sh}}\left(\Omega\right)$
TiO <sub>2</sub>	21.58	1.05	66.73	15.13	82.32	16 465.43
In <sub>2</sub> S <sub>3</sub>	20.08	1.04	67.09	14.02	76.40	9920.95

reagent) was added to it. Later, 225 μL carbon disulphide (CS<sub>2</sub>) (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<sup>-1</sup> and 50 mmol L<sup>-1</sup> In-complex precursors, respectively. For In<sub>2</sub>S<sub>3</sub> thin films, different concentrations of Incomplex 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 In<sub>2</sub>S<sub>3</sub> 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.

TiO<sub>2</sub> 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 N<sub>2</sub>, and annealed for 30 min at 200 °C on a hot plate.

#### Device assembly

The PSC adopted the structure of FTO/TiO2 or In2S3/CH3NH3-PbI<sub>3</sub>/Spiro-OMeTAD/Au. All TiO<sub>2</sub>/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 CH<sub>3</sub>NH<sub>3</sub>I was purchased from Xi'an Polymer Light Technology Corp (99.5%). First, 1.1064 g PbI<sub>2</sub> and 0.3816 g CH<sub>3</sub>NH<sub>3</sub>I were disolved in 1.4 mL γ-butyrolactone (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 (TiO<sub>2</sub> or In<sub>2</sub>S<sub>3</sub>) 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<sup>-1</sup>) lithium bis imide acetonitrile solution) was deposited by spin-coating (5000 rpm for 30 s) as the hole transport layer on top of pervoskite film. Finally, a 100 nm-thick gold electrode was deposited by thermal evaporation using a shadow mask to form an active area of 9 mm<sup>2</sup>.

## Characterizations

X-ray diffraction was used to monitor perovskite film formation (XRD; DX-2700) via Cu-K $\alpha$  radiation ( $\lambda = 1.5416$  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-40S2-CE, San-Ei Electric, AM 1.5 G filter at 100 mW cm<sup>-2</sup>), 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<sup>-1</sup> in forward and backward scan mode.

## Conclusion

In conclusion, we have demonstrated a convenient, simple solution processable approach for the fabrication of In<sub>2</sub>S<sub>3</sub> film as the ETL for high-performance planar perovskite solar cells. In<sub>2</sub>S<sub>3</sub> 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 In<sub>2</sub>S<sub>3</sub> ETL compared to that obtained using TiO<sub>2</sub>. Meanwhile, In<sub>2</sub>S<sub>3</sub> 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

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