Anti-solvent spin-coating for improving morphology of lead-free $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ perovskite films

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Abstract

Methylammonium iodide bismuthate $((\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9)$ (MIB) perovskite has attracted research attention because of its low toxicity and stability in air. However, MIB perovskite also has its inherent defects, e.g., MIB films have too many pinholes and large indirect band gap. Our group has also done some efforts to successfully improve the performance of MIB-based PSC. One of the recent works focused on the use of diethyl ether (DEE) as anti-solvent to improve film compactness and reduce pinhole defects. The characterization indicated that the films treated by DEE (DEE/MIB) were compact with fewer pinholes. The devices fabricated with DEE/MIB based on mesoporous TiO_2 (mp- TiO_2) architecture exhibited good performance in terms of V_{oc} (885 mV), J_{sc} (0.807 mA cm^{-2}), and FF (49.71%), with a power conversion efficiency of 0.343%, which were much higher than that of the contrast test and results of our previous work. The present devices also exhibited superior long-term stability in ambient air (approximately 30% humidity) of more than 200 days.

Keywords $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ (MIB) · Anti-solvent spin-coating · Lower toxicity · Longer stability

1 Introduction

During the fabrication of perovskite film, it tends to agglomerate into crystal lumps because of the high surface tension. Gaps are then formed between perovskite lumps, resulting in a greater loss of incident light [1]. Therefore, a superior crystal film is the key to achieve high-quality perovskite solar cells (PSCs) [2]. An inferior perovskite film has a great impact on charge separation, transport, and photoelectric conversion performance [3]. A uniform film can not only absorb incident light, but also avoid direct contact between the hole transport layer and the electron transport layer as well as the serious problem of charge recombination. Therefore, exploring and optimizing the process of fabricating perovskite films are

important to control the surface coverage of crystal film and crystal size, thus producing superior consecutive film without pinholes.

To obtain high-quality films, researchers have explored different methods such as one-step spin-coating (1-S method), two-step spin-coating (2-S method), and chemical vapor deposition [4–6]. Although vapor deposition can produce dense films, the preparation process needs a certain vacuum and high temperature, which has the disadvantage of time-consuming and energy-consuming. The 2-S methods will make the reaction between the reactants insufficient. The 1-S method has the advantage of low cost as well as simple and easy operation, but it has poor repeatability, and cannot control the thickness and morphology of the perovskite layer. Consequently, the

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grain size of perovskite is uneven, pinholes are formed in perovskite layer, and the substrate is not fully covered [7], which result in poor photoelectric properties of the devices. Therefore, fabrication of compact films by the 1-S method is important, which can be achieved by choosing mixing solvent [8, 9], adding additive [10, 11], and anti-solvent treatment [12, 13]. Among these methods, anti-solvent treatment is widely used because it can accelerate the crystallization of perovskite crystal, resulting in extremely dense and compact film. The most common anti-solvents are methylbenzene, dichloromethane, diethyl ether (DEE), chlorobenzene (CB), ethyl acetate (EA), n-hexane, and trichloromethane [14–18]. Given that the solubilities of PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ (MAI) vary in *N,N*-dimethylformamide (DMF), during the perovskite formation, DMF volatilizes slowly and PbI_2 (whose solubility is low) will separate out from DMF firstly, and then, the $\text{CH}_3\text{NH}_3\text{I}$ attaches to the separated PbI_2 , which results in a perovskite crystal morphology similar to that of PbI_2 crystal [3, 19]. The solution can be extracted instantly via dropping anti-solvent, when using spin-coating method to fabricate perovskite films, making PbI_2 and MAI supersaturated and precipitate at the same time, which can eliminate PbI_2 and MAI segregation.

Li developed a new method using CB to treat PbI_2 film during 2-S method and successfully acquired compact and equable perovskite film [20]. Considering that the solubilities of solute and solvent are different, DMF can be removed quickly; PbI_2 could crystallize quickly, and reduce the volume of the PbI_2 film at the same time. When the PbI_2 film is dipped in a MAI solution, the mesoscopic architecture PbI_2 film provides enough space for the reaction of PbI_2 and MAI, so that the reaction does not occur on the PbI_2 film surface.

