

Controllable Crystallization of $\text{CH}_3\text{NH}_3\text{Sn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ Perovskites for Hysteresis-Free Solar Cells with Efficiency Reaching 15.2%

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While Sn–Pb alloyed perovskites have been considered as an effective approach to broaden the absorption spectrum, it is still challenging to modify the crystallization (and thus morphology, crystallinity, and orientation) in a controllable manner and thus boost the efficiency of Sn–Pb alloyed perovskite solar cells. Here, it is unveiled that controlling the crystallization of $\text{CH}_3\text{NH}_3\text{Sn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ films can be simply realized by adjusting the amount of dimethyl sulfoxide in precursors, which has not been reported in Sn–Pb alloyed perovskite systems. The remarkable perovskite crystallinity enhancement by the 20-fold enhanced (110) plane intensity in the X-ray diffraction spectrum of $\text{CH}_3\text{NH}_3\text{Sn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ and the preferred (110) orientation with the texture coefficient enhanced by 2.6 times to reach 0.88 are demonstrated. Importantly, it is discovered that the introduction of dimethyl sulfoxide avoids the formation of the colloidal coagulation observed in prolonged-storage precursors and ameliorates inhomogeneous Sn/Pb distributions in resultant perovskite films. Through optimizing perovskite films and device structures, hysteresis-free planar-heterojunction $\text{CH}_3\text{NH}_3\text{Sn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ solar cells with the efficiency reaching 15.2%, which are the most efficient Sn–Pb alloy-based perovskite solar cells, are achieved.

As for the recent widely studied materials of hybrid organometallic halide perovskites, alloying is also effective to modify the absorption wavelength region. The most widely used $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{SnI}_3$ have the absorption edge at about 800 and 950 nm, respectively.^[3,4] Interestingly, the Sn–Pb alloyed perovskite materials can extend the absorption edge to over 1000 nm.^[4–6] For instance, $\text{CH}_3\text{NH}_3\text{Sn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ perovskite solar cells (PVSCs) constructed on mesostructured substrates can harvest the light in the wavelength up to 1060 nm.^[5–7] However, due to the reducibility of Sn(II), the required experimental conditions for Sn and Sn–Pb-based materials are typically more rigorous than for the pure Pb-based ones. It is still challenging to control the film formation and crystallinity of Sn–Pb-based perovskite materials, which hinders the enhancement of device performances.^[3,5,8] More works on the film formation and microstructure control

of Sn-contained perovskite materials are required to improve device performances toward those reported in pure Pb-based PVSCs. Importantly, some fundamental issues in the Sn-contained system, such as Sn and Pb distributions, need to be addressed for understanding and improving device performances.

Herein, we introduce dimethyl sulfoxide (DMSO) to realize the film formation and microstructure control of Sn–Pb alloyed perovskite films. By controlling the crystallization rate, the $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ films show the large enhancement of perovskite crystallinity with the 20-fold enhanced (110) peak intensity and the strong (110) preferred orientation with the texture coefficient improved by 2.6 times to a value of 0.88. Smooth and pinhole-free Sn–Pb alloyed perovskite films on planar substrates are successfully fabricated. Furthermore, the introduction of DMSO is found to prevent the formation of the colloidal coagulation observed in prolonged-storage precursors and ameliorate inhomogeneous Sn/Pb distributions. Finally, hysteresis-free planar-heterojunction $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ PVSCs achieve the power conversion efficiency (PCE) of 15.2%, which is, to the best of knowledge, the highest value among Sn–Pb alloyed PVSCs.^[4–6,9,10]

1. Introduction

Inorganic-compound semiconductors such as cadmium telluride (CdTe), copper indium selenide (CIS), and gallium arsenide (GaAs) are widely recognized as excellent materials for photovoltaic devices.^[1,2] To further improve their device performances by matching the solar spectrum, introducing congeners to form alloyed compounds is an effective method. By partially replacing indium in CIS with gallium, the bandgap can be reduced and the absorption spectrum can be extended to the longer wavelength. These alloyed copper indium gallium selenide (CIGS) solar cells have the comparable efficiency with polycrystalline silicon solar cells.^[1]

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2. Results and Discussion

2.1. Formation of Sn–Pb Alloyed Perovskites

While there are very limited studies in controlling the crystallization (and thus morphology, crystallinity, and crystal orientation) of Sn–Pb alloyed perovskites, which are important for achieving high-performance perovskite solar cells, we introduce DMSO to form high-quality $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskites with the smooth surface, high crystallinity, and preferential orientation through the controlled crystallization of SnI_2 – PbI_2 in *N,N*-dimethylformamide (DMF).

