LETTER

Realizing a Cosolvent System for Stable Tin-Based Perovskite Solar Cells Using a Two-Step Deposition Approach

Saeed Shahbazi, Meng-Yu Li, Amir Fathi, and Eric Wei-Guang Diau*

ACCESS | Metrics & More | Article Recommendations | SI Supporting Information

ABSTRACT: Applying a two-step procedure and solvent engineering, we fabricated a stable tin-based perovskite, formamidinium tin triiodide ($FASnI_3$), solar cell for lead-free photovoltaic applications. The first step was deposition of a SnI_2 layer with the solvent dimethyl sulfoxide; the second step was application of a cosolvent system containing hexafluoro-2-propanol (HFP), isopropyl alcohol (IPA), and chlorobenzene (CB) in a 5:5:2 ratio to deposit the FAI layer on the SnI_2 layer. The traditional IPA solvent prevented the formation of a stable $FASnI_3$ layer such that a stable device could not be fabricated. HFP was hence used to form hydrogen bonds with IPA and FAI to retard the crystal growth of $FASnI_3$; CB served as the antisolvent. Ethylenediammonium dihypophosphite in the first step was an effective reducing agent to increase the efficiency of power conversion from ∼5% to ∼7% with great reproducibility and stability over 4000 h.
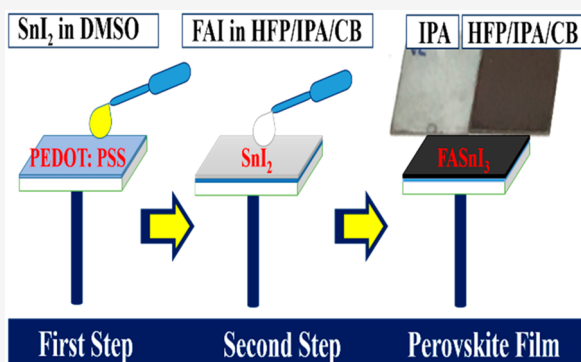
Tin-based perovskite solar cells (PSCs) have attracted a great deal of attention due to their recent rapid progress as promising alternatives to lead-free PSC to resolve the toxic issue of lead for their lead-based analogues.[1−4] The active perovskite layer can be fabricated with deposition in either one step or two. The two-step sequential deposition has been widely applied for lead perovskites as the method itself is more flexible for controlling the nucleation and crystal growth than the one-step approach for easily scaled industrial production.[5] However, for the tin perovskites, the active layers were fabricated with deposition in one step for most devices.[6−8] Only one report[9] of fabrication of a formamidinium tin triiodide ($FASnI_3$) layer uses a two-step method with a solvent, isopropyl alcohol (IPA), applied for the second step as for lead perovskites.[10,11] As IPA can easily deteriorate the tin-based perovskite layer, as reported elsewhere,[4,12−15] finding a suitable solvent or cosolvent system that is compatible with tin-based perovskites to yield a uniform film seems necessary. Even though Mitzi and co-workers[16] used a two-step dip-coating method to fabricate Sn-based perovskites with a cosolvent system containing IPA and toluene, the stability of the tin perovskites remains a challenging issue. Here we report a two-step deposition method using a novel cosolvent system for the second step to fabricate $FASnI_3$ devices with stability and performance superior to those of the devices fabricated

using one-step deposition. Ethylenediammonium dihypophosphite ($EDAP_2$) was applied in the first step as a coadditive with tin fluoride (SnF_2) as an additive to achieve a power conversion efficiency (PCE) of ∼7%.