Solvent engineering and compositional engineering [21–23] indicate that Bismuth-based perovskite crystal structure is not simply a regular perovskite structure formed by replacing lead in lead-based perovskite with element Bi. Because Bi^{3+} is trivalent and Pb^{2+} is bivalent, Bi substitutes for Pb to form a perovskite-like structure consisting of two coplanar octahedral $(\text{Bi}_2\text{I}_9)^{3-}$ group surrounded by cations, which results in a hexagonal lamellar structure of Bismuth-based perovskite crystal. During spin-coating, the crystal growth preferentially grows along the C axis, which causes the morphology of Bi-based perovskite thin films being a porous structure formed by the accumulation of hexagonal crystals. Therefore, the nucleation and growth of bismuth-based perovskite crystals must be controlled if we want to get a better Bismuth-based perovskite film.

Sawanta fabricated $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ PSCs based on mp- TiO_2 architecture and achieved a PCE of 0.069% [15]. After

treating with CB, they obtained dark-color films, large grain size, and high PCE of 0.356%. The performance of the devices was better than the devices fabricated by traditional 1-S method, with V_{oc} , J_{sc} , and FF of 0.653 V, 1.1 mA cm^{-2} , and 49.6%, respectively. Optical absorption measurement exhibits a strong absorption band about 550 nm, and the band gap is approximately 2.1 eV. The reason may be that adding CB reduces the nucleation rate of MIB and controls the crystal growth process, thereby decreasing the grain boundary number and improving the quality of MIB films. As a result, the performance of PSCs based on MIB films is further improved. Therefore, treatment of MIB films with anti-solvent is beneficial and needs further investigation.

Because mixed solvents (DMF, DMSO) are advantageous to the preparation of Perovskite thin films [21], DMSO is advantageous to the anti-solvent effect [22], and the use of DEE as anti-solvent to treat the MIB film and to investigate the performance of devices has not been explored. Hence, in this work, CB and DEE was used as anti-solvent to treat MIB films and obtain high-quality films, which were then applied to mp- TiO_2 architecture organic–inorganic hybrid PSCs as optical absorption layer. The performances of the devices based on the films treated by different anti-solvents and fabricated by traditional 1-S method were further compared. X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), UV–Vis spectrophotometry (UV–Vis), and current density–voltage (*J*–*V*) curves were used to characterize the films and explore the influence of film compactness on the performance of the devices.

2 Experimental

2.1 MIB film fabrication

The $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ precursor solution (1 mol L^{-1}) was obtained by mixing methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$, 99%, Shanghai Mater Win New Materials Co., Ltd.) and BiI_3 (99.999%, Sigma-Aldrich Co., LLC) at a ratio of 1.5:1 in 1 mL of DMF (99.8%, Shanghai Mater Win New Materials Co., Ltd)/dimethyl sulfoxide (DMSO, 99.8%, Shanghai Mater Win New Materials Co., Ltd.) solvent mixture (4:1 by volume) and filtered through a syringe filter of $0.45 \mu\text{m}$ after stirring in dark (sealed). The precursor solution was deposited on top of the mesoporous TiO_2 (mp- TiO_2) film through spin-coating method at 2000 rpm (revolutions per minute) for 6 s followed by 4000 rpm for 30 s. Then, 100

Fig. 1 Scheme of the fabrication process of the MIB layer based on the mp-TiO₂ by anti-solvent spin-coating

μL of CB (99.9%, Sigma-Aldrich Co., LLC) or DEE (99.9%, Sigma-Aldrich Co., LLC) was pipetted onto the substrate in the process of high-speed spin-coating, followed by annealing on a hot plate at 100 °C for 30 min (Fig. 1).

2.2 Fabrication of solar cell

Conductive fluorine-doped tin oxide (FTO)-coated glasses (sheet resistance 14 Ω/square), as the devices substrates, were cleaned by ultra-sonication for 20 min in deionized water and detergent mixture, deionized water, ethanol, acetone, and isopropanol, respectively. Then, the substrates were treated by ultraviolet ozone cleaner (UVO) for 25 min after drying. Direct-frequency magnetron sputtering (DFMS) was used to deposit the compact TiO₂ (cp-TiO₂) layer onto the substrates at 100 W for 30 min. The cp-TiO₂ films were annealed at 500 °C for 15 min. After cooling the substrates to room temperature, the mp-TiO₂ was deposited by spin-coating at 4000 rpm for 30 s on the top of cp-TiO₂ layer using a commercial TiO₂ paste (18-NRT, Mater Win) diluted in ethanol (1:4, weight ratio). After drying at 100 °C, the films were heated to 500 °C for 60 min to form mp-TiO₂. Then, the MIB films were fabricated by the method mentioned above. Subsequently, 30 μL of HTM was pipetted for onto the top of MIB film and spin-coated at 3000 rpm for 30 s, and then oxidized in the air for approximately 8 h. Finally, the gold counter electrodes were deposited to obtain the final devices by thermal evaporation.

