

# Toward All Room-Temperature, Solution-Processed, High-Performance Planar Perovskite Solar Cells: A New Scheme of Pyridine-Promoted Perovskite Formation

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Since their first report in 2009, perovskite solar cells (PVSCs) have drawn enormous attention with remarkably high efficiency and prospective for low-cost photovoltaic applications.<sup>[1–10]</sup> A new certified efficiency of PVSC reaches 22.1%,<sup>[11]</sup> and the theoretical efficiency limit has been estimated to be 31% taking into account the photon recycling design through a detailed balance model.<sup>[12]</sup> This renders them very promising candidates to be used for next-generation photovoltaics.

Currently, most state-of-the-art PVSCs require a series of distinct processes (e.g., high-temperature sintering/annealing, high bombardment energy through sputtering, and ultrahigh vacuum) to fabricate efficient carrier-transport layers (e.g., TiO<sub>2</sub>,<sup>[13–15]</sup> Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS),<sup>[16–21]</sup> NiO<sub>x</sub>,<sup>[22–25]</sup>) and perovskite absorbers (e.g., CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>).<sup>[5,21,26–29]</sup> Various processing conditions involving multiple process steps in forming layers of multilayered PVSCs will increase the fabrication complexity, throughput, energy consumption, and cost.<sup>[30]</sup> The high annealing temperature may also be a concern for device fabrication on flexible substrates.<sup>[31]</sup> In addition, thermal annealing for an extended period of time is known to cause the perovskite decomposition, which degrades the device performance and stability.<sup>[5,32–34]</sup> Meanwhile, simple and scalable device fabrication is among the critical issues for the practical application of PVSCs,<sup>[30,31]</sup> low

temperature and solution-processed methods for each layer of PVSCs are highly desirable. While there is a very limited study in room-temperature solution-processed PVSCs and only an *n-i-p* planar structure of ZnO/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/spiro-OMeTAD has been reported with power conversion efficiency (PCE) of 15.7% on glass substrate,<sup>[35]</sup> its device stability is still a concern such as the potential reaction between ZnO and perovskite.<sup>[36]</sup> Up to now, it is still challenging to fabricate room-temperature solution-processed PVSCs with high performance and good stability.

The growth of perovskite film is a critical step to produce high efficiency and stable PVSCs.<sup>[2,4–9,12–20,29]</sup> Considering CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>-based PVSCs, the two-step dipping deposition provides an efficient and low-cost route toward large-scale production of PVSCs.<sup>[5,6,31]</sup> However, when PbI<sub>2</sub> is deposited on a flat substrate, it tends to form a layered and dense film. Therefore, there is a concern of uncompleted conversion of PbI<sub>2</sub> to perovskite during the exposure to CH<sub>3</sub>NH<sub>3</sub>I solution in a short time. The unreacted PbI<sub>2</sub> in the final device will reduce photovoltaic performances and stability.<sup>[5]</sup> While prolonging the reaction time seems to be a good method to address this issue, the dissolution and uncontrollable morphology of perovskites are detrimental to the device performances. These drawbacks make it difficult to fabricate scalable planar PVSCs by a conventional sequential deposition method. Although thermal annealing is an effective tool to accelerate the conversion of PbI<sub>2</sub> into perovskite,<sup>[32–34]</sup> layer-dependent fabrication complexity and energy consumption may hinder upscaling of the PVSCs.<sup>[31]</sup> Although other ligands (e.g., dimethyl sulfoxide, 4-*tert*-butylpyridine and *N*-methyl-2-pyrrolidone) have been reported to control the crystallization of perovskite by forming PbI<sub>2</sub>(ligand)<sub>x</sub> or CH<sub>3</sub>NH<sub>3</sub>I-ligand-PbI<sub>2</sub> intermediates,<sup>[5,37]</sup> high-temperature thermal annealing (≥100 °C) is required to remove the ligands for forming high-quality perovskites.

In this work, we propose a new scheme of pyridine (Py)-promoted formation of high-quality perovskite films at room temperature for the first time. In addition, we demonstrate the approach of employing an all room-temperature solution process to fabricate the *p-i-n* planar structure of NiO<sub>x</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/C<sub>60</sub> for achieving high performance and stable PVSCs. Our results show that room-temperature-processed PVSCs with PCE reaching 17.10% on indium tin oxide (ITO) coated glass substrate are achieved, which is the best results for PVSCs fabricated by all room-temperature solution-processed techniques to date. In addition, our all room-temperature solution-processed technique enables the fabrication of