To prepare high-quality Sn–Pb alloyed perovskite films, we introduced DMSO into the mixed solvent for perovskite precursors. On top of the role as a solvent, DMSO serves as a relatively stronger capping agent for SnI_2 and PbI_2 , which can retard the crystallization of these metal iodides to hybrid perovskites.^[3,11] As described in the Experimental Section, we dissolved PbI_2 , $\text{CH}_3\text{NH}_3\text{I}$ (MAI), and SnI_2 sequentially in pure DMF or mixed solvents. We named the studied four systems in this work as DMSO-0, DMSO-25, DMSO-50, and DMSO-75, corresponding to the volume percentage of DMSO of 0%, 25%, 50%, and 75%, respectively, in the mixed solvents. To form dense and pinhole-free $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskites, the effects of the DMSO amount in the raw precursors on the crystallization of Sn–Pb alloyed perovskite films are also investigated.

Interestingly, during the film formation, films coated from Sn–Pb alloyed precursors became light brown immediately after washed by the antisolvent and then gradually turned into dark brown, which is completely different from the pure Pb-based system in which a transparent MAI– PbI_2 –DMSO intermediate formed at the same stage using the similar approach.^[11,12] This can be explained by the fact that SnI_2 reacts faster with MAI to form organometallic halide perovskites than PbI_2 does.^[13] By reducing the amount of DMSO in the mixed solvent, the reaction from precursors to perovskites becomes faster due to the weaker bonding ability and more volatile property of DMF. Our results show that, in the case of DMSO-0, the films even turned dark immediately after being washed by

the antisolvent. Consequently, our results show that DMSO can be used to control the crystallization of $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskites and thus determine the film formation.

2.2. Morphology, Crystallinity, and Orientation of Sn–Pb Alloyed Perovskites

The surface morphologies of deposited Sn–Pb alloyed perovskite films formed from various DMSO concentration-based precursors are shown in Figure 1. Clearly, all these films show uniform grains without any pinholes and 100% surface coverage on planar substrates. Compared with perovskites produced from precursors containing DMSO in Figure 1b–d, DMSO-0-based perovskite films (Figure 1a) are relatively rough with the roughness of 65 nm, which was confirmed by the atomic force microscope (AFM) measurement (Figure S1, Supporting Information). Distinctively, perovskite films produced from DMSO-25, DMSO-50, and DMSO-75-based precursors present compact and smooth films with the roughness of only 11, 12, and 6 nm, respectively.

Interestingly, the introduction of DMSO in the raw precursors can significantly increase the grain/crystal size of Sn–Pb perovskites. DMSO-25 and DMSO-50-based films achieve large grain sizes of about 250 and 200 nm, respectively, while DMSO-0-based films show small grain sizes of about 100 nm. Excess DMSO in the raw precursor (DMSO-75) causes the small grain size, as shown in Figure 1d. Meanwhile, the crystal sizes of Sn–Pb perovskites calculated by the Scherrer equation from X-ray diffraction (XRD) patterns (Figure 1e) are 22, 69, 47, and 29 nm, for the cases of DMSO-0, DMSO-25, DMSO-50, and DMSO-75, respectively. This change of perovskite grain/crystal sizes can be further confirmed by AFM images (Figure S1, Supporting Information). The underlying mechanism for growing Sn–Pb alloyed perovskites with different grain sizes will be discussed later.

The XRD measurement was employed to investigate the crystallinity and orientation of fabricated Sn–Pb perovskite films. Remarkably, compared with DMSO-0-based perovskites,

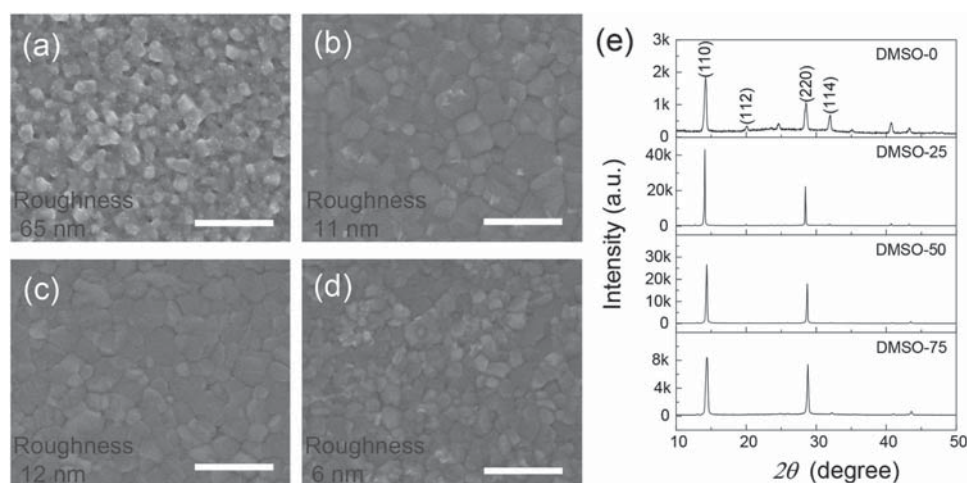


Figure 1. Top-view scanning electron microscope (SEM) images of Sn–Pb alloyed perovskite films produced from different DMSO/DMF ratios based precursors: a) DMSO-0, b) DMSO-25, c) DMSO-50, d) DMSO-75; and e) corresponding XRD patterns. The scale bars are 500 nm.