2.3 Characterization

Elements analysis was carried out by XPS (Thermo Fisher) on a Scientific Escalab 250Xi instrument with monochromatized Al K-Alpha radiation. The XRD patterns of MIB films fabricated on mp-TiO₂ FTO glass were collected using a Bruker-AXS D8 Advance from 10° to 60° (2 θ) at room temperature. AFM (Nanoscope-IIIa) and FE-SEM (Jeol JEM 6510LV) were employed to characterize the surface roughness and surface morphology. The UV-Vis absorption measurements were obtained by a UV-3600 spectrophotometer (Shimadzu). The spectral test range is 300–900 nm, the light source slit width is 5 nm, and the test interval is 1 nm. The *J*–*V* characteristics were analyzed under simulated AM 1.5 G (100 mW cm^{−2} irradiance) using a solar simulator (NEWPORT, 91192-1000) and a source meter (Keithley 2400, USA). Photoluminescence (PL) spectra and time-resolved PL (TRPL) decay measurement were measured by Fluo Time 300 (Pico Quant Ltd., Germany) with an excitation of 520 nm at room temperature (20.0 MHz, 25.0 ps), and instrument test parameters: room temperature; 485 nm picosecond pulsed laser (LDH-P-C-485 nm); 530 nm filter; emission wavelength 536 nm; total output average power 2 mW. Test results were analyzed using FluoFit analysis software.

3 Results and discussion

Figure 2a shows the solution of MIB/DMF (vivid red). Figure 2b shows the annealed films fabricated by traditional 1-S method treated with CB and DEE, respectively. As

Fig. 2 Actual image of **a** MIB solution and **b** MIB films fabricated by 1-S method, untreated with anti-solvent, treated with CB and DEE, respectively

shown in Fig. 2, it is obvious that the color of the film fabricated by traditional 1-S method is lighter than the other two films; DEE/MIB is the most conspicuous, which would lead to a better compactness and stronger intensity of optical absorption, and thus, the device based on the film would have a higher PCE.

The elemental composition and valence of the near-surface atoms of the MIB films fabricated on bare FTO glass were analyzed by XPS. Figure 3f shows the peaks of I, Bi, C, N, and O. The peaks of $I\ 3d_{3/2}$ (630.44 eV) and $I\ 3d_{5/2}$ (618.98 eV) are attributed to the spin orbital of I^- . The peaks $Bi\ 4f_{5/2}$ (163.98 eV) and $Bi\ 4f_{7/2}$ (158.65 eV) can be attributed to the characteristic signals of Bi^{3+} , which indicated that Bi was mainly in the 3^+ oxidation state. Moreover, the peak of $Bi\ 4f_{7/2}$ can be attributed to both Bi–O and Bi–I bonds [24]. Two characteristic peaks of C1s in Fig. 3c with the binding energy of 285.78 and 284.68 eV corresponded, respectively, to C–N and C–C bonds in $CH_3NH_3^+$ [25, 26]. The N1s signal peak at 402.08 eV (Fig. 3d) was from $CH_3NH_3^+$. These results indicated that the MIB was successfully synthesized.

The XRD patterns of MIB fabricated on mp-TiO₂ layer are shown in Fig. 4 to further confirm MIB formation. The diffraction peaks of 12.5°, 16.2°, 37.6°, and 41.56°, according with previous work [26–28], indicated that the MIB fabricated by 1-S method belong to the hexagonal system with the P63/mmc space group [29], which confirmed the formation of the MIB perovskite. In addition, a peak of anatase TiO₂ around 42.5° was observed, which indicated that the film of MIB did not cover the substrate completely. In the XRD patterns of MIB films without treatment by anti-solvent, a weak diffraction peak of BiI_3 can be observed, which were not detected in the samples treated by anti-solvent, which suggested an almost completely transformation of BiI_3 into MIB. In the XRD patterns of CB/MIB and DEE/MIB, the peak of

anatase TiO₂ was very weak, which indicated that the films were more compact.