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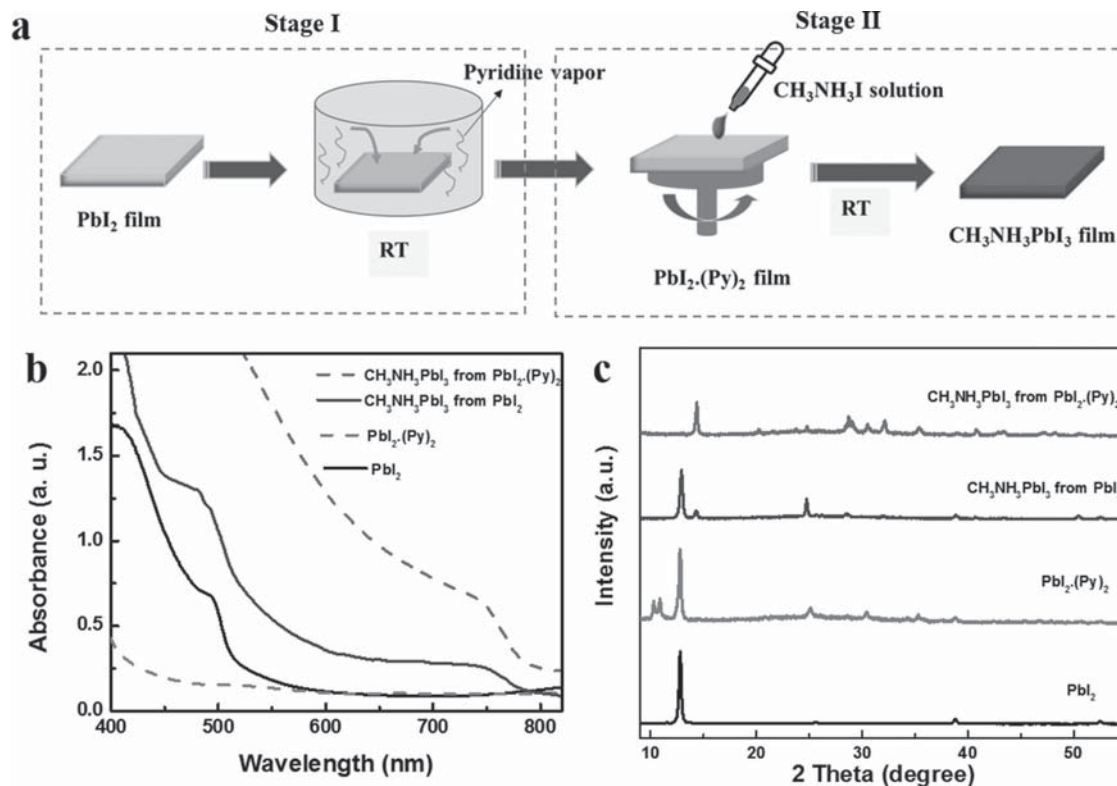
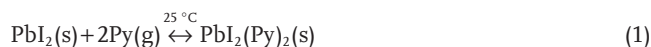


**Figure 1.** a) Schematics of the pyridine-promoted formation of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  film. b) UV-vis spectra of  $\text{PbI}_2$  film,  $\text{PbI}_2\cdot(\text{Py})_2$  film, and relevant perovskite films. c) XRD of  $\text{PbI}_2$  film,  $\text{PbI}_2\cdot(\text{Py})_2$  film, and relevant perovskite films.

flexible PVSCs with high PCE of 14.19% and remarkable power-weight of  $23.26 \text{ W g}^{-1}$ . Furthermore, the PVSC is very stable that can maintain 95% of its original PCE after being stored 1000 h in an ambient environment. This work not only reveals the great potential for preparing room-temperature-processed high-quality perovskite films but also represents an important step for achieving high-performance and low-cost PVSCs.

**Figure 1a** shows the process for pyridine-promoted formation of perovskite films. The fabrication of perovskite films mainly contains two stages, namely, (I) pyridine-induced formation of nanostructured  $\text{PbI}_2\cdot(\text{Py})_2$  films and (II) perovskite film formation facilitated by ligand exchange reaction. A key finding of our work is that the judicious introduction of pyridine greatly facilitates the room temperature conversion of  $\text{PbI}_2$  to the perovskite in a short time.

**Stage I. Pyridine-induced formation of nanostructured  $\text{PbI}_2\cdot(\text{Py})_2$  films:** The nanostructured  $\text{PbI}_2\cdot(\text{Py})_2$  film is synthesized in situ by solid-gas reactions between  $\text{PbI}_2$  film and pyridine vapors at room temperature (Equation (1))



The content of Py in the  $\text{PbI}_2\cdot(\text{Py})_2$  complex was estimated by thermogravimetric analysis (TGA). TGA was suitable for this purpose because the only volatile species in the  $\text{PbI}_2\cdot(\text{Py})_2$  powder was Py. The TGA results of  $\text{PbI}_2\cdot(\text{Py})_2$  are shown in Figure S1 (Supporting Information). The  $\text{PbI}_2\cdot(\text{Py})_2$  complex exhibited a one-step decomposition process with weight loss of

25.41% at  $135.49^\circ\text{C}$ . In other words, the weight proportion of Py in the  $\text{PbI}_2\cdot(\text{Py})_2$  complex is 25.41%. Then, we can get the coordination ratio of  $\text{PbI}_2$  and Py is 1:2.

