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ABSTRACT

Herein, a very simple, solvent free, scalable, and single-step approach to prepare organometal halide perovskite powders via mechanochemical synthesis followed by the deposition of perovskite films by spin coating is reported. This work particularly deals with various parameters that influence the crystallization process and morphology (hyperbranched) of methylammonium lead iodide films. Moreover, the influence of growth temperature on the morphology and the transition from tetragonal to cubic structure are investigated. The mechanosynthesized perovskite provides hyperbranched morphology and crystalline films in a hexagonal shape and serves as a better precursor for the absorber layer in perovskite solar cells.

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I. INTRODUCTION

Semiconducting nanostructured absorber layer has been playing an important role in enhancing the efficiency of solar cells due to its low reflection, high photon absorption, efficient energy conversion, and low charge carrier recombination properties. Organometal halide perovskites are one of the most promising light harvesting materials for photovoltaic applications because of high power conversion efficiency (PCE).^{1–3} Perovskite solar cell (PSC) is composed of a counter electrode/hole transporting material (HTM)/perovskite material/mesoporous TiO₂/electron transport layer (ETL) coated on a conductive substrate. Kojima *et al.*⁴ reported methylammonium lead iodide (MAPbI₃) crystals as the light-absorbing material in a liquid electrolyte, such as an iodine/triiodide redox couple. Lee *et al.*⁵ and Kim *et al.*⁶ had employed spiro-OMeTAD as an organic HTM instead of liquid electrolyte, which improved the PCE of the cells and its stability.

The synthesis of complex-shaped perovskite nanoparticles (NPs) such as one-dimensional (nanowires and nanorods), two-dimensional (platelets and sheets) from organic-inorganic perovskite compounds was reported by various researchers.^{7,8} However, researchers are interested in developing thin film perovskite materials by simple, cost-effective, and precise techniques that serve as an alternative to chemical synthesis (two-step process). Spin coating is a unique and precise method to develop thin films in which a centrifugal force is used to produce uniform films.⁹ The photovoltaic properties are strongly dependent on the fabrication process, purity of HTM, ETL, interfacial microstructures, and crystal structures of the compounds.

Numerous papers have been published on highly efficient perovskite solar cells.^{10,11} However, an in-depth understanding of the one-step deposition and its influence on the physical properties such as crystal structure, optical property, and morphology of the perovskite is needed for its effective utilization in perovskite solar