AFM measurement further compares the surface topography and roughness of the MIB films fabricated on mp-TiO₂ by different methods. Figure 5a shows the surface topography of the MIB films fabricated by traditional 1-S method, in which numerous holes are observed in the film. The large roughness of 188 nm is shown in Fig. 4a-1. Figure 4b and b-1 shows a better surface topography of CB/MIB film, which is more compact with the roughness reduced to 33.1 nm. Figure 4c and c-1 exhibits the highest compactness and smooth surface of DEE/MIB film with the smallest roughness of 27.5 nm and largest grain. These results indicated that the films treated by anti-solvent are more compact and smoother.

To validate the above analysis, the surface morphology of different MIB films was characterized by SEM. The images in Fig. 6 show that the compact and crystal morphology of the film untreated with anti-solvent (Fig. 6a) is inferior so that the mp-TiO₂ layer can be observed. The grain size is the smallest, which in good agreement with the XRD result of the strong TiO₂ peaks, which will cause many defects in the films ('traps'), increase the exciton recombination rate, even cause shunting paths in the device and limiting the ultimate efficiency. Figure 6b and c shows SEM images of CB/MIB and DEE/MIB, respectively. The films are more compact, and the size of the crystal increases distinctly as compared with Fig. 6a. The compactness and grain size of the DEE/MIB are best in this study; this may be ascribed to different solubility of BiI_3 and MAI. When no anti-solvent is used, DMF slowly volatilizes, and low-solubility BiI_3 precipitates first, and then high-solubility MAI precipitates to cause nucleation and growth unevenness of the perovskite crystal. As anti-solvent, DEE has a lower boiling point and stronger extraction ability than CB. DEE can faster extract DMF and volatilize, so that iodide and MAI can be supersaturated at the same time, which is more favorable for MIB nucleation. In the presence of DMSO, a BiI_3 -DMSO-MAI mesophase is formed. After heating, the DMSO is removed and the MIB crystals are gradually grown to form a uniform and dense MIB film. Hence, the perovskite layer has the largest coverage, which may increase the absorption intensity and PCE. Figure 6a-1 to c-1 shows the cross-sectional images of different films, which show that the films treated by anti-solvent are more compact, with thickness of about 300 nm.

The absorption spectra of the MIB films on the FTO substrate are shown in Fig. 7a. The absorption range of all films was between 300–600 nm, and the absorption edge was about in 700 nm. Compared with other films,

Fig. 3 The high-resolution XPS spectra of as-made MIB film on bare FTO substrate: **a** I 3d, **b** Bi 4f, **c** C 1f, **d** N 1s, **e** O 1s, and **f** overview XPS spectra of MIB

the absorption intensity of the DEE/MIB was the strongest because of their high crystallinity and high coverage, which can be supported by the SEM images. Moreover, the absorption intensity of crystals enhanced with the increase

in grain size [30]. The stronger absorption intensity produces more excitons, which is beneficial to the device performance. Figure 7b shows the Tauc curves of DEE/MBI. We calculated the band gap of DEE/MBI (2.16 eV) by plotting

Fig. 4 XRD patterns of MIB fabricated on mp-TiO₂ layer, untreated with anti-solvent, treated with CB and DEE, respectively

the diagram of $(\alpha h\nu)^2$ against $h\nu$ obtained from the UV-Vis absorption spectra.

Figure 8a, c, and d shows the different diagrams of MIB PSCs, including cp-TiO₂ layer, mp-TiO₂ layer, MIB layer, HTM layer, and Au counter electrode. The valence band (-5.9 eV) of MIB is lower than the work functions of Spiro-OMe TAD, and thus, the holes can be transported easily through perovskite layer and collected by the gold electrode. The conduction band (-3.8 eV) of MIB matched well with that of TiO₂ (-4.2 eV). The wider pattern of energy conductor of TiO₂ facilitates the electron transfer from MIB layer to TiO₂ layer [31].

All fabrication procedures of devices were carried out in ambient atmosphere, with humidity of $> 50\%$. The photoelectric performance of all devices was evaluated under simulated AM 1.5 G (100 mW cm^{-2}). The $J-V$ characteristics of MIB PSCs based on the films treated with different anti-solvent are shown in Fig. 9, and the relevant parameters of the photoelectric performance are shown in Table 1. The highest PCE of the devices based on the MIB films fabricated by transitional 1-S method is 0.082%, with the V_{oc} , J_{sc} , and FF of 715 mV, 0.300 mA cm^{-2} , and 38.23%, respectively. The PCE of the devices based on the MIB films treated with anti-solvent enhanced obviously. The devices based on the CB/MIB film exhibited a PCE of 0.185%, and the V_{oc} (844 mV), J_{sc} (0.502 mA cm^{-2}), and FF (43.67%) were also enhanced. As expected, the devices based on DEE/MIB film exhibited the highest PCE of 0.343%. These devices also had the best photoelectric performance in terms of V_{oc} (885 mV), J_{sc} (0.807 mA cm^{-2}), and FF (49.71%). The best performance of the devices fabricated by DEE/MIB film can be attributed to the smoother, lower defects, and more compacter MIB layer with larger grain and lower charge trap density.