The formation of  $\text{PbI}_2\cdot(\text{Py})_2$  complex was further confirmed from UV-vis spectra (Figure 1b) and X-ray powder diffraction (XRD) pattern (Figure 1c). Owing to the low volatility of pyridine whose boiling points is  $115^\circ\text{C}$ , the yellow-colored  $\text{PbI}_2$  changes to colorless within 100 s upon the exposure to pyridine vapors. (The conversion rate was monitored by UV-vis spectra.) After the treatment of initial  $\text{PbI}_2$  film by pyridine vapor, the film not only exhibits Bragg peaks associated with  $\text{PbI}_2$  crystal (001) planes at  $12.55^\circ$  but also shows other new peaks at lower angles ( $<12.55^\circ$ ), indicating the formation of the  $\text{PbI}_2\cdot(\text{Py})_2$  insertion complex. Meanwhile, the XRD peaks at low angles ( $<12.55^\circ$ ) also indicate that the  $\text{PbI}_2\cdot(\text{Py})_2$  complex has longer interlayer spacing along the *c*-axis, which is beneficial to the substitution of  $\text{CH}_3\text{NH}_3\text{I}$  [20,29] as described in Stage II.

We also investigate the formation of  $\text{PbI}_2\cdot(\text{Py})_2$  films by using scanning electron microscopy (SEM) as shown in Figure 2. It can be found that the untreated  $\text{PbI}_2$  forms dense platelet shaped crystals (Figure 2a). The layered structure impairs their complete conversion to perovskite. [5,6] Differently, as shown in Figure 2b, the  $\text{PbI}_2\cdot(\text{Py})_2$  film shows a uniform and nanoporous morphology, which is also verified by transmission electron microscopy (TEM). During the treatment by pyridine vapor, the bulk  $\text{PbI}_2$  platelets (Figure 2c) change to porous  $\text{PbI}_2\cdot(\text{Py})_2$  nanocrystals (Figure 2d), which will contribute to the formation of high-quality perovskite films.

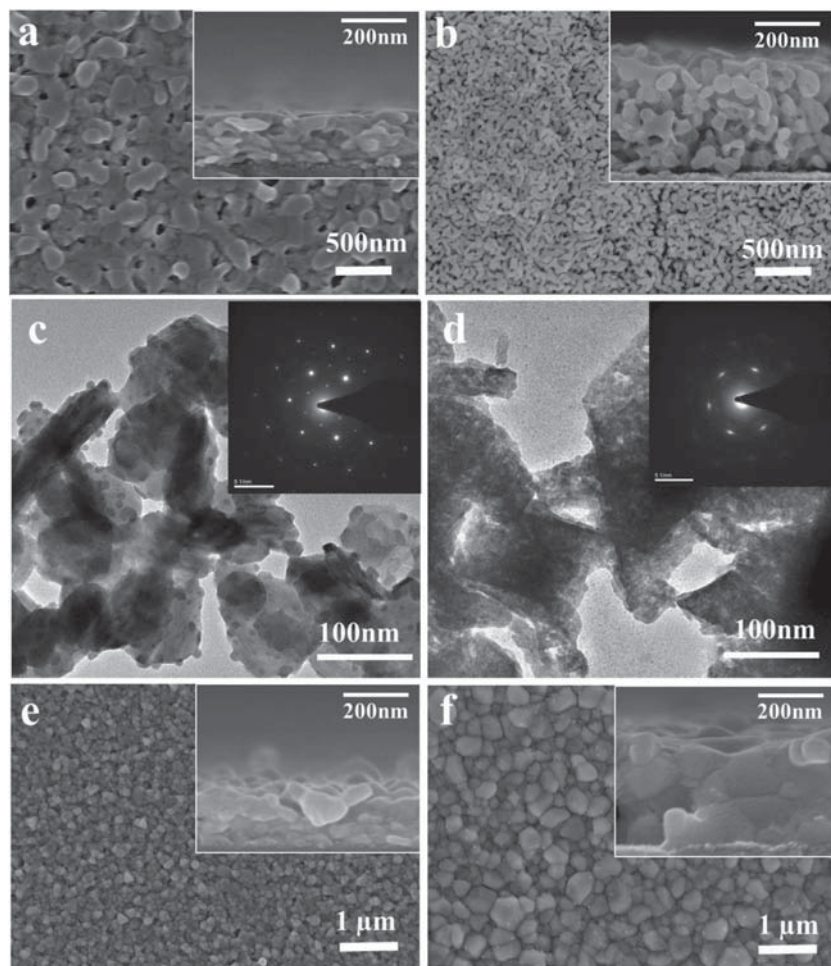
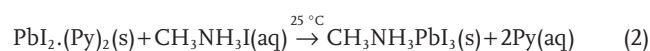


**Figure 2.** Top-view SEM images of a) pristine  $\text{PbI}_2$  and b)  $\text{PbI}_2(\text{Py})_2$  films. TEM images of c)  $\text{PbI}_2$  and d)  $\text{PbI}_2(\text{Py})_2$  powder. Top-view SEM images of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  films from e)  $\text{PbI}_2$  and f)  $\text{PbI}_2(\text{Py})_2$  films.