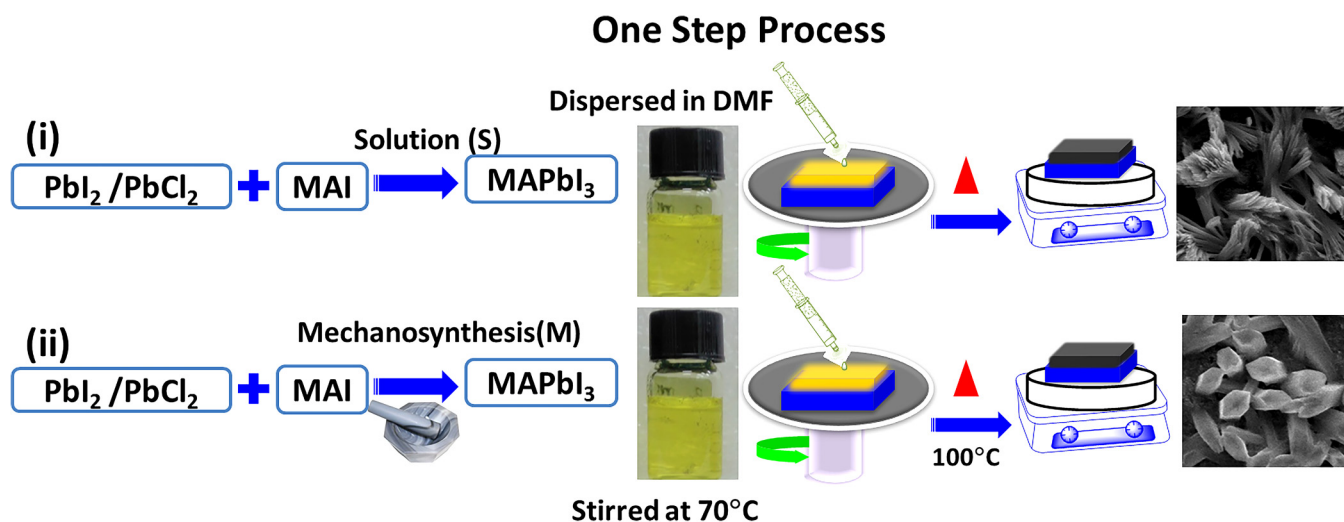


FIG. 1. Schematic representation of the one-step deposition for MAPbI₃ films.

cells. The commonly used methods to prepare MAPbI₃ thin films are spin coating, sequential deposition, vapor-assisted solution deposition, sequential vacuum deposition, coevaporation, and so on.^{12–16} However, it is still a challenge to obtain highly crystalline perovskite films. Hence, several modification routes like solvent engineering, fast deposition-crystallization, and addition of different additives¹⁷ had been reported to achieve crystalline films.

Mechanochemical synthesis is one of the versatile methods that has been utilized in recent years to synthesize perovskite powders in various nanostructures and its corresponding devices from the perovskite films.¹⁸ For instance, the pioneering work was reported by Prochowicz *et al.*, where they presented a facile mechanochemical route for the synthesis of MAPbI₃ and fabricated perovskite solar cell with enhanced PCE.¹⁹ The preparation of

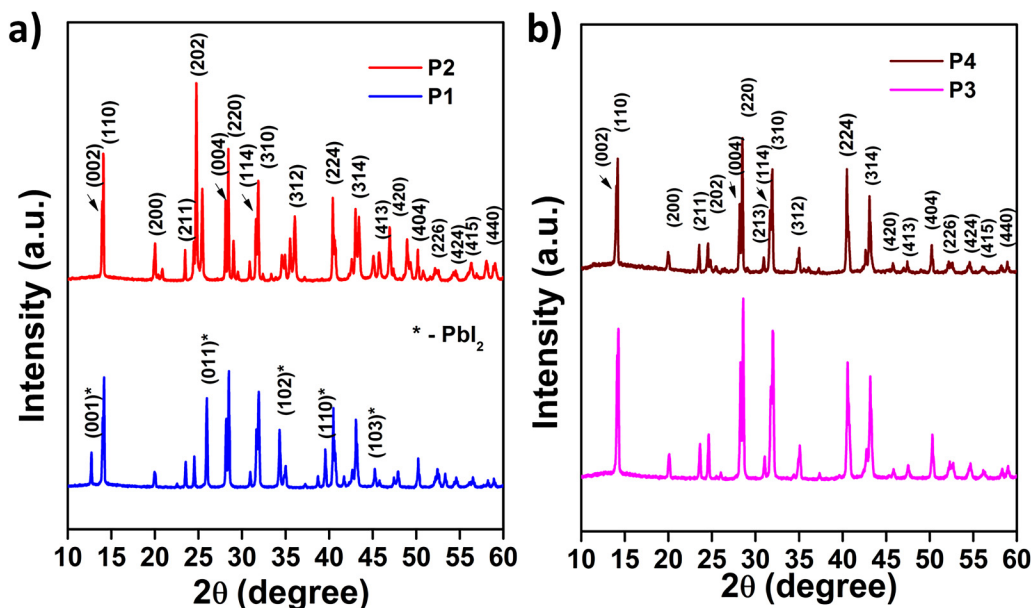


FIG. 2. XRD patterns of MAPbI₃ powders obtained by (a) solvent intervened synthesis (P1 and P2) and (b) solvent free mechanochemical synthesis (P3 and P4).

perovskite inks from the mechanochemically synthesized perovskites was also reported by the same group in 2017 for the formation of highly crystalline films. The devices obtained from mechanoperovskite exhibited lower hysteric behavior owing to the slow charge recombination and low interfacial trap density of the highly crystalline perovskite films.²⁰ The mechanochemical synthesis was also employed to obtain mixed halide perovskites^{21,22} and all-inorganic perovskites in recent years.²³