Eight devices based on DEE/MIB film were selected in a batch of devices fabricated in same experiment condition and processes to test the repeatability. The corresponding photoelectric parameters are shown in Fig. 10 and Table 2. The PCE of 85.7% of the devices was over 0.3%, and the V_{oc} , J_{sc} , and FF of these devices were almost higher than 800 mV, 0.8 mA cm^{-2} , and 43%, respectively, which indicated that the devices based on DEE/MIB film had good repeatability.

PCE decay was measured to test the stability of the devices based on DEE/MIB film. As shown in Fig. 11 and

Fig. 5 AFM 2D topography images and 3D views of as-made MIB films **a** and **a-1** untreated with anti-solvent, **b**, **b-1** and **c**, **c-1** CB/MIB and DEE/MIB, respectively

Fig. 6 **a–c** Top-view FE-SEM images, and **a-1** to **c-1** cross-sectional FE-SEM image of the MIB films untreated with anti-solvent, CB/MIB and DEE/MIB, respectively

Table 3, the PCE of these devices remained high at 0.3% in ambient air (approximately 30% humidity) for 200 days, although the devices showed a decaying trend. The small PCE decrease of 7.58% indicated that the PSCs based on DEE/MIB film exhibited excellent long-term stability.

The J - V curves demonstrated that the devices based on films treated by anti-solvent have a high FF, which indicated that the films treated by anti-solvent had fewer defects. However, the PCE of all devices was still low. Besides the high exciton binding energy, the internal defects of MIB films are also an important factor influencing the FF and PCE values [32, 33]. To further investigate the defect state of the films, PL curves were obtained on the quartz glass substrates, as shown in Fig. 12. The strongest photoluminescence intensity of DEE/MIB film revealed that DEE/MIB had less nonradiative recombination, which indicated fewer trap density states of DEE/MIB. Therefore, the devices based on DEE/MIB have the highest FF. However, all carrier lifetime of the MIB film fabricated in this work is much smaller than that of Pb-based perovskite films. Hence, the performance of all devices based on the MIB films should be optimized further.

Table 3 summarizes the photoelectric properties of all bismuth-based perovskite solar cells (MIB PSCs) prepared by using anti-solvent methods in previous studies and in our work. Sawanta and co-workers improved the performance of MIB PSCs by treatment with chlorobenzene [15]. Our work mainly used chlorobenzene and diethyl ether as anti-solvents to treat MIB films. Then, we compared different MIB films in terms of morphology, internal defects, and photoelectric performance. When we used diethyl ether

Fig. 7 **a** UV-Vis spectra of the different MIB films, **b** indirect band gap Tauc plot of DEE/MIB

Fig. 8 **a** Device structure and **b** energy level diagram of the MIB PSCs, **c** cross-sectional FE-SEM image of the MIB PSCs, **d** 3D diagram of MIB PSCs matched with (a) and (c)

Fig. 9 *J*-*V* curves of the PSCs based on the MIB films treated with different anti-solvent under simulated AM 1.5 G (100 mW cm^{-2})

Table 1 Device parameters of PSCs based on the MBI films treated with different anti-solvent under simulated AM 1.5 G (100 mW cm^{-2})

Samples	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
MBI	715	0.300	38.23	0.082
CB/MBI	844	0.502	43.67	0.185
DEE/MBI	885	0.807	49.71	0.343

(DEE) as anti-solvent instead of CB, the devices exhibited superior performance in terms of V_{oc} (885 mV), J_{sc} (0.807 mA cm^{-2}), FF (49.71%), and PCE (0.343%). The PCE of the devices in our work is comparable with that of devices reported by Sawanta, but the devices treated by DEE in our work have higher V_{oc} and FF. In our work, all performances of the MIB PSCs treated by DEE are higher than the devices

Fig. 10 Histograms of photovoltaic parameters for 8 devices (the same batch of samples) based on DEE/MIB, under simulated AM 1.5 G (100 mW cm^{-2} irradiance)

Table 2 Photoelectric parameters for eight devices based on DEE/MBI

Samples	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
1	850	0.791	43.73	0.294
2	889	0.802	42.58	0.307
3	865	0.794	46.45	0.319
4	845	0.786	49.38	0.328
5	880	0.801	47.67	0.336
6	874	0.803	48.73	0.342
7	885	0.807	49.71	0.343
8	885	0.807	49.71	0.343

treated by CB. Compared to our previous works [34, 35], the performance of MIB PSCs treated by anti-solvents is much higher than those of the devices fabricated by traditional method. The photoelectric properties of the devices treated by DEE are also the best among all devices.

