

New Methylamine-Iodine-Mediated Solvent-Free Approach of Hybrid Perovskite Synthesis via the Redox Conversion of Metallic Lead Films

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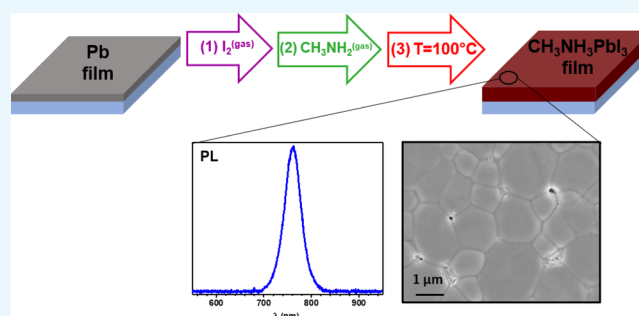


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ABSTRACT: The fast progress of lab-scale perovskite solar cells makes the problem of upscaling of perovskite thin-film deposition more and more acute; therefore, the development of new methods for perovskite deposition is highly desired. In this work, we proposed a new solution-free preparation approach for hybrid perovskite films based on the in situ generation of methylammonium iodide from methylamine and iodine vapors in the presence of an organic reducing agent conjugated with a redox process of metallic lead conversion with iodine vapor. At first, we demonstrated that either metallic lead or lead iodide powders can readily react with the solution of methylamine and iodine in the presence of isopropyl alcohol acting as a reducing agent, resulting in a phase-pure polycrystalline $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite. A possible mechanism of underlying chemical processes has been proposed. In order to convert the predeposited thin films of metallic lead to $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite, a protocol of sequential treatment by iodine and methylamine vapors was proposed. Finally, we revealed the optimal conditions of processing, which were proven to be facile and robust for the sake of the better control of perovskite grain morphology.



INTRODUCTION

Hybrid lead halide perovskites, being an innovative class of semiconductors with exceptional optoelectronic properties,^{1,2} attract great attention as novel thin-film polycrystalline light-absorbing materials for the emerging class of so-called perovskite solar cells (PSCs).³ After 10 years of sustained progress, the power conversion efficiency (PCE) of PSCs reached 25.5%, surpassing the benchmark of polycrystalline silicon solar cells. The operational stability of PCE, which is frequently considered as the “Achilles heel” of lead halide perovskites, has also demonstrated significant progress reaching up to 9000 h of working without a significant decay.⁴ Nevertheless, preparation of large-area perovskite thin films with uniform thickness and coverage (so-called “upscaling”) remains difficult if using the existing techniques of deposition from solutions such as spin-coating.⁵ The problem of upscaling is particularly challenging for nonflat substrates, such as textured silicon wafers which are one of the main technological challenges to achieve large-area high-efficiency perovskite-silicon tandem solar cells.^{6,7}

Recently, a novel promising strategy has been proposed for the formation of thin perovskite films by the chemical conversion of a predeposited layer of metallic lead^{8–10} using reactive polyiodide melts (RPMs) acting simultaneously as either an oxidizer or the source of organic cations and iodine. However, these approaches faced the difficulty of RPMs dosing

by virtue of their high recrystallizing ability.¹¹ In this regard, it is of great interest to develop a synthetic approach for the conversion and controlled crystallization of hybrid perovskites, starting from metallic lead and gas-phase reagents as precursors, enabling the formation of perovskite films with an improved morphology.

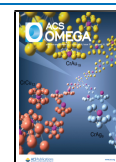
From a chemical point of view, the simplest set of gas-phase reagents that can introduce the lacking components to some solid-phase lead precursors (Pb or PbI_2) are methylamine (CH_3NH_2) and I_2 vapor. Remarkably, both the precursors also result in complete or partial liquefaction and also recrystallization of hybrid iodide perovskites, which results in an additional gas posttreatment effect for secondary grain growth in perovskite thin films to reduce the number of grain boundaries and diminish the surface defect concentration.^{11–14}

In this work, we demonstrated a proof-of-concept of the new approach for hybrid perovskite preparation based on a conjugated redox reaction of metallic lead, iodine, and methylamine in the presence of an organic reducing agent.