DMSO-25, DMSO-50, and DMSO-75-based Sn–Pb perovskites achieve significantly enhanced diffraction intensities of (110) plane by over 20, 14, and 4-folds, respectively. This indicated the enhancement of perovskite crystallinity. With the increase of DMSO amount, intensities of alloyed Sn–Pb perovskites gradually decrease. This is quite similar to the case of the pure Pb-based system, in which the excess DMSO molecules lead to uncrystallized PbI_2 film and thus lower perovskite crystallinity.^[14] Consequently, a suitable DMSO amount in the mixed solvent can effectively control the crystallinity of alloyed Sn–Pb perovskites.

The preferred orientation of the film is characterized by the texture coefficient.^[15] The texture coefficient of the (110) plane relative to (112) plane (TC_{110}) can be derived by

$$TC_{110} = \frac{I_{110}/I_{110}^0}{I_{110}/I_{110}^0 + I_{112}/I_{112}^0} \quad (1)$$

where I_{110} and I_{112} are the respective measured XRD intensities of the (110) and (112) planes at the peak height. I_{110}^0 and I_{112}^0 are the respective powder diffraction intensities of each plane. Since 25% Sn-based perovskite $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ does not change the crystal structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$, I_{110}^0 and I_{112}^0 are extracted from powder diffraction intensities of $\text{CH}_3\text{NH}_3\text{PbI}_3$.^[16] The estimated TC_{110} for DMSO-0, DMSO-25, DMSO-50, and DMSO-75-based perovskites are 0.34, 0.81, 0.88, and 0.74, respectively. Distinctly, the higher value of TC_{110} for the mixed solvent based Sn–Pb alloyed perovskites suggests that the introduction of DMSO will effectively enhance the orientation of the main plane. Moreover, by controlling the DMSO amount, the perovskite orientation of the main plane can be easily modified. Preferred (110) orientation was further confirmed by the increased bandgap of $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ films (Figure S2, Supporting Information), which is consistent with the density functional theory calculations that energy gap for the (110) surfaces is larger than other surfaces.^[17] As a consequence, alloyed Sn–Pb-based perovskites with high crystallinity and preferential orientation are expected to facilitate the carrier transport ability (Figure S3, Supporting Information), and thus boost PVSCs with $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ as the light absorber.^[18,19]

2.3. Colloidal System and Reaction Mechanism

In this section, the underlying crystallization of Sn–Pb alloyed perovskites is studied. Importantly, the DMSO functions of eliminating a colloidal coagulation in prolonged-storage DMSO-0 precursors and ameliorating inhomogeneous Sn/Pb distributions will be demonstrated.

The colloidal-based perovskite growth can be employed to explain the crystallization of Sn–Pb perovskites as shown in Figure 2a.^[20] Apart from the high viscosity and lower vapor pressure than DMF, DMSO can also coordinate PbI_2 or SnI_2 to form relatively stable intermediates.^[3,13] After redundant solvents are removed during spin-coating, the capped metal iodide colloidal cluster (confirmed by the Tyndall scattering shown in Figure 2b) and MAI in the wet film will begin to grow perovskites. In the case of DMSO-0-based precursors, MAI will take the position of DMF and react with SnI_2 and PbI_2 . The DMF-capped clusters can offer massive reaction sites between MAI and $\text{SnI}_2/\text{PbI}_2$. The relatively rapid reaction rate will divide the large colloid cluster into pieces, resulting in small perovskite grains, poor crystallinity, and random orientation. For the DMSO/DMF mixed precursors, the surface of clusters is mainly capped with DMSO, owing to the higher affinity of DMSO toward metal iodides than that of DMF. Under such relatively slow reaction rates, the clusters will be divided into a few parts, thus leading to larger sizes of perovskite grains, enhanced crystallinity, and preferred orientation.^[21] However, the excess DMSO will dissolve the PbI_2 and SnI_2 colloidal clusters into smaller sizes.^[22] This accounts for the fact that the grain sizes in DMSO-75-based perovskites are smaller than