4 Conclusions

This work introduced DEE as anti-solvent in 1-S method for the first time to improve MIB films for fabricated PSCs. MIB, CB/MIB, and DEE/MIB films were prepared and tested. Results showed that DEE/MIB was the most compact, with the largest grains and lowest roughness. The device based

Fig. 11 J - V curves of MIB PSC based on DEE/MIB under simulated AM 1.5 G (100 mW cm^{-2} irradiance), **a** measured immediately and **b** measured after exposed to humid dark environment without any sealing (> 30% relative humidity) for 200 days

on DEE/MIB exhibited the best photoelectric property, which should attribute to the strong extraction function DEE, which can extract the solvent of perovskite immediately. Given that the boiling point of DEE is lower than that of CB, DEE can volatilize at room temperature, which can remove DMF to facilitate the separation of BiI_3 and MAI. The PSCs based on DEE/MIB achieved highest PCE

Table 3 Photoelectric parameters of MBI based PSCs in different works

Device structure	Anti-solvent	PCE (%)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)
cp-TiO ₂ /mp-TiO ₂ /(CH ₃ NH ₃) ₃ Bi ₂ I ₉ /Spiro-OMe TAD/Au [15]	Chlorobenzene	0.356	0.653	1.100	49.60
cp-TiO ₂ /mp-TiO ₂ /(CH ₃ NH ₃) ₃ Bi ₂ I ₉ /C [32] ^a	–	0.054	0.895	0.255	24.00
cp-TiO ₂ /TiO ₂ -NRAs/(CH ₃ NH ₃) ₃ Bi ₂ I ₉ /Spiro-OMe TAD/Au [33] ^a	–	0.150	0.593	0.691	36.61
cp-TiO ₂ /mp-TiO ₂ /(CH ₃ NH ₃) ₃ Bi ₂ I ₉ /Spiro-OMe TAD/Au ^a	Ether	0.343	0.884	0.807	49.72

^aOur work **Fig. 12** Photoluminescence spectra of MIB film treated with different anti-solvent