In this work, we have performed a viable route to prepare perovskite ink and an easy way to fabricate thin film via a single-step deposition using the ink ($\text{CH}_3\text{NH}_3\text{I-PbI}_2$ and $\text{CH}_3\text{NH}_3\text{I-PbCl}_2$ complex) because of its cost-effectiveness, simplicity, and easy fabrication. We also demonstrated an effective way to obtain high quality perovskite films with different morphology depending upon the processing conditions. The current work also reports two different morphologies such as paper fan and hexagonal rodlike structure for MAPbI_3 thin films with uniform surface coverage. In this solidification process, solvent evaporation was accompanied by crystallization during spin coating to form $\text{CH}_3\text{NH}_3\text{I-PbI}_2$ and $\text{CH}_3\text{NH}_3\text{I-PbCl}_2$ complex. As-deposited film was then crystallized by post heat treatment at 100°C , resulting in two different morphologies covering the substrate fully without pinholes. Solution processability of these materials is another key property that makes them very attractive for solid state PSC. The main objective of the study is to obtain good quality films based on the structure, surface, electrical, and optical of the materials.

II. EXPERIMENT

Polycrystalline organometal halide perovskites were synthesized via two routes such as solvent intervened as well as solvent free synthesis, which was recently reported by our group.²⁴

- (i) Solvent intervened synthesis: 4.6 g of lead iodide powder was added to the solution containing 3.2 g of methylammonium iodide (MAI) in 50 ml of isopropyl alcohol in the molar ratio of 1:2. Similarly, 1.4 g of lead chloride was added to the solution containing 2.4 g of MAI in the molar ratio of 1:3 taken in another beaker stirred at 50°C for 30 min. Finally, the solid was washed with ethanol followed by diethyl ether to get pure product and dried at 80°C to free from solvents, named as P1 and P2.
- (ii) Solvent free solid state synthesis: perovskites were synthesized by grinding of MAI (0.026M) and PbI_2 (0.013M) and then MAI (0.042M) and PbCl_2 (0.014M) in a mortar for 10 min.¹¹ Then, the resulting powders were gently heated up to 80°C in order to improve the crystalline nature. It was found that the color of both the powders completely turned into black, indicating the complete formation of perovskite. Finally, the resulting solid was washed with ethanol and diethyl ether to get pure MAPbI_3 , which are named as P3 and P4.

The as-prepared MAPbI_3 (P1–P4) (300 mg) were dissolved in 2 ml of dimethylformamide (DMF) in a separate vial and vigorously stirred at 70°C to prepare the perovskite stock solution of