**Stage II. Perovskite film formation facilitated by ligand exchange reaction:** The room-temperature crystallized perovskite films are fabricated by dipping the as-formed  $\text{PbI}_2(\text{Py})_2$  porous films into  $\text{CH}_3\text{NH}_3\text{I}$  solution for 20 s at room temperature (see Figure 1a). Through the conversion of  $\text{PbI}_2(\text{Py})_2$  to  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , the pyridine molecules intercalated in  $\text{PbI}_2$  will be replaced by external  $\text{CH}_3\text{NH}_3\text{I}$ , owing to its affinity toward  $\text{PbI}_2$  is higher than that of pyridine (Equation (2))



The formation of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  films was confirmed by UV-vis spectra and XRD. As shown in Figure 1b,c, the  $\text{PbI}_2(\text{Py})_2$  film is converted into  $\text{CH}_3\text{NH}_3\text{PbI}_3$  completely in 20 s. By contrast, untreated  $\text{PbI}_2$  is incompletely converted into  $\text{CH}_3\text{NH}_3\text{PbI}_3$  with a large amount of  $\text{PbI}_2$  residue, which can be confirmed by the XRD patterns (Figure 1c). Figure 2e,f shows the top-view SEM images of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  films produced from untreated  $\text{PbI}_2$  and porous  $\text{PbI}_2(\text{Py})_2$  films. As expected, the morphology of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  films depends on their starting  $\text{PbI}_2$  film in the two-step dipping method.<sup>[5,6,27]</sup> The

$\text{CH}_3\text{NH}_3\text{PbI}_3$  films prepared from untreated  $\text{PbI}_2$  are rough and have small grains, voids, and cracks. Notably, the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  film prepared from  $\text{PbI}_2(\text{Py})_2$  film exhibits a uniform/smooth morphology and hundred nanometer sized grains.

To further improve the crystallinity of perovskite crystals prepared from  $\text{PbI}_2(\text{Py})_2$  complexes, we adopted the  $\text{CH}_3\text{NH}_2/\text{CH}_3\text{OH}$  mixed vapor treatment for 1–2 s at room temperature (see Figure S2, Supporting Information). It should be noted that we directly used commercial  $\text{CH}_3\text{NH}_2$  solution in methanol, which was simpler than the previous study.<sup>[38]</sup>

Regarding the detailed understanding of pyridine role in perovskite formation, we have studied the possible reaction mechanisms from the kinetics point of view. In terms of kinetics, the reaction rate between  $\text{CH}_3\text{NH}_3\text{I}$  and  $\text{PbI}_2(\text{Py})_x$  ( $x = 0$  or 2) is a function of the rate constant and reactants' concentration,<sup>[39]</sup> as shown in Equation (3)

$$v = Ae^{-E_a/RT} [\text{CH}_3\text{NH}_3\text{I}]^m [\text{PbI}_2(\text{Py})_x]^n \quad (3)$$

where  $A$  is constant,  $v$  and  $E_a$  are the reaction rate and the activation energy of reaction of perovskite formation, respectively.  $\alpha$  and  $\beta$  are the order of  $\text{CH}_3\text{NH}_3\text{I}$  and  $\text{PbI}_2(\text{Py})_x$ , respectively. For different pathways, the initial reactant concentration and reaction temperature (room temperature) are the same. Therefore, the reaction rate is determined by the activation energy. The  $E_a$  of a reaction can be considered as the height of the potential barrier separating two minima of potential energy (of the reactants and products of a reaction). Therefore, the smaller the  $E_a$  of a reaction, the faster the reaction rate.

We further conduct theoretical calculations of activation energies based on density functional theory (DFT). Detailed calculation procedures and crystallographic structures are provided in the Experimental Section and Figure S3 (Supporting Information), respectively. The corresponding calculated  $E_a$  for forming perovskite from conventional and pyridine-promoted pathways is summarized in Table 1. Based on the DFT calculation results, the reaction coordinate diagram of the perovskite formation via different pathways is presented in Figure 3. In the conventional pathway, the formation of perovskite needs to overcome a large energy barrier ( $E_a = 1.004$  eV). Interestingly, in our pyridine-promoted pathway, the formation of perovskite undergoes

**Table 1.** The calculated activation energies.

| Perovskite formation pathway | Reaction scheme                                                            | Activation energy $E_a$ [eV] |
|------------------------------|----------------------------------------------------------------------------|------------------------------|
| Conventional                 | $\text{PbI}_2 \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3$              | 1.004                        |
| Pyridine-promoted            | $\text{PbI}_2 \rightarrow \text{PbI}_2(\text{Py})_2$                       | 0.095                        |
|                              | $\text{PbI}_2(\text{Py})_2 \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3$ | 0.741                        |

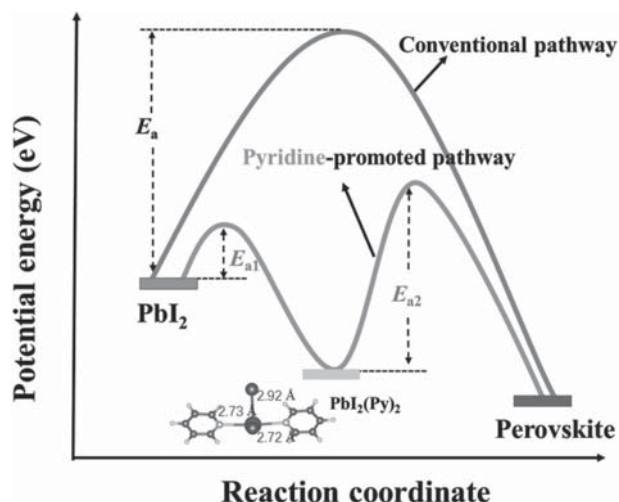


**Figure 3.** The reaction coordinate diagram of the perovskite formation via conventional pathway and pyridine-promoted pathway.