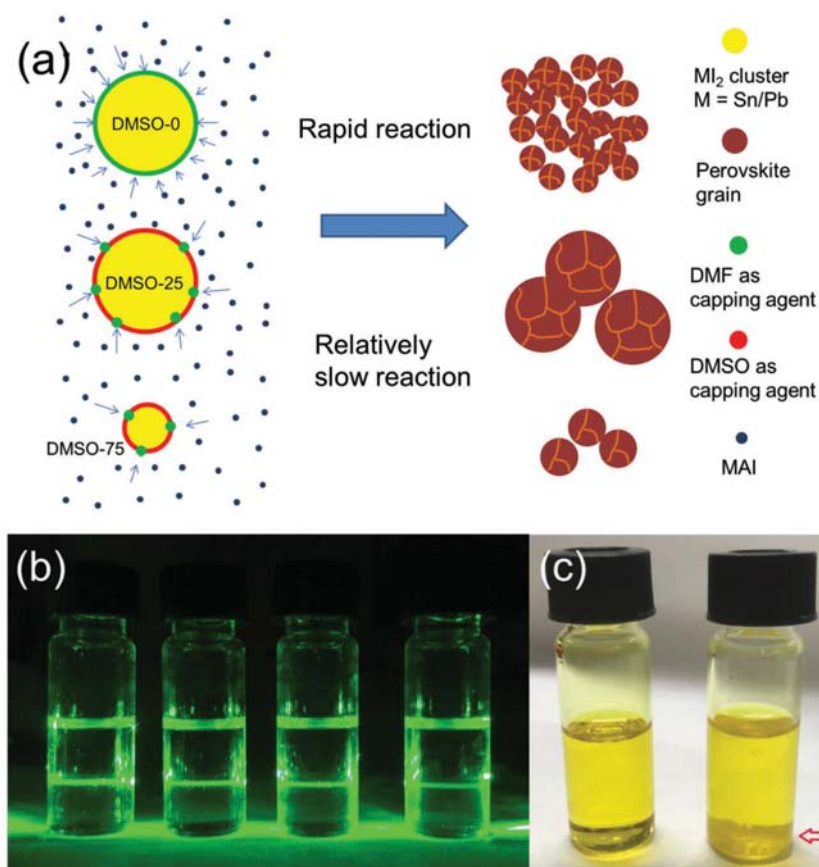


Figure 2. a) Schematic diagram of the reaction mechanism of Sn–Pb alloyed perovskites from different DMSO/DMF solvent ratios; b) photographs of the Tyndall effect in Sn–Pb perovskite precursors, DMSO-0, DMSO-25, DMSO-50, and DMSO-75 from left to right; c) photographs of (left) DMSO-25-based precursors and (right) colloidal coagulation phenomenon in the prolonged-storage DMSO-0-based precursors.

that of DMSO-25-based perovskites. Consequently, by adjusting the DMSO amount in the raw precursors, the reaction sites between MAI and $\text{SnI}_2\text{-PbI}_2$ will be effectively controlled, which results in different grain sizes of alloyed Sn–Pb perovskites and thus its different morphologies.

Importantly, a unique phenomenon in alloyed Sn–Pb perovskite systems was observed in our results. As indicated by the red arrow in Figure 2c, some white insolubles in the prolonged-storage DMSO-0-based precursors will form, while the DMSO-25-based precursors in the left vial maintain clear. It should be noted that the insolubles may not be re-dissolved in the excess amount of DMF or DMSO. Apparently, the insolubles are a typical colloidal coagulation, rather than precipitation, caused by mixing two different colloidal systems, which are SnI_2 and PbI_2 in this case. Meanwhile, this coagulation was not observed when the percentage of DMSO in the mixed solvent was over 25%. This implies that the introduction of DMSO in the mixed solvents eliminates the formation of a colloidal coagulation observed in pure DMF-based precursors and then forms relatively stable Sn–Pb mixed iodide colloids, which is highly preferred in practical applications.

Another concern is that the colloidal nature of Sn–Pb-based precursors may cause nonuniformly mixed Sn–Pb in precursors and thus affect the element distributions in the final Sn–Pb alloyed perovskites. Indeed, alloyed materials-based CIGS solar cells with inhomogeneous distributions of In and Ga can cause bandgap fluctuations and result in open-circuit voltage losses.^[23] To have a deep understanding of Sn–Pb alloyed materials, we scraped the perovskite film off and dispersed the obtained perovskite powders in toluene to study Sn and Pb distributions. From the transmission electron microscopy (TEM) image in Figure 3a, all the grains have sizes of hundred nanometers and shapes without shattered. The individual perovskite particles are then studied by energy dispersive X-ray spectroscopy (EDS) integrated to the TEM system. It should be noted that ten individual particles just like those shown in Figure 3b were randomly selected in EDS analysis to avoid any unexpected interference signal from adjacent particles. The results of Sn element mapping are summarized in Table 1; the Sn percentages (defined as the ratio of Sn atoms over the total atoms of Sn and Pb) in Sn–Pb alloyed perovskites are not constant. In the case of pure DMF-based films (i.e., DMSO-0), the Sn percentage fluctuated significantly from 10.0% to 36.4% with the standard deviation (SD) of 8.61%. When DMSO is added, in the DMSO-25 system, the Sn percentage shows much narrower fluctuation from 14.7% to 31.7% with a smaller SD of 5.02%. Further increasing the DMSO amount in DMSO-50 and DMSO-75 systems, the Sn percentages change from 11.2% to 26.9% with the SD of