A scheme of the experimental procedure appears in Figure 1. In the first step, dimethyl sulfoxide (DMSO) served as the solvent for deposition of the SnI_2 layer in the presence of SnF_2 (20%) as an effective additive to prevent Sn^{2+} oxidation;[13,14] DMSO is known to form a stable complex SnI_2·3DMSO as an intermediate at this stage (Figure 1).[17] In the second step, the cosolvent system of hexafluoro-2-propanol (HFP), IPA, and chlorobenzene (CB) in a 5:5:2 optimal ratio served to deposit the FAI layer on top of the SnI_2/DMSO layer. In our experiments, the pure IPA solvent prevented formation of a stable $FASnI_3$ layer and a pale film was formed during spin coating. In contrast, with the cosolvents in the second step, a dark film appeared after annealing. We expected that H-bonding interactions among HFP, IPA, and FAI (Figure 1)
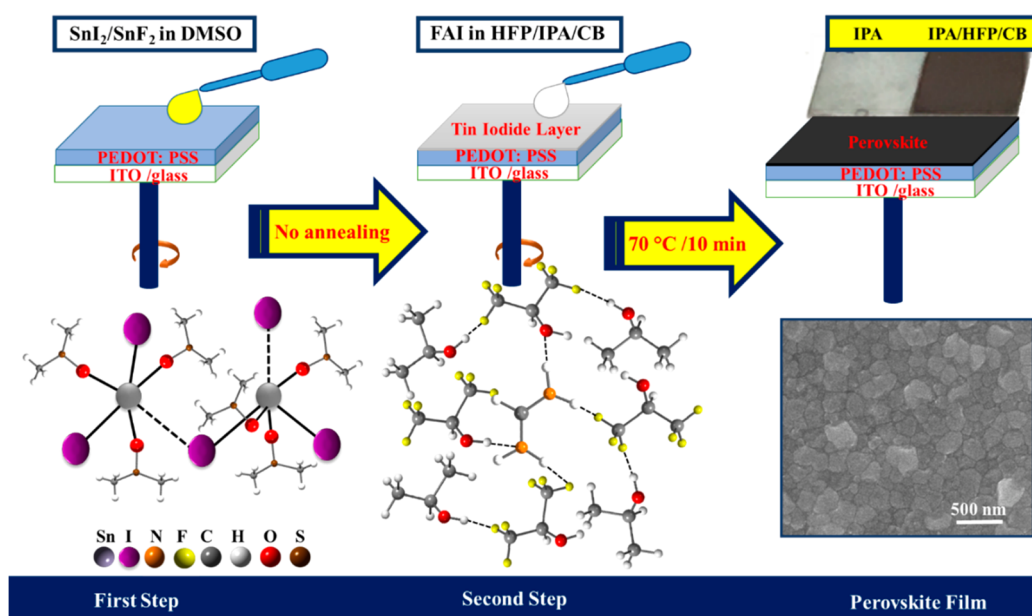
Figure 1. Scheme of the preparation of the $FASnI_3$ film with a two-step sequential deposition. In the first step, SnI_2/SnF_2 in DMSO was deposited on a PEDOT:PSS/ITO glass substrate to form a $SnI_2 \cdot 3DMSO$ complex. In the second step, FAI in a mixed HFP/IPA/CB cosolvent system was deposited to form a hydrogen-bonded framework to retard crystal growth between SnI_2 and FAI so that a uniform $FASnI_3$ film would form, as the SEM image shows; using only the IPA solvent did not produce the dark phase of $FASnI_3$ as shown in the inset.

stabilized the second layer to prevent the quick penetration of IPA so as not to destroy the $SnI_2 \cdot 3DMSO$ intermediate; the existence of CB acted as an antisolvent for the extraction of the residual DMSO in the first layer during annealing.[18] As a result, the cosolvent system retarded the crystal growth between SnI_2 and FAI and facilitated the formation of a film to produce a uniform $FASnI_3$ layer.

To confirm the formation of hydrogen bonds in our cosolvent system, we carried out Fourier transform infrared (FTIR) and ^{1}H nuclear magnetic resonance (NMR) measurements; the corresponding results are shown in Figures S1 and S2, respectively. For the FTIR spectra in the range of 1050−1350 cm^{-1}, we observed the characteristic C−F stretching vibrations from HFP shifted to a lower-wavenumber region compared to those of pure HFP peaks, which is attributed to the hydrogen bonding interaction between HFP and IPA. For the NMR measurements in the range of 8.0−9.5 ppm, the singlet resonance peak attributed to the NH_2 groups in the FAI and FAI/IPA mixtures split into doublet peaks in the FAI/HFP and FAI/HFP/IPA mixtures. The reason for this difference is that the NH_2 groups have a more electronegative environment for the FAI/HFP and FAI/HFP/IPA mixtures than for the FAI and FAI/IPA mixtures due to the formation of hydrogen bonds.