two-stage reactions:  $\text{PbI}_2(\text{Py})_2$  formation and perovskite formation. Since  $E_{a1}$  is very small with a value of 0.095 eV,  $\text{PbI}_2$  will quickly react to form  $\text{PbI}_2(\text{Py})_2$  (which supported by our experimental results described previously that yellow-colored  $\text{PbI}_2$  changes to colorless within a very short time 100 s).  $E_{a2}$  of the pyridine-promoted pathway from  $\text{PbI}_2(\text{Py})_2$  to perovskite is only 0.741 eV, which is substantially lower than that of the conventional pathway ( $E_a = 1.004$  eV), which indicates that the formation rate of perovskite is faster through our pyridine-promoted pathway, as shown in the experimental results above (Figure 1c). Therefore, a high-quality perovskite film can be

readily obtained at room temperature and short fabrication time through our pyridine-promoted pathway, which contributes the continuous and large-scale production of PVSCs.

To realize all room-temperature solution-processed PVSC, we introduce room-temperature solution-processed  $\text{NiO}_x$  film,<sup>[40]</sup>  $\text{C}_{60}$ , and Bis- $\text{C}_{60}$  surfactant as hole transport layer (HTL), electron transport layer (ETL), and interface layer, respectively, to fabricate PVSCs with the *p-i-n* planar configuration of  $\text{ITO}/\text{NiO}_x/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{C}_{60}/\text{Bis-C}_{60}/\text{Ag}$ . We also fabricated the control PVSC based on pristine  $\text{PbI}_2$  film (absence of  $\text{PbI}_2(\text{Py})_2$ ) for comparison (Figure S4, Supporting Information) and investigated the effect of  $\text{CH}_3\text{NH}_2/\text{CH}_3\text{OH}$  treatment on the device performance (Figure S5, Supporting Information). As shown in Figure 4a, the best device based on  $\text{PbI}_2(\text{Py})_2$  exhibited a short-circuit current density ( $J_{sc}$ ) of  $22.60 \text{ mA cm}^{-2}$ , a open-circuit voltage ( $V_{oc}$ ) of 1.05 V, and an fill factor (FF) of 0.721, corresponding to a PCE of 17.10%. The incident photon-to-current efficiency (IPCE) spectrum is shown in Figure 4b. The integration of the IPCE over the AM 1.5 solar emission spectrum produces photocurrent that is consistent with the  $J_{sc}$  derived from the corresponding *J-V* curve (see Figure S6, Supporting Information), showing negligible spectral mismatch of our solar simulator with the standard solar light. We also monitored the power output with time (Figure 4c). The photocurrent stabilizes within seconds to  $\approx 19.4 \text{ mA cm}^{-2}$ , yielding a stabilized PCE of 17.07%, measured after 100 s. In order to investigate the reproducibility of PVSC fabrication we made, 30 separate devices were fabricated and tested. The histograms of the device efficiencies are presented in Figure 4d. Approximately 85% of the cells show PCE over 15%.

Concerning the hysteresis of our PVSCs, we have measured the devices under different scan directions and scan rates. The