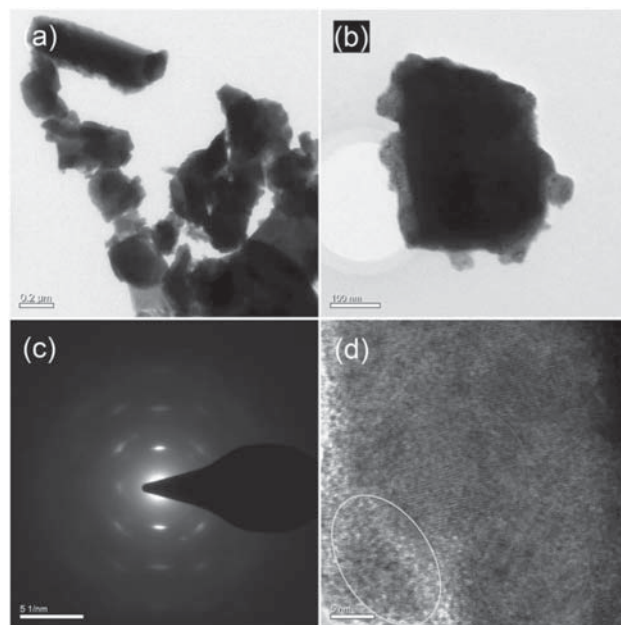


Figure 3. TEM images of a) dispersed perovskites scraped from their films, and b) individual perovskite particles; c) SAED pattern and d) TEM image of the perovskite particles in (b).

4.36%, and from 16.3% to 30.2% with the SD of 4.23%, respectively. Consequently, the results show that the Sn–Pb alloyed perovskites are inhomogeneous under the high spatial resolution on a 100 nm scale, which is similar to the reported CIGS system^[23] and thus would affect the device performances as studied later. Importantly, the introduction of DMSO ameliorates inhomogeneous distributions that will improve the film quality and device performances.

Meanwhile, inhomogeneous Sn/Pb distributions can partially affect the quality of perovskite films because of some delicate differences between SnI_2 and PbI_2 . For instance, due to the different crystal textures of PbI_2 and SnI_2 , the relatively large segregation of SnI_2 and PbI_2 in DMSO-0 precursors will favor low crystallinity and random orientation in the resultant perovskite films, as shown in Figure 1. After the introduction of DMSO, the SnI_2 and PbI_2 will mix better and thus facilitate the formation of perovskites with high crystallinity and preferred orientations. Urbach energy is used to characterize the energetic disorder level of semiconductors,^[10,24] which was estimated to be 19.0, 17.6, 16.8, and 17.1 meV for DMSO-0, DMSO-25, DMSO-50, and DMSO-75-based films, respectively. It further confirms that the presence of DMSO increases the energetic order level of $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ films.

Table 1. The Sn percentage (defined as the ratio of Sn atoms over the total atoms of Sn and Pb) in DMSO-0, DMSO-25, DMSO-50, and DMSO-75-based individual perovskite particles.

Samples	1	2	3	4	5	6	7	8	9	10	Avg.	SD
DMSO-0	23.3	17.7	33.2	22.4	13.8	36.4	30.0	16.2	10.0	25.4	22.8	8.61
DMSO-25	20.3	18.6	22.1	26.1	19.5	21.3	16.7	31.7	14.7	25.8	21.7	5.02
DMSO-50	26.0	20.5	22.0	20.2	23.6	18.8	26.9	20.0	11.2	22.0	21.1	4.36
DMSO-75	21.5	19.9	24.1	16.3	30.2	17.8	18.6	16.4	21.6	17.8	20.4	4.23