The $FASnI_3$ devices were fabricated according to an inverted planar heterojunction solar cell architecture [indium−tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS)/$FASnI_3$/C_{60}/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP)/Ag]. Four parameters must be considered to optimize the device performance. First, the concentration of SnI_2 in the first step was optimized to be 0.7 M according to the $J-V$ characterizations shown in Figure S3; the corresponding X-ray diffraction (XRD) data for concentrations of 0.6−1.0 M are shown in Figure S4. Second, no annealing is necessary for the first step, according to the scanning electron microscopy (SEM) images (Figure S5) and

the corresponding $J-V$ characterizations (Figure S6). Third, the amount of FAI in the second step was optimized to be 15 mg in 1.2 mL of the HFP/IPA/CB cosolvent with a 5:5:2 ratio, according to the XRD (Figure S7) and SEM images (Figure S8) for 10−30 mg of FAI; the corresponding $J-V$ characterizations are shown in Figure S9. No perovskite film was formed for an IPA ratio of >60%; the film quality was poor for an HFP ratio of >60% (Figure S10). To understand the effect of CB in this cosolvent system, the devices were made in the presence and absence of CB in the second step. The corresponding perovskite films show better morphology for the former than for the latter (Figure S11), and the current density and PCE increase significantly in the presence of CB (Figure S12). As HFP has a low boiling point (58 °C) at normal pressure,[19] pure HFP quickly evaporated, which led to rapid crystal growth to form a poor film. Fourth, the loading duration of FAI in the second step was optimized to be 30 s, according to the $J-V$ characterizations shown in Figure S13; the corresponding SEM images for loading durations of 10−50 s appear in Figure S14. The $FASnI_3$ device with 20% SnF_2 as the additive eventually attained a PCE of 4.9%, which is greater than that reported using pure IPA as a solvent for the second step.[9]