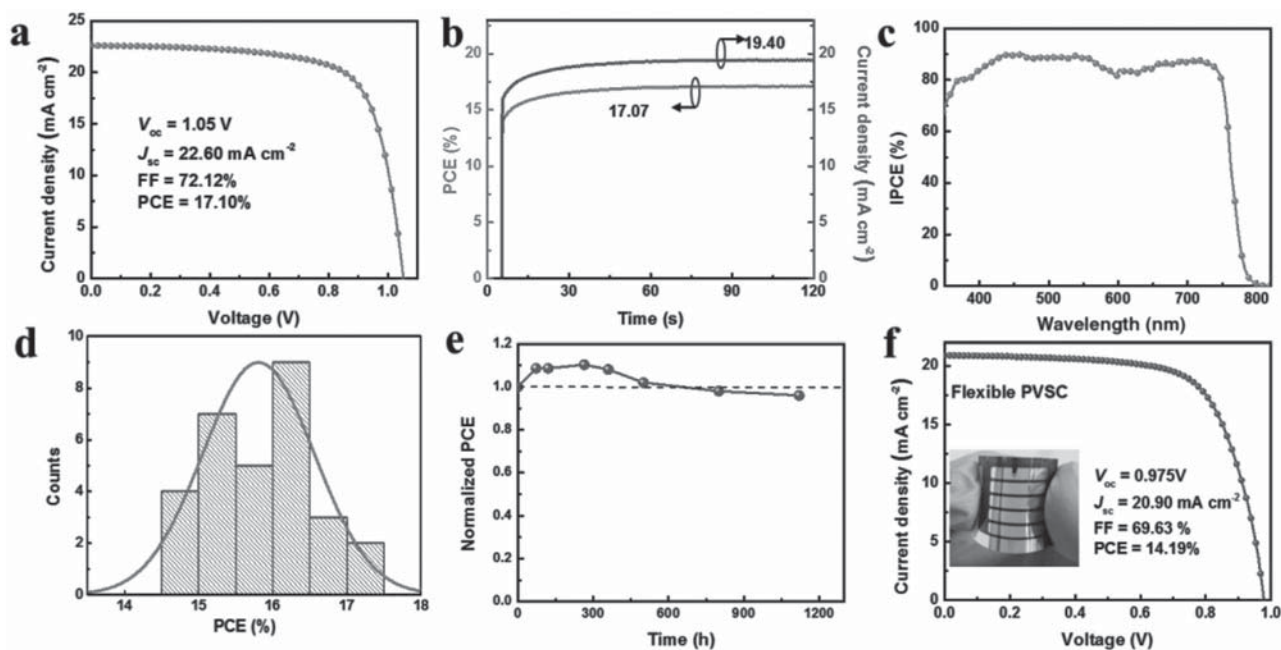


**Figure 4.** a) *J-V* curves and b) photocurrent output and PCE at the maximum power point (0.88 V) for the best PVSCs from  $\text{PbI}_2(\text{Py})_2$  film. c) IPCEs of a typical PVSC from  $\text{PbI}_2(\text{Py})_2$  film. d) The PCE distribution histogram of  $\text{PbI}_2(\text{Py})_2$ -based PVSCs. e) The PCE evolution of an encapsulated device stored in ambient air (45%–65% humidity, 20–28 °C) for different numbers of days. f) *J-V* curve and the photograph (inserted) of a  $\text{PbI}_2(\text{Py})_2$ -based flexible PVSC.

**Table 2.** Summary of the performance of the reported room temperature processed perovskite solar cells (our results are included for comparison).

| Solar cell configurations                                                                                              | $J_{sc}$ [mA cm <sup>-2</sup> ] | $V_{oc}$ [V] | FF    | PCE [%] | Power-per-weight [W g <sup>-1</sup> ] | Ref.      |
|------------------------------------------------------------------------------------------------------------------------|---------------------------------|--------------|-------|---------|---------------------------------------|-----------|
| Glass/FTO/ZnO/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /spiro-MeOTAD/Ag                                        | 20.4                            | 1.03         | 0.749 | 15.70   | –                                     | [35]      |
| Glass/ITO/ZnO/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /spiro-MeOTAD/Ag                                        | 11.0                            | 0.97         | 0.677 | 7.66    | –                                     | [42]      |
| Glass/ITO/PEDOT:PSS/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /PC <sub>60</sub> BM/Ca/Al                        | 13.11                           | 0.91         | 0.781 | 9.32    | –                                     | [43]      |
| Glass/ITO/C <sub>60</sub> /CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /spiro-MeOTAD/Au                           | 18.90                           | 1.10         | 0.754 | 15.70   | –                                     | [44]      |
| Glass/ITO/NiO <sub>x</sub> /CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /C <sub>60</sub> /Bis-C <sub>60</sub> /Ag | 22.60                           | 1.05         | 0.721 | 17.10   | –                                     | This work |
| PET/ITO/PEDOT:PSS/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /PC <sub>60</sub> BM/Ca/Al                          | 14.98                           | 0.92         | 0.49  | 6.80    | –                                     | [43]      |
| PET/ITO/ZnO/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /spiro-MeOTAD/Ag                                          | 13.4                            | 1.03         | 0.739 | 10.2    | –                                     | [35]      |
| PET/ITO/NiO <sub>x</sub> /CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /C <sub>60</sub> /Bis-C <sub>60</sub> /Ag   | 20.90                           | 0.975        | 0.696 | 14.19   | 23.26                                 | This work |

corresponding  $J$ – $V$  curves are shown in Figure S7 (Supporting Information). To quantitatively compare the hysteresis effect across different samples, a modified hysteresis index (HI) is adopted<sup>[41a]</sup>

$$HI = \frac{J_{RS}(0.8V_{oc}) - J_{FS}(0.8V_{oc})}{J_{RS}(0.8V_{oc})} \quad (4)$$

where  $J_{RS}$  ( $0.8 V_{oc}$ ) and  $J_{FS}$  ( $0.8 V_{oc}$ ) represent the photocurrent density at 80% of the  $V_{oc}$  for the reverse scan (from open circuit to short circuit) and forward scan (from short circuit to open circuit), respectively. According to Equation (4), the calculated HI of the PVSCs measured under different scan rates was below 0.05 as depicted in Figure S6 (Supporting Information), which indicates that our room-temperature solution-processed PVSCs show negligible hysteresis. The negligible hysteresis of our room temperature processed PVSCs should be due to the highly crystalline perovskite films and rapid charge extraction by the fullerene.<sup>[41]</sup>

Besides, we have checked the stability of the devices fabricated by our room temperature approach. As shown in Figure 4e, the encapsulated device demonstrated good stability over a period of 1000 h in ambient condition maintaining over 95% of its initial efficiency.