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We proved the possibility to obtain $\text{CH}_3\text{NH}_3\text{PbI}_3$ in the form of thin films and powders from metallic lead and lead iodide, discussed the similarities and differences of the proposed approach for liquid and gaseous media, and revealed the underlying chemical processes.

RESULTS AND DISCUSSION

In order to convert metallic lead into the archetypal perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$, the aforementioned methylamine and iodine

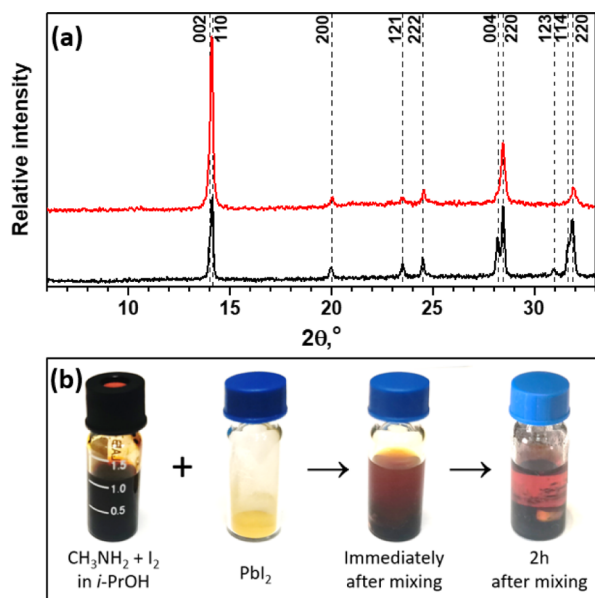
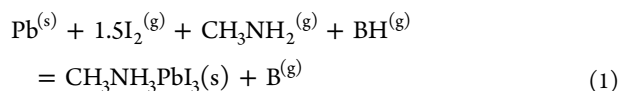
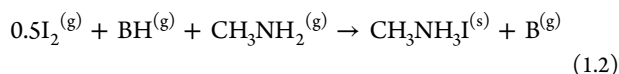


Figure 1. (a) XRD pattern of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ powder obtained from PbI_2 powder in the bulk (black) and of the film obtained by the sequential treatment of the PbI_2 film by the same reagents (red). The positions of the tetragonal phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$ reflections are shown by vertical black dotted lines. (b) Photos of vials with the (I) initial mixture of CH_3NH_2 , I_2 , and *i*-PrOH in the nonpolar solvent; (II) PbI_2 powder; and (I) and (II) immediately after mixing and after stirring at 70 °C for 2 h.

should be combined with an organic reducing agent donating the proton upon oxidation, such as a hydroxy group of primary and secondary alcohols. This third component provides coupled reactions of iodine reduction and methylamine protonation to form the target methylammonium cation. The general equation of the proposed chemical conversion process can be written as follows



where BH and B are the organic reducing agent and its corresponding oxidized (dehydrogenated) form, respectively. The conversion process can be represented as a sum of two redox subreactions



with a subsequent immediate reaction of PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ to form methylammonium lead iodide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$.