To enhance the device performance, we used $EDAP_2$ as a coadditive in the first step. This coadditive has the same organic cation as $EDAI_2$, but instead of iodine, the hypophosphite anion was used to serve as a reducing agent to enhance the efficiency and stability of the device.[20] The XRD results (Figure S15) indicated that increasing the amount of $EDAP_2$ from 1 to 2−4 mg decreased the crystallinity; the 1 mg device had the best performance (Figure S16). The hypophosphite anions can suppress the oxidation of Sn^{2+}, which is evident in the X-ray photoelectron spectra (XPS) shown in Figure S17. As a result, the device performance increased from a PCE of 4.9% to 6.8% according to the $J-V$ curves shown in Figure 2a; the corresponding IPCE spectra
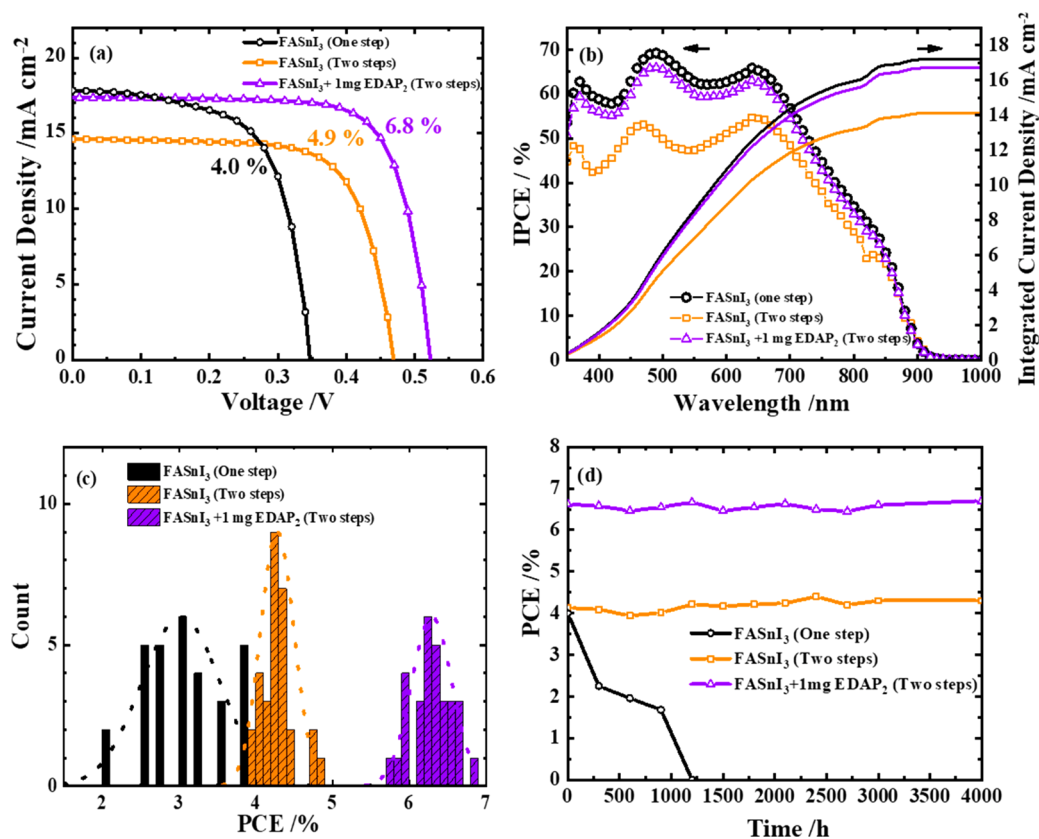
Figure 2. (a) $J-V$ curves, (b) IPCE spectra with integrated current density, (c) performance histograms, and (d) long-term dark-storage stability of devices in a glovebox, for all devices made of FASnI$_3$ (one step), FASnI$_3$ (two steps), and FASnI$_3$ with 1 mg of EDAP$_2$ (two steps). The data of FASnI$_3$ (one step) were taken from ref 6.

appear in Figure 2b. The devices made of the two-step procedure showed a negligible effect of hysteresis (Figure S18) with great stabilized PCE and photocurrent densities in 120 s (Figure S19). PCE histograms of 30 devices fabricated under the same experimental conditions (the corresponding photovoltaic parameters are listed in Tables S1−S3) for devices made of FASnI$_3$ (one step),[6] FASnI$_3$ (two steps), and FASnI$_3$ with 1 mg of EDAP$_2$ (two steps) are shown in Figure 2c. Figure 2d shows the long-term stability of these three devices, for which only devices made of the two-step method were sustained for >4000 h in the dark. Furthermore, the device made of FASnI$_3$ and 1 mg of EDAP$_2$ (two steps) also showed great enduring stability and retained 95% of the original PCE for 2 days and >80% after 70 h, under ambient air conditions (60% relative humidity) without encapsulation (Figure S20). We have hence demonstrated that EDAP$_2$ is an excellent coadditive as a reducing agent to suppress effectively the Sn^{2+}/Sn^{4+} oxidation for the device made with a two-step procedure to attain great performance and stability.

In conclusion, IPA has been broadly applied as a solvent in the second step of a sequential deposition to fabricate stable lead perovskites,[10,11] but IPA has strong interactions with SnI$_2$ that prevent formation of a high-quality tin perovskite layer. To tackle this problem, we developed a cosolvent system containing HFP, IPA, and CB in a 5:5:2 ratio in the second step to dissolve FAI upon formation of a hydrogen-bonded framework to retard the reaction between FAI and SnI$_2$ so that a uniform FASnI$_3$ layer was produced. When EDAP$_2$ served as the coadditive with SnF$_2$ as the additive in the first deposition step with DMSO as a solvent, the device achieved a PCE of

6.8% with great reproducibility and stability. For the first time, a stable FASnI$_3$ solar cell has been produced via a two-step deposition, which may provide us more flexibility to control the film quality and crystal structure, via varying halides and coadditives in the first step and cocations and bulky organic cations in the second step, for further development of tin-based perovskite solar cells with enhanced device performance and stability.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.0c01190.