Furthermore, in comparison to the previous studies toward room temperature fabrication of PVSCs,<sup>[35,42–44]</sup> our cells are more efficient and stable (see Table 2). In particular, the  $J_{sc}$  of our PVSCs is higher by  $\approx 1$ – $2$  mA cm<sup>-2</sup> as compared to previous studies. The  $J_{sc}$  value of 21–23 mA cm<sup>-2</sup> is closer to that of the annealed conventional champion cells with  $n$ - $i$ - $p$  configuration of TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/spiro-OMeTAD.<sup>[45]</sup>

Regarding the origin of the high  $J_{sc}$  of our room-temperature solution-processed PVSCs, we have investigated the crystallinity and morphology of the perovskite film. As shown in Figure S2a (Supporting Information), our room temperature crystallized perovskite film shows high purity (PbI<sub>2</sub> residue-free) and high crystallinity with dominated (110) orientation, which is better than that prepared from the thermal annealing process.<sup>[32–34]</sup> Figure S2b–d (Supporting Information) shows the top-view and cross-sectional SEM images and that the perovskite film is pinhole-free and ultrasmooth with large grains (300–600 nm). The results are similar to that prepared by the thermal annealing process.<sup>[32–34,40]</sup> The grain sizes of the room temperature crystallized perovskite film estimated from the top-view image (Figure S2b, Supporting

Information) are 200–600 nm width, which is close to that calculated from the cross-sectional image (Figure S2c, Supporting Information). Interestingly, the length of the grains is equal to the thickness of the film ( $\approx 330$  nm) and the film uniformity expands to several tens of micrometer as displayed in Figure S2d (Supporting Information), which can facilitate charge transport to electrodes because of the reduction of defects and trap states at grain boundaries.<sup>[19]</sup> Our results conclude that high electronic quality perovskite film can be obtained through a room-temperature solution-processed technique.

By taking advantage of the room temperature techniques, we have further fabricated flexible PVSCs utilizing ITO/Polyethylene terephthalate (PET) as the conductive transparent electrode. Figure 4f shows the  $J$ – $V$  curve of the PVSCs using flexible ITO/PET substrates under AM 1.5G irradiation and the photograph of a flexible PVSC. The best flexible PVSC exhibits a  $V_{oc}$  of 0.975 V, a  $J_{sc}$  of 20.90 mA cm<sup>-2</sup>, and an FF of 69.63%, corresponding to a PCE of 14.19%, which is the highest PCE of the flexible PVSCs fabricated by room-temperature solution-processed techniques to date. In addition, our flexible PVSCs show remarkable power-per-weight of 23.26 W g<sup>-1</sup> (the detailed calculations are presented in Table S1, Supporting Information). It implies that high-performance and lightweight PVSCs can also be obtained through a room-temperature solution-processed techniques.

In summary, we have demonstrated a new room-temperature solution-processed technique to fabricate low-cost perovskite-based photovoltaics. Highly crystalline and pure CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> films are formed at room temperature through the judicious design of PbI<sub>2</sub>·(Py)<sub>2</sub> precursor films. Our theoretical studies of the perovskite formation mechanism through kinetics well describe the experimental results. Remarkably, we find that the devices based on PbI<sub>2</sub>·(Py)<sub>2</sub> film show the best photovoltaic performance with PCE of 17.10% on rigid substrate. Our devices show also negligible hysteresis and maintain stable performance during 1000 h exposure to an ambient environment. In addition, our room-temperature solution-processed technique enables the fabrication of lightweight flexible PVSCs with high PCE of 14.19% and remarkable power-per-weight of 23.26 W g<sup>-1</sup>. This work not only proves the feasibility of producing highly efficient PVSCs enabled by all room-temperature solution-processed techniques but also opens a new avenue to realize the large-scale production of low-cost perovskite-based photovoltaics.

## Experimental Section

All the chemicals and materials were purchased and used as received unless otherwise noted.  $\text{CH}_3\text{NH}_3\text{I}$  was purchased from Dyesol and used as received.  $\text{PbI}_2$  (99%) and pyridine (99.8%) were purchased from Sigma-Aldrich. Bis- $\text{C}_{60}$  surfactant was kindly provided by Prof. A. Jen.  $\text{NiO}_x$  NCs inks were synthesized according to our previous report<sup>[40]</sup> with a small modification. Briefly, 3 g  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dispersed in 60 mL deionized water to obtain a dark green solution. The pH of the solution was adjusted to 10 by adding 0.5 mol  $\text{L}^{-1}$  NaOH solution. After stirring for 5 min, the colloidal precipitation was thoroughly washed with deionized water twice and ethanol once, respectively, and dried at 80 °C overnight. The obtained green powder was grinded and then calcined at 270 °C for 2 h to obtain a dark-black powder. The  $\text{NiO}_x$  NCs ink with concentration of 20 mg  $\text{mL}^{-1}$  was prepared by dispersing the obtained  $\text{NiO}_x$  NCs in deionized water.