and long-term stability. This study also showed that the MIB films can be improved through optimization of process parameters and selection of appropriate anti-solvent.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Shi Z, Guo J, Chen Y, Li Q, Pan Y, Zhang H, Huang W (2017) Lead-free organic-inorganic hybrid perovskites for photovoltaic applications. *Adv Mater* 29(16):1605005–1605033. <https://doi.org/10.1002/adma.201605005>
- Eperon GE, Burlakov VM, Docampo P, Goriely A, Snaith HJ (2014) Morphological control for high performance, solution-processed planar heterojunction perovskite solar cells. *Adv Funct Mater* 24(1):151–157. <https://doi.org/10.1002/adfm.201302090>
- Xiao M, Huang F, Huang W, Dkhissi Y, Zhu Y, Etheridge J, Gray-Weale A, Bach U, Cheng YB, Spiccia L (2014) A fast deposition-crystallization procedure for highly efficient lead iodide perovskite thin-film solar cells. *Angew Chem Int Ed* 53(37):9898–9903. <https://doi.org/10.1002/ange.201405334>
- Kim HS, Lee CR, Im JH, Lee KB, Moehl T, Marchioro A, Grätzel M (2012) Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%. *Sci Rep* 2:591–597. <https://doi.org/10.1038/srep00591>
- Burschka J, Pellet N, Moon SJ, Humphry-Baker R, Gao P, Nazeeruddin MK, Grätzel M (2013) Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature* 499(7458):316–319. <https://doi.org/10.1038/nature12340>
- Chen Q, Zhou H, Hong Z, Luo S, Duan HS, Wang HH, Yang Y (2013) Planar heterojunction perovskite solar cells via vapor-assisted solution process. *J Am Chem Soc* 136(2):622–625. <https://doi.org/10.1021/ja411509g>
- Liu M, Johnston MB, Snaith HJ (2013) Efficient planar heterojunction perovskite solar cells by vapour deposition. *Nature* 501(7467):395–398. <https://doi.org/10.1038/nature12509>
- Kim HB, Choi H, Jeong J, Kim S, Walker B, Song S, Kim JY (2014) Mixed solvents for the optimization of morphology in solution-processed, inverted-type perovskite/fullerene hybrid solar cells. *Nanoscale* 6(12):6679–6683. <https://doi.org/10.1039/c4nr00130c>
- Heo JH, Song DH, Im SH (2014) Planar CH₃NH₃PbBr₃ hybrid solar cells with 10.4% power conversion efficiency, fabricated by controlled crystallization in the spin-coating process. *Adv Mater* 26(48):8179–8183. <https://doi.org/10.1002/adma.201403140>
- Chen CC, Hong Z, Li G, Chen Q, Zhou H, Yang Y (2015) One-step, low-temperature deposited perovskite solar cell utilizing small molecule additive. *J Photon Energy* 5(1):057405–057413. <https://doi.org/10.1117/1.JPE.5.057405>
- Song X, Wang W, Sun P, Ma W, Chen ZK (2015) Additive to regulate the perovskite crystal film growth in planar heterojunction solar cells. *Appl Phys Lett* 106(3):033901–033901-5. <https://doi.org/10.1063/1.4906073>
- Jeon NJ, Noh JH, Kim YC, Yang S, Ryu S, Seok SI (2014) Solvent engineering for high-performance inorganic–organic hybrid perovskite solar cells. *Nat Mater* 13(9):897–903. <https://doi.org/10.1038/nmat4014>
- Seo J, Park S, Kim YC, Jeon NJ, Noh JH, Yoon SC, Seok SI (2014) Benefits of very thin PCBM and LiF layers for solution-processed p-i-n perovskite solar cells. *Energy Environ Sci* 7(8):2642–2646. <https://doi.org/10.1039/C4EE01216J>
- Byravan MM, Song S, Pyeon L, Kang G, Lee GY, Park T (2017) Simple post annealing-free method for fabricating uniform, large grain-sized, and highly crystalline perovskite films.