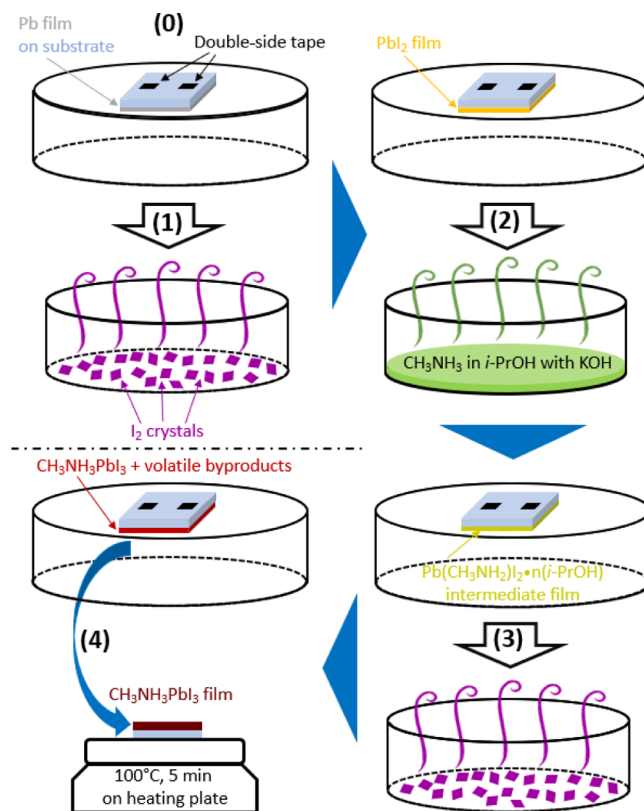


Figure 2. General scheme of the proposed process of Pb to $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite chemical conversion: (0) the predeposited Pb film (~60 nm) on a substrate [glass or fluorine-doped tin oxide (FTO)] is fixed on top of a Petri dish and then kept over iodine powder in the bottom dish (1), resulting in the formation of the PbI_2 film (2), which is exposed to CH_3NH_2 and *i*-PrOH mixed vapor and again (3) treated by I_2 vapor as explained in stage (1). Finally, the obtained film is annealed in a hot plate (4) to complete the single-phase perovskite formation.

To be a good reducing agent, the BH reagent should have redox potential significantly lower than that of iodine (<0.54 V). At the same time, both species of the BH/B redox couple should have low partial pressure to ensure the ease of diffusion transport through the vapor phase and elimination when the reaction of perovskite formation is completed. An obvious good choice of the BH reagent is some volatile primary or secondary alcohols, especially isopropanol (*i*-PrOH), which is the most inert to perovskites among other volatile alcohols.¹⁵

As a first proof of idea, we conducted reaction 1 in the model system, containing PbI_2 powder dispersed in the liquid medium of the inert solvent (toluene) with dissolved CH_3NH_2 , I_2 , and *i*-PrOH in a molar ratio of 1.5:1:2. The orange powder of lead iodide turns black immediately when the precursor solution was added, which implies the fast proceeding of reaction 2 (Figure 1a). After 2 h of vigorous stirring at 60 °C, the initially intensely colored solution due to the high concentration of iodine becomes noticeably lighter due to the reduction of iodine. According to X-ray diffraction (XRD) phase analysis, the black precipitate obtained after 4 h of the reaction is represented by the single-phase $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite (Figure 1b).

Thus, it was shown that a mixture of methylamine, iodine, and isopropanol can provide complete chemical conversion of

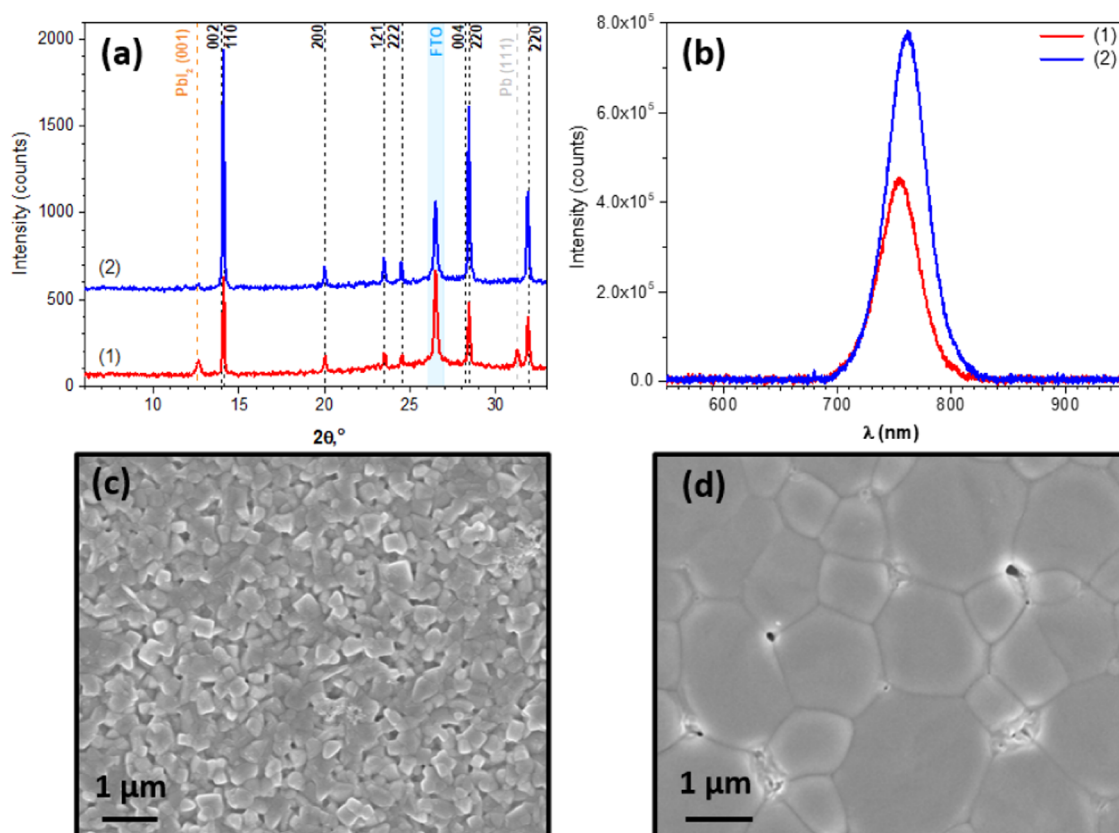
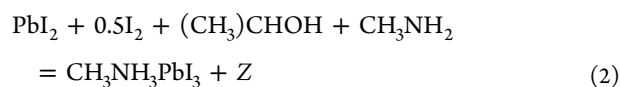