> Experimental section, current−voltage characteristics, XRD, SEM, XPS, and photovoltaic parameters (PDF)

■ AUTHOR INFORMATION

Corresponding Author

    Eric Wei-Guang Diau − *Department of Applied Chemistry and Institute of Molecular Science and Center for Emergent Functional Matter Science, National Chiao Tung University, Hsinchu 30010, Taiwan;* ⓞ orcid.org/0000-0001-6113-5679; Email: diau@mail.nctu.edu.tw

Authors

    Saeed Shahbazi − *Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan*

Meng-Yu Li − *Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan*

Amir Fathi − *Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan;* ⊙ orcid.org/0000-0002-2528-8405

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsenergylett.0c01190

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Jiang, X.; Wang, F.; Wei, Q.; Li, H.; Shang, Y.; Zhou, W.; Wang, C.; Cheng, P.; Chen, Q.; Chen, L.; et al. Ultra-High Open-Circuit Voltage of Tin Perovskite Solar Cells via an Electron Transporting Layer Design. *Nat. Commun.* **2020**, *11* (1), 1245.

(2) Nishimura, K.; Kamarudin, M. A.; Hirotani, D.; Hamada, K.; Shen, Q.; Iikubo, S.; Minemoto, T.; Yoshino, K.; Hayase, S. Lead-Free Tin-Halide Perovskite Solar Cells with 13% Efficiency. *Nano Energy* **2020**, *74*, 104858.

(3) Diau, E. W.-G.; Jokar, E.; Rameez, M. Strategies To Improve Performance and Stability for Tin-Based Perovskite Solar Cells. *ACS Energy Lett.* **2019**, *4*, 1930−1937.

(4) Konstantakou, M.; Stergiopoulos, T. A Critical Review on Tin Halide Perovskite Solar Cells. *J. Mater. Chem. A* **2017**, *5* (23), 11518−11549.

(5) Guo, F.; He, W.; Qiu, S.; Wang, C.; Liu, X.; Forberich, K.; Brabec, C. J.; Mai, Y. Sequential Deposition of High-Quality Photovoltaic Perovskite Layers via Scalable Printing Methods. *Adv. Funct. Mater.* **2019**, *29* (24), 1900964.

(6) Jokar, E.; Chien, C.-H.; Fathi, A.; Rameez, M.; Chang, Y.-H.; Diau, E. W.-G. Slow Surface Passivation and Crystal Relaxation with Additives to Improve Device Performance and Durability for Tin-Based Perovskite Solar Cells. *Energy Environ. Sci.* **2018**, *11* (9), 2353−2362.

(7) Jokar, E.; Chien, C.-H.; Tsai, C.-M.; Fathi, A.; Diau, E. W.-G. Robust Tin-Based Perovskite Solar Cells with Hybrid Organic Cations to Attain Efficiency Approaching 10%. *Adv. Mater.* **2019**, *31* (2), 1804835.

(8) Akmal Kamarudin, M.; Hirotani, D.; Wang, Z.; Hamada, K.; Nishimura, K.; Shen, Q.; Toyoda, T.; Iikubo, S.; Minemoto, T.; Yoshino, K.; Hayase, S. Suppression of Charge Carrier Recombination in Lead-Free Tin Halide Perovskite via Lewis Base Post-Treatment. *J. Phys. Chem. Lett.* **2019**, *10* (17), 5277−5283.