- Nano Energy 34:181–187. <https://doi.org/10.1016/j.nanoen.2017.02.017>
15. Mali SS, Kim H, Kim DH, Kook Hong C (2017) Anti-solvent assisted crystallization processed methylammonium bismuth iodide cuboids towards highly stable lead-free perovskite solar cells. *Chem Sel* 2(4):1578–1585. <https://doi.org/10.1002/slct.201700025>
 16. Yin M, Xie F, Chen H, Yang X, Ye F, Bi E, Han L (2016) Annealing-free perovskite films by instant crystallization for efficient solar cells. *J Mater Chem A* 4(22):8548–8553. <https://doi.org/10.1039/C6TA02490D>
 17. Lin N, Qiao J, Dong H, Ma F, Wang L (2015) Morphology-controlled $\text{CH}_3\text{NH}_3\text{PbI}_3$ films by hexane-assisted one-step solution deposition for hybrid perovskite mesoscopic solar cells with high reproducibility. *J Mater Chem A* 3(45):22839–22845. <https://doi.org/10.1039/C5TA04051E>
 18. Kara K, Kara DA, Kirbiyik C, Ersoz M, Usluer O, Briseno AL, Kus M (2016) Solvent washing with toluene enhances efficiency and increases reproducibility in perovskite solar cells. *RSC Adv* 6(32):26606–26611. <https://doi.org/10.1039/C5RA27122C>
 19. Bae S, Han SJ, Shin TJ, Jo WH (2015) Two different mechanisms of $\text{CH}_3\text{NH}_3\text{PbI}_3$ film formation in one-step deposition and its effect on photovoltaic properties of OPV-type perovskite solar cells. *J Mater Chem A* 3(47):23964–23972. <https://doi.org/10.1039/C5TA06870C>
 20. Li M, Yan X, Kang Z, Liao X, Li Y, Zheng X, Zhang Y (2017) Enhanced efficiency and stability of perovskite solar cells via anti-solvent treatment in two-step deposition method. *ACS Appl Mater Interfaces* 9(8):7224–7231. <https://doi.org/10.1021/acsami.7b01136>
 21. Shin SS, Correa Baena JP, Kurchin RC (2018) Solvent-engineering method to deposit compact bismuth-based thin films: mechanism and application to photovoltaics. *Chem Mater* 30(2):336–343. <https://doi.org/10.1021/acs.chemmater.7b03227>
 22. Ahn N, Son DY, Jang IH (2015) Highly reproducible perovskite solar cells with average efficiency of 18.3% and best efficiency of 19.7% fabricated via Lewis base adduct of lead (II) iodide. *J Am Chem Soc* 137(27):8696–8699. <https://doi.org/10.1021/jacs.5b04930>
 23. Hoefler SF, Rath T, Fischer R (2018) A zero-dimensional mixed-anion hybrid halogenobismuthate (III) semiconductor: structural, optical, and photovoltaic properties. *Inorg Chem* 57(17):10576–10586. <https://doi.org/10.1021/acs.inorgchem.8b01161>
 24. Hoyer RL, Brandt RE, Osherov A, Stevanović V, Stranks SDMW, Wilson Poindexter JR (2016) Methylammonium bismuth iodide as a lead-free, stable hybrid organic-inorganic solar absorber. *Chem Eur J* 22(8):2605–2610. <https://doi.org/10.1002/chem.201505055>
 25. Fabian DM, Ardo S (2016) Hybrid organic-inorganic solar cells based on bismuth iodide and 1,6-hexanediammonium dication. *J Mater Chem A* 4(18):6837–6841. <https://doi.org/10.1039/C6TA00517A>
 26. Öz S, Hebig JC, Jung E, Singh T, Lepcha A, Olthof S, Jan F, Gao Y, German R, van Loosdrecht PH, Meerholz K (2016) Zero-dimensional $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ perovskite for optoelectronic applications. *Sol Energy Mater Sol C* 158:195–201
 27. Eckhardt K, Bon V, Getzschmann J, Grothe J, Wisser FM, Kaskel S (2016) Crystallographic insights into $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$: a new lead-free hybrid organic-inorganic material as a potential absorber for photovoltaics. *Chem Commun* 52(14):3058–3060. <https://doi.org/10.1039/C5CC10455F>
 28. Johansson MB, Zhu H, Johansson EM (2016) Extended photo-conversion spectrum in low-toxic bismuth halide perovskite solar cells. *J Phys Chem Lett* 7(17):3467–3471. <https://doi.org/10.1021/acs.jpclett.6b01452>
 29. Lyu M, Yun JH, Cai M, Jiao Y, Bernhardt PV, Zhang M, Wang L (2016) Organic-inorganic bismuth (III)-based material: a lead-free, air-stable and solution-processable light-absorber beyond organolead perovskites. *Nano Res* 9(3):692–702. <https://doi.org/10.1007/s12274-015-0948-y>
 30. Li X, Bi D, Yi C, Décoppet D, Luo J, Zakeeruddin SM, Mi Grätze (2016) A vacuum flash-assisted solution process for high-efficiency large-area perovskite solar cells. *Science* 353(6294):58–62. <https://doi.org/10.1126/science.aaf8060>
 31. Yusoff ARBM, Nazeeruddin MK (2016) Organohalide lead perovskites for photovoltaic applications. *J Phys Chem Lett* 7(5):851–866. <https://doi.org/10.1021/acs.jpclett.5b02893>
 32. Ran C, Wu Z, Xi J, Yuan F, Dong H, Lei T, Hou X (2017) Construction of compact methylammonium bismuth iodide film promoting lead-free inverted planar heterojunction organohalide solar cells with open-circuit voltage over 0.8 V. *J Phys Chem Lett* 8(2):394–400. <https://doi.org/10.1021/acs.jpclett.6b02578>
 33. Hutter EM, Eperon GE, Stranks SD, Savenije TJ (2015) Charge carriers in planar and meso-structured organic-inorganic perovskites: mobilities, lifetimes, and concentrations of trap states. *J Phys Chem Lett* 6(15):3082–3090. <https://doi.org/10.1021/acs.jpclett.5b01361>
 34. Kong M, Hu H, Wan L, Chen M, Gan Y, Wang J, Wang S (2017) Nontoxic $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ perovskite solar cells free of hole conductors with an alternative architectural design and a solution-processable approach. *RSC Adv* 7(56):35549–35557. <https://doi.org/10.1039/C7RA04924B>
 35. Chen M, Wan L, Kong M, Hu H, Gan Y, Wang J, Wang S (2018) Influence of rutile- TiO_2 nanorod arrays on Pb-free $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ -based hybrid perovskite solar cells fabricated through two-step sequential solution process. *J Alloys Compd* 738:22–431. <https://doi.org/10.1016/j.jallcom.2017.12.188>

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