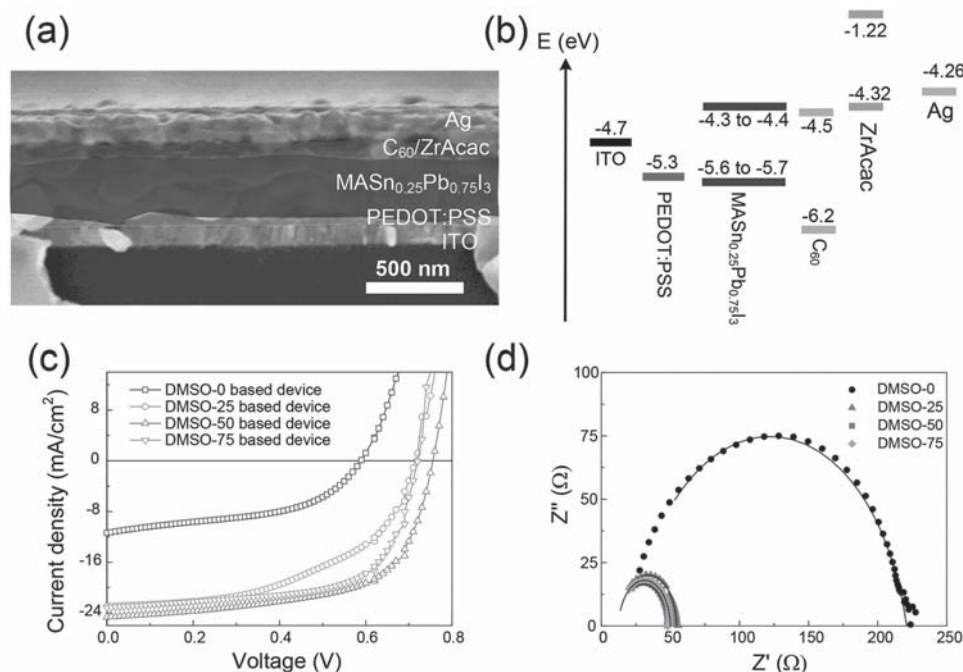


Figure 4. Device structure and performances. a) Cross-sectional SEM image and b) energy-level diagram of Sn–Pb alloyed PVSCs. c) Typical current density as a function of voltage curves (J – V) and d) the electrical impedance spectroscopy of Sn–Pb alloyed PVSCs measured at V_{oc} .

By further investigation of the perovskite particles, the selected area electron diffraction (SAED) pattern in Figure 3c is neither a bright spot nor a full ring, which reveals that the particles are composed of some smaller crystals rather than one piece of single crystal. As shown in the TEM image in Figure 3d, crystalline phase (circled in top and right) and amorphous phase (circled in the lower left corner) are connected in a particle. The intensity difference in the XRD patterns (Figure 1e) can be explained by the various amorphous ratios in different samples. These intuitive results confirmed the results from SEM (grain sizes) and XRD (crystal sizes) that each large perovskite grain (hundreds of nanometers) is composed of smaller crystals (tens of nanometers) and an amorphous part.

2.4. Device Performances

In this section, we will use $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskite films to fabricate planar-heterojunction PVSCs and discuss the change of device performances with the perovskite crystallization. By further optimizing the electron transport layer, we demonstrate efficient $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ PVSCs with the PCE of 15.2% and no hysteresis.

We use $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ alloyed perovskite films to fabricate planar-heterojunction PVSCs with the device structure of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS)/ $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ /C₆₀/zirconium(IV) acetylacetonate (ZrAcac)/Ag. The cross-sectional SEM device image of DMSO-25 perovskite shown in Figure 4a exhibits the dense and pinhole-free perovskite film, which is beneficial for achieving efficient perovskite solar cells. Figure 4b shows the energy band diagram for the planar-structured device. The valence band (VB) positions of

fabricated $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskites determined by ultraviolet photoelectron spectroscopy (UPS) are shown in Figure S4 (Supporting Information). The VB and conduction band (CB) positions of $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ are summarized in Table S1 (Supporting Information). As shown in Figure 4b, the introduction of hole and electron transport layers (PEDOT:PSS and C₆₀) can offer an appropriate energy-level alignment with Sn–Pb alloyed perovskites for efficient carrier extraction.

The J – V characteristics of $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ PVSCs prepared from various DMSO/DMF solvents (i.e., DMSO-0, DMSO-25, DMSO-50, and DMSO-75) are shown in Figure 4c, and the photovoltaic parameters are summarized in Table 2. DMSO-0-based PVSCs achieve lowest short-circuit current (J_{sc}) of 11.16 mA cm^{−2}, open-circuit voltage (V_{oc}) of 0.48 V, fill factor (FF) of 38.04%, and thus lowest PCE of 2.16%. Distinctively, PVSCs produced from mixed solvent-based precursors show the simultaneous enhancement of all J_{sc} , V_{oc} , FF, and thus PCE. Since the VB and CB adjustments of different $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ films were little (see Figure 4b and Table S1, Supporting Information), the influence of interfacial energy-level alignments

Table 2. Photovoltaic parameters of Sn–Pb alloyed PVSCs under AM1.5G illumination using $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskites from different DMSO/DMF solvent ratios based precursors.

Precursors	J_{sc} [mA cm ^{−2}]	V_{oc} [V]	FF [%]	PCE [%]
DMSO-0	11.16 ± 1.77	0.48 ± 0.07	38.04 ± 9.67	2.16 ± 1.13
DMSO-25	23.15 ± 0.49	0.69 ± 0.04	60.27 ± 8.27	9.51 ± 1.07
DMSO-50	24.27 ± 0.64	0.73 ± 0.05	59.91 ± 5.93	10.70 ± 1.79
DMSO-75	22.57 ± 1.07	0.71 ± 0.03	64.20 ± 1.33	10.21 ± 0.78

on device performances could be excluded in this case. The significant performances improvement should be ascribed to the formation of dense and smooth perovskites, enhanced crystallinity, preferred orientations, and ameliorated inhomogeneous Sn/Pb distributions.^[18,25] After the introduction of DMSO, $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ PVSCs produced from DMSO-50 precursors achieve the largest J_{sc} of 24.27 mA cm^{-2} , compared with 23.15 and 22.57 mA cm^{-2} for PVSCs produced from DMSO-25 and DMSO-75 precursors, respectively. The largest J_{sc} for DMSO-50-based PVSCs can be partially explained by the highest texture coefficient of 0.88, which suppresses recombination losses at grain boundaries.^[18]