Figure 3. (a) XRD pattern and (b) photoluminescence spectra of the perovskite films on the glass obtained from the metallic lead film (1) by one full cycle of treatment (stages 1–4, Figure 1) and (2) with an additional cycle of treatment by CH_3NH_2 and I_2 . (c,d) Scanning electron microscopy (SEM) images of thin films (1) and (2).

lead iodide to perovskite due to the occurrence of a coupled redox reaction between the reagents in liquid media



where Z represents some products of *i*-PrOH oxidation. We expect that the main products can be acetone and various derivatives of its further interaction with iodine as a result of the following iodoform reaction (such as acetic acid and iodoform; see reactions I and II in the Supporting Information).

Then, we demonstrated the possibility of proceeding reaction 2 in the gas phase. In this case, the simultaneous exposure by iodine, methylamine, and isopropanol is difficult by virtue of different vapor pressures of the precursors at a given temperature. Therefore, the film was sequentially treated first with vapors of a concentrated solution of CH_3NH_2 in *i*-PrOH and then with I_2 vapor (the scheme of the process is given in Figure 2). Both the stages are carried out in Petri dishes at room temperature. At the first stage, the initially orange PbI_2 film first changes its color to dull yellow due to the formation of a layered complex with the composition $\text{Pb}(\text{CH}_3\text{NH}_2)_2\text{I}_2$,¹⁶ and then, the absorption of *i*-PrOH and excessive methylamine yields liquefaction of the layer and makes it transparent. At the second stage, the resulting transparent film was instantly transferred into an atmosphere of iodine vapor and kept for 3–5 min. After that, the film acquires a reddish-brown color typical for the thin layers of the perovskite; remarkably, its XRD pattern demonstrates only the

reflections of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (Figure 1). To eliminate all volatile byproducts and residual reagents, a short postannealing stage was applied at the end of the process.

In the case of metallic lead as a precursor, it is primarily needed to oxidize it to lead iodide, followed by the conversion to perovskite according to the scheme described above. It should be noted that the reaction of metallic lead with iodine vapor proceeds rather slowly even at elevated temperatures. To accelerate it, a few drops of a concentrated aqueous solution of HI are added to the Petri dish with crystalline iodine. However, the film of lead iodide resulting from such gas-phase oxidation seems to be too dense and may not fully react with methylamine. As a result, after a full cycle of conversion and annealing, the perovskite film still contains residual PbI_2 and Pb (Figure 3a). This problem can be overcome by interrupting the first stage of oxidative iodination of the lead film before its complete conversion and introducing an additional cycle of treatment with methylamine and iodine, allowing the residual Pb and PbI_2 to react completely to give a single-phase perovskite (Figure 3a).