(9) Zhu, Z.; Chueh, C.-C.; Li, N.; Mao, C.; Jen, A. K.-Y. Realizing Efficient Lead-Free Formamidinium Tin Triiodide Perovskite Solar Cells via a Sequential Deposition Route. *Adv. Mater.* **2018**, *30* (6), 1703800.

(10) Burschka, J.; Pellet, N.; Moon, S.-J.; Humphry-Baker, R.; Gao, P.; Nazeeruddin, M. K.; Grätzel, M. Sequential Deposition as a Route to High-Performance Perovskite-Sensitized Solar Cells. *Nature* **2013**, *499* (7458), 316−319.

(11) Im, J.-H.; Jang, I.-H.; Pellet, N.; Grätzel, M.; Park, N.-G. Growth of CH$_3$NH$_3$PbI$_3$ Cuboids with Controlled Size for High-Efficiency Perovskite Solar Cells. *Nat. Nanotechnol.* **2014**, *9* (11), 927−932.

(12) Gu, F.; Zhao, Z.; Wang, C.; Rao, H.; Zhao, B.; Liu, Z.; Bian, Z.; Huang, C. Lead-Free Tin-Based Perovskite Solar Cells: Strategies Toward High Performance. *Sol. RRL* **2019**, *3* (9), 1900213.

(13) Hao, F.; Stoumpos, C. C.; Guo, P.; Zhou, N.; Marks, T. J.; Chang, R. P. H.; Kanatzidis, M. G. Solvent-Mediated Crystallization of CH$_3$NH$_3$SnI$_3$ Films for Heterojunction Depleted Perovskite Solar Cells. *J. Am. Chem. Soc.* **2015**, *137* (35), 11445−11452.

(14) Ke, W.; Stoumpos, C. C.; Kanatzidis, M. G. Unleaded" Perovskites: Status Quo and Future Prospects of Tin-Based Perovskite Solar Cells. *Adv. Mater.* **2019**, *31* (47), 1803230.

(15) Yokoyama, T.; Cao, D. H.; Stoumpos, C. C.; Song, T.-B.; Sato, Y.; Aramaki, S.; Kanatzidis, M. G. Overcoming Short-Circuit in Lead-Free CH$_3$NH$_3$SnI$_3$ Perovskite Solar Cells via Kinetically Controlled Gas−Solid Reaction Film Fabrication Process. *J. Phys. Chem. Lett.* **2016**, *7* (5), 776−782.

(16) Liang, K.; Mitzi, D. B.; Prikas, M. T. Synthesis and Characterization of Organic−Inorganic Perovskite Thin Films Prepared Using a Versatile Two-Step Dipping Technique. *Chem. Mater.* **1998**, *10* (1), 403−411.

(17) Lee, S. J.; Shin, S. S.; Kim, Y. C.; Kim, D.; Ahn, T. K.; Noh, J. H.; Seo, J.; Seok, S. Il Fabrication of Efficient Formamidinium Tin Iodide Perovskite Solar Cells through SnF$_2$−Pyrazine Complex. *J. Am. Chem. Soc.* **2016**, *138* (12), 3974−3977.

(18) Jeon, N. J.; Noh, J. H.; Kim, Y. C.; Yang, W. S.; Ryu, S.; Seok, S. Il Solvent Engineering for High-Performance Inorganic−Organic Hybrid Perovskite Solar Cells. *Nat. Mater.* **2014**, *13* (9), 897−903.

(19) Kida, T.; Sato, S.; Yoshida, H.; Teragaki, A.; Akashi, M. 1,1,1,3,3,3-Hexafluoro-2-Propanol (HFIP) as a Novel and Effective Solvent to Facilely Prepare Cyclodextrin-Assembled Materials. *Chem. Commun.* **2014**, *50* (91), 14245−14248.

(20) Cao, J.; Tai, Q.; You, P.; Tang, G.; Wang, T.; Wang, N.; Yan, F. Enhanced Performance of Tin-Based Perovskite Solar Cells Induced by an Ammonium Hypophosphite Additive. *J. Mater. Chem. A* **2019**, *7* (46), 26580−26585.