Furthermore, DMSO-50-based PVSCs achieve the largest V_{oc} of 0.73 V, compared with 0.69 and 0.71 V for PVSCs produced from DMSO-25 and DMSO-75 precursors, respectively. The V_{oc} losses correlate with the recombination paths inside devices, which can be physically characterized by the recombination resistance R_{rec} .^[26] Electrical impedance spectroscopy was used to characterize the charge transport properties of solar cells, as shown in Figure 4d and Figure S5 (Supporting Information). The equivalent circuit consisted of R_{rec} and the contact resistance R_{co} is shown in Figure S6 (Supporting Information). Sn–Pb alloyed PVSCs all show the close value of R_{co} , originating from the same hole/electron transport layers (PEDOT:PSS and C_{60}). The R_{rec} values of DMSO-0, DMSO-25, DMSO-50, and DMSO-75-based PVSCs are 186, 40, 34, and 37 Ω , respectively. Evidently, DMSO-0-based PVSCs present the largest R_{rec} , while DMSO-50-based PVSCs show the smallest R_{rec} . Therefore, DMSO-50-based PVSCs achieve the largest V_{oc} of 0.73 V (Table 2). Peculiar features of V_{oc} between DMSO-25 and DMSO-75-based PVSCs should be attributed to ameliorated inhomogeneous Sn/Pb distributions for DMSO-75-based perovskites (Table 1).^[23] Consequently, PVSCs using DMSO-50 perovskites with the smooth surface, high crystallinity, preferred orientation, and ameliorated inhomogeneous Sn/Pb distributions achieve the highest PCE of 10.7%.

Since the interface engineering has been demonstrated to significantly influence the device performances,^[27] we introduce a nanocomposite electron transport layer consisting of PC_{61}BM and C_{60} to maximize the PCE of DMSO-50-based $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ PVSCs. It was found that PVSCs using $\text{PC}_{61}\text{BM}:\text{C}_{60}$ (3:1 by weight) achieved the highest PCE with the increased value of J_{sc} , V_{oc} , and FF, as shown in Figure S7 and Table S2 (Supporting Information). The improvement of J_{sc} and V_{oc} for PVSCs using $\text{PC}_{61}\text{BM}:\text{C}_{60}$ should be ascribed to the efficient perovskite surface passivation by $\text{PC}_{61}\text{BM}:\text{C}_{60}$, which leads to the reduced recombination at the interfaces of perovskites/electron transport layers and then increase the carrier lifetime confirmed by the photovoltage decay (see Figure S8, Supporting Information).^[28] Additionally, PVSCs with $\text{PC}_{61}\text{BM}:\text{C}_{60}$ electron transport layer achieved a smaller series resistance of $2.2 \Omega \text{ cm}^2$ and a larger shunt resistance of $6700 \Omega \text{ cm}^2$ ($2.4 \Omega \text{ cm}^2$ series resistance and $256 \Omega \text{ cm}^2$ shunt resistance for PVSCs with C_{60} electron transport layer), resulting in the increased

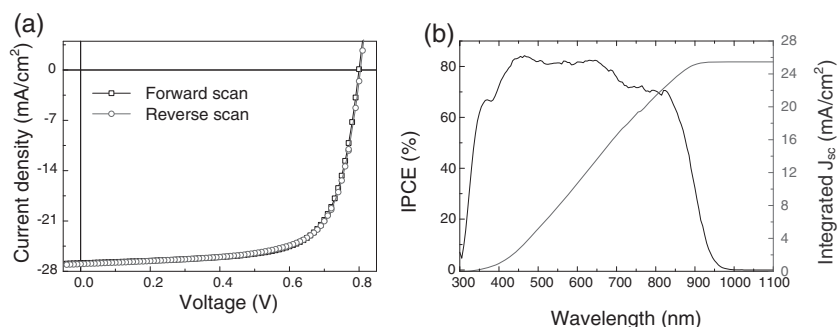


Figure 5. a) J - V curves of Sn–Pb alloyed PVSCs using $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskites from DMSO-50-based precursors. The PVSCs were measured by forward (from short circuit to open circuit) and reverse (from open circuit to short circuit) scans under AM1.5G illumination. b) IPCE spectra and integrated J_{sc} . Integrated J_{sc} is 25.5 mA cm^{-2} .