**Solar Cell Fabrication:** ITO-coated glass substrates or ITO-coated PET substrates (17 × 17 mm) were cleaned and then ultraviolet–ozone treated for 20 min. Then, the  $\text{NiO}_x$  NCs aqueous ink (20 mg  $\text{mL}^{-1}$  in deionized water) was spin-coated on precleaned ITO glass to form  $\text{NiO}_x$  films. The resultant  $\text{NiO}_x$  films were used to fabricate devices without annealing process or other treatments. The  $\text{PbI}_2$  precursor was prepared by dissolving 450 mg  $\text{PbI}_2$  powder in 1 mL DMF and then spin coated on the  $\text{NiO}_x$  substrate at 4000 rpm for 100 s. The formed  $\text{PbI}_2$  film was covered by a glass petri dish. Around 10  $\mu\text{L}$  of pyridine was added at the edge of the petri dish. Since the boiling point of pyridine is only 115 °C, pyridine vaporized in the petri dish and reacted with the  $\text{PbI}_2$  film to form  $\text{PbI}_2(\text{Py})_2$  intermediate. The duration of pyridine vapor treatment was 100 s. The resulting  $\text{PbI}_2(\text{Py})_2$  intermediates were then dipped in a solution of 15 mg  $\text{CH}_3\text{NH}_3\text{I}$  per mL 2-propanol for 20 s, rinsed with 2-propanol, and dried by  $\text{N}_2$  gas. For the champion cell, the  $\text{PbI}_2$  precursor was modified using a formulation of 28 mg  $\text{PbCl}_2$  and 462 mg  $\text{PbI}_2$  per mL DMF, and the crystallization of resulting  $\text{CH}_3\text{NH}_3\text{PbI}_3$  films was improved by  $\text{CH}_3\text{NH}_2/\text{CH}_3\text{OH}$  mixed vapor treatment for 1–2 s. Subsequently, the  $\text{C}_{60}$  (20 mg  $\text{mL}^{-1}$  dissolved in dichlorobenzene) and Bis- $\text{C}_{60}$  surfactant (2 mg  $\text{mL}^{-1}$  in 2-propanol) were sequentially deposited by spin coating at 1000 rpm for 60 s and 3000 rpm for 30 s, respectively. Finally, the device was completed with the evaporation of Ag contact electrodes (120 nm) through a shadow mask. The active area of this electrode was fixed at 6  $\text{mm}^2$ . For flexible devices, glass slides (17 × 17 mm) coated with a thin layer of PDMS (Sylgard 184 Silicone Elastomer, Dow Corning, spin-coated at 5000 rpm for 60 s from a solution of 10:1 v/v PDMS base to hardener, diluted 1:2 v/v in hexane, and subsequently annealed at 150 °C for 30 min) served as support for the ITO-coated PET substrates. The polymer film adheres through weak van der Waals forces only, enabling all subsequent processing steps (spin coating, dipping, and vacuum evaporation). After fabrication, the devices can be peeled off the support without causing damage. All devices were fabricated in a glove box.

**Measurement and Characterization:** Simulated AM 1.5 sunlight was generated using a Newport AM 1.5G solar simulator (100  $\text{mW cm}^{-2}$ ), calibrated with an ISO 17025-certified KG3-filtered silicon reference cell. The spectral mismatch factor was calculated to be less than 1%. The  $J$ – $V$  curves were recorded from 0 to 1.1 V using a Keithley 2650 apparatus with scan rate being 0.10  $\text{V s}^{-1}$ . The IPCE measurement was performed by a system combining xenon lamp, a monochromator (SpectraPro-2150i, Acton Research Corporation), a chopper, two optical filters (320 and 570 nm), and a lock-in amplifier (SR830, Stanford Research Systems) together with a calibrated silicon photodetector (Hamamatsu mono-Si cell). SEM images were recorded using a LEO 1530 scanning electron microscope. TEM was performed using a Philips Tecnai G2 20 S-TWIN instrument. The crystal phases were investigated by a Siemens D5005 X-ray diffraction system ( $\text{CuK}\alpha$  radiation,  $\lambda = 1.54056 \text{ \AA}$ ). UV–vis absorption spectra were measured using a home-built goniometer.

**DFT Calculations:** All the calculations were carried out using first-principles methods based on DFT. The projector augmented wave potentials<sup>[46]</sup> and Perdew–Burke–Ernzerhof<sup>[47]</sup> functions were implemented using the Vienna Ab initio Simulation Package.<sup>[48]</sup> The

orbitals Pb (5d, 6s, 6p), I (5s, 5p), C (2s, 2p), N (2s, 2p), H (1s), O (2s, 2p), and S (3s, 3p) were treated as valences in the calculation. The wave functions were expanded in plane waves with a kinetic energy cutoff of 500 eV. A  $k$ -point set generated by the  $15 \times 15 \times 11$  Monkhorst–Pack mesh was employed. For partial occupancies, the Gaussian smearing method was adopted. The convergence criterion of the self-consistent calculations for ionic relaxations was  $10^{-5}$  eV between two consecutive steps. With the conjugate gradient method, all atomic positions were optimized until the atomic forces were lower than 0.005 eV  $\text{\AA}^{-1}$ .

## Supporting Information

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

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