Remarkably, both CH_3NH_2 and I_2 act not only as reagents but also as recrystallizing agents for the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite. Figure S1a,b in the Supporting Information shows that treatment with both iodine vapor and methylamine vapor leads to the secondary grain growth; however, in the first case, the film becomes too rough due to the strong faceting of the grains, and in the second case, many pinholes and inclusions on the surface are noticeable. In contrast, the perovskite film obtained after successive treatment by I_2 and CH_3NH_2 has much larger grains attaining up to 1–2 μm

(Figure 3d) with a relatively small number of pinholes observed in contrast to the small-grained and wrinkled film obtained after the first processing cycle (Figure 3c). The average thickness of the resulted perovskite layer is about 570 nm. The contact between the obtained perovskite layer and the glass substrate is smooth and contains no cavities (Figure S2). The additional treatment cycle also enhances the photoluminescence of the perovskite film (Figure 3b).

Noteworthy, CH_3NH_2 and I_2 placed together readily interact with the formation of a dark viscous liquid. Most likely, this liquid is an adduct of iodine with methylamine, analogous to the known butylamine-iodine molecular complexes.¹⁷ In a pure form, this liquid readily reacts not only with lead iodide but also with metallic lead to form a perovskite, thus exhibiting properties similar to RPMs. The formation of this adduct is undesirable due to possible internal redox reactions and its high corrosive capacity. Therefore, the treatment processes with methylamine and iodine should be separated in time and place.

In conclusion, we proposed a new synthetic approach to obtain the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite from metallic lead by means of consequent gas treatment. A unique feature of the approach is the simultaneous in situ generation of the methylammonium cation and iodine anion due to the conjugated redox reaction of methylamine, iodine, and an auxiliary organic component. This approach allows us to obtain the phase-pure thin films of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite with large grains from both the Pb and PbI_2 precursor film. In contrast to the solution-based methods of perovskite deposition, this approach has no limitations associated with either the relief or shape of the substrate or with the presence of solvent-sensitive underlying layers.¹⁸ Therefore, further optimization of the method is of great interest for developing a technology for the scalable deposition of perovskite films.

MATERIALS AND METHODS

Lead iodide (PbI_2 , 99.999%, Sigma-Aldrich) was commercially purchased and used without further purification. Concentrated (30%) methylamine solution in isopropanol was purchased from Ltd Labsintez (Russia) and was stored in a refrigerator at 0 °C to avoid the volatilization of CH_3NH_2 .

Perovskite Film Fabrication. Glass and FTO substrates were cleaned with a detergent, flushed with distilled water, and then sequentially washed in ultrasonic baths with acetone, isopropyl alcohol, and distilled water. Substrates were further cleaned using UV ozone for 15 min prior to their use.

Thin films of Pb with a target thickness of 62 nm were deposited on FTO substrates by the thermal evaporation of metallic Pb (99.99%) in vacuum at a deposition rate of 0.1 nm/s as described by Belich et al. in ref 9. After the deposition, the samples were transferred into an Ar-filled glovebox.

All further treatment operations were also carried out in the glovebox in the sequence described in the main text. The methylamine vapor treatment was conducted in a Petri dish filled with CH_3NH_2 concentrated solution in *i*-PrOH with KOH additives (to ensure the dryness of vapors).

Characterization. The XRD measurements were performed using a Bruker D8 ADVANCE diffractometer ($\text{Cu } \alpha$, $\lambda = 1.5406 \text{ \AA}$) in the range of $2\theta = 3\text{--}35^\circ$ with 0.02° step and 0.1 s step time for perovskite films. The morphology of the films was investigated using a Carl Zeiss NVision 40 field-emission scanning electron microscope (Oxford instruments).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c02061>.

SEM images of the surface morphology, cross-section of the perovskite films obtained after additional treatment, and equations of the plausible reactions occurring in a solution of methylamine and iodine in isopropanol (PDF)

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Author Contributions

Concept and original draft preparation, S.A.F.; experimental data acquisition, analysis, and visualization, A.S.S. and S.A.F.; and supervision, result discussion, and manuscript editing, E.A.G and A.B.T. All authors have read and agreed to the published version of the manuscript.

Notes

The authors declare no competing financial interest.

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