FF.^[29] Figure 5a shows the J - V curves for DMSO-50-based $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ PVSCs measured by forward (from short circuit to open circuit) and reverse (from open circuit to short circuit) scans. Importantly, negligible hysteresis was observed in our devices. Specifically, under the forward scan, devices achieved a V_{oc} of 0.80 V, J_{sc} of 26.2 mA cm^{-2} , and FF of 72.5%, corresponding to the PCE of 15.2%; while under the reverse scan, the devices achieved a V_{oc} of 0.81 V, J_{sc} of 26.4 mA cm^{-2} , and FF of 71.4%, corresponding to the PCE of 15.2%. The incident photon-to-electron conversion efficiency spectra and integrated J_{sc} over an AM 1.5G spectrum for planar-heterojunction PVSCs were shown in Figure 5b. The integrated J_{sc} of 25.5 mA cm^{-2} from the incident photon-to-current efficiency (IPCE) spectrum matches well the value derived from the corresponding J - V measurement. Moreover, $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ PVSCs red-shift the spectral response onset to $\approx 95 \text{ nm}$, indicating potential applications as the bottom cell to absorb the long-wavelength light in tandem solar cells. To the best of our knowledge, the high PCE for our $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ PVSCs is larger than that of Sn–Pb alloyed PVSCs constructed on mesoporous TiO_2 ^[4–6] and that of the very recently reported planar-heterojunction Sn–Pb alloyed PVSCs (see Table S3, Supporting Information).^[9,10]

3. Conclusions

In conclusion, we demonstrate high-quality $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskites with smooth surface, high crystallinity, and preferential orientation through the controlling crystallization of $\text{SnI}_2\text{-PbI}_2$ in the mixed solvent of DMSO and DMF. The introduction of DMSO also prevents the formation of the colloidal coagulation observed in prolonged-storage DMSO-0-based precursors and ameliorates inhomogeneous Sn/Pb distributions in the resultant perovskite films (and thus reduces V_{oc} losses). Through optimizing perovskites and employing a nanocomposite electron transport layer, hysteresis-free planar-heterojunction $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ PVSCs achieve the efficiency of 15.2%. Consequently, efficient $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ PVSCs achieved here highlight the importance of engineering mixed solvents-based precursors in Sn–Pb alloyed perovskite systems and its broad spectral response covering near ultraviolet–visible–near infrared region enables its potential use in multijunction solar cells.

4. Experimental Section

Synthesis of Sn–Pb Alloyed Perovskite Precursors: To prepare precursors of Sn–Pb alloyed perovskites, 345.7 mg PbI_2 (0.75 mmol) and 159 mg $\text{CH}_3\text{NH}_3\text{I}$ (1 mmol) first dissolved in 1 mL mixed polar solvents of DMF and DMSO. DMSO volume ratios were tuned including 0%, 25%, 50%, and 75%, respectively. After stirring at room temperature for 30 min, solutions became transparent. The solutions were then added to a vial with 93.1 mg SnI_2 (0.25 mmol) and stirred at 80 °C for 1 h before use. It should be noticed that all the SnI_2 involved steps were operated in a nitrogen-filled glove box to avoid oxidation.

Device Fabrication: ITO glass substrates were cleaned with deionized water, acetone, and ethanol. After 15 min ultraviolet–ozone treatment, PEDOT:PSS was spin-coated on the treated ITO substrates at 2000 rpm and annealed at 130 °C for 10 min to form solid-state films. The Sn–Pb alloyed perovskite precursors prepared in the last section were spin-coated on ITO/PEDOT:PSS substrates at the rate of 1000 rpm for 10 s at the first stage and 5000 rpm for 40 s at the second stage. 300 μL toluene as the antisolvent was slowly dripped on the substrates at the first 10 s of the second stage (at 20 s of the whole spin-coating time). Then, the spin-coated thin films were annealed at 100 °C for 10 min for the conversion of the precursors to perovskite films. Subsequently, 20 mg mL^{-1} hybrid PC_{61}BM and C_{60} with different weight ratios dissolved in 1,2-dichlorobenzene were spin-coated on perovskite films at 800 rpm, followed by spin-coating 2 mg mL^{-1} ZrAcac in isopropanol at 4000 rpm. Finally, 140 nm silver was deposited atop through the thermal evaporation under a vacuum of 10^{-4} Pa. The device structure of Sn–Pb alloyed PVSCs is ITO/PEDOT:PSS/ $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3/\text{PC}_{61}\text{BM}:\text{C}_{60}/\text{ZrAcac}/\text{Ag}$.

Characterization and Measurement: The morphologies of perovskite films were measured by Hitachi S4800 field-emission SEM and NT-MDT NTEGRA Spectra AFM. The microscopic structure and element composition of perovskite grains were investigated by using FEI Tecnai G2 20 scanning field-emission TEM. The UPS of perovskite films were investigated by using Kratos AXIS Ultra DLD spectrometer. For the measurements of device performances, solar-simulated AM 1.5G sunlight was generated using an Abet AM 1.5G solar simulator (100 mW cm^{-2}). The current density as a function of voltage curves was recorded using a Keithley 2635 sourcemeter. The electrical impedance spectroscopy was measured under illumination using Autolab instruments. Urbach energy of perovskite films was extracted from the IPCE spectrum. A mask with a window of 0.06 cm^2 was adopted to define the photoactive area of the solar cells.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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