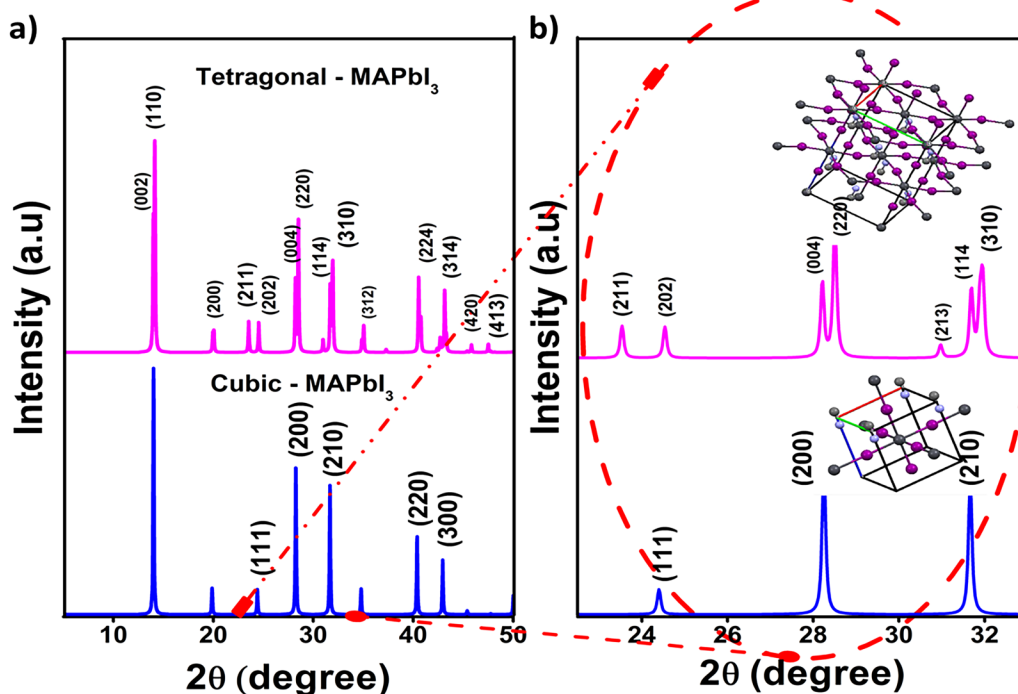


FIG. 3. (a) XRD patterns of MAPbI_3 extracted from ICSD and (b) its enlarged view.

$\text{CH}_3\text{NH}_3\text{I}-\text{PbI}_2$ and $\text{CH}_3\text{NH}_3\text{I}-\text{PbCl}_2$ complex. These processes resulted in the formation of yellow color solutions, suggesting the formation of $\text{PbI}_2/\text{PbCl}_2$ -DMF adducts²⁵ respectively. Thus, the prepared perovskite inks were deposited onto the nanoporous TiO_2 (P25) layer by spin coating. The as-deposited films were dried at room temperature for 10 s, in which the film appeared colorless and started to crystallize slowly. The dried film was immediately heated up to 100 °C under controlled environment for 10 min where the color of the film was changed to dark brown indicating the nucleation of perovskite crystals (shown in Fig. 1). These crystals were grown in the tetragonal crystal system with various morphologies, which are described in detail in Sec. III. To avoid the formation of secondary phases, films were grown at 150 °C for 10 min, in order to understand the temperature-dependent growth process of MAPbI_3 . Also, a commercially available MAPbI_3 perovskite precursor was purchased from Ossilla (Ossilla-I101) and prepared the film for comparison.

III. RESULTS AND DISCUSSION

In the sequential deposition process, the composition control is more difficult during the ion exchange processes. Therefore, the experiment was performed using perovskite ink via the spin coating technique. The as-prepared perovskites (chemical, solid state reaction) (before making ink) were subjected to XRD in order to understand the crystalline phase of the materials and is shown in Figs. 2(a) and 2(b). MAPbI_3 shows strong diffraction peaks at 2θ positions of 14.18°, 24.88°, 28.50°, 31.95°, and 40.46° corresponding to (110), (202), (220), (310), and (224) planes, respectively, representing the tetragonal phase. It is inferred that the perovskite synthesized from solvent intervened method leads to the presence of unreacted PbI_2 . However, the perovskites obtained from mechano-synthesis showed a better diffraction pattern having a tetragonal phase of the perovskite structure. Mechano-perovskite will be useful to provide high quality perovskite thin films with relatively larger crystalline grains.

To understand the crystal system, the standard data were extracted from ICSD 250735 (cubic) and 250379 (tetragonal) using mercury software. Figure 3(a) shows the XRD patterns of cubic and tetragonal system, where the splitting of peaks is clearly seen in the tetragonal system at different 2θ positions shown in Fig. 3(b). These standard data were very helpful in comparing the experimental values. XRD analysis of single-step spin-coated perovskite films (as shown in Fig. 4) exhibits primary peaks at higher angles, which exactly matched with tetragonal perovskite structure. In addition to that, we observed a low intensity peak at 12.5° corresponding to PbI_2 (001) plane. This may be due to insufficient thermal energy or a small variation in the composition of the films.

In order to avoid PbI_2 and secondary phase diffraction, spin-coated films were grown at 150 °C. Figure 5(a) shows the XRD of annealed MAPbI_3 film, in which, reflections with strong intensity were observed. It clearly indicates a well-crystallized and highly oriented MAPbI_3 perovskite film formation with the cubic system. This annealing process avoids the formation of the complex crystal structure and also improves the crystalline quality, air stability, and morphology of MAPbI_3 crystals. From that, we concluded that a MAPbI_3 film grown at 150 °C showed good crystalline nature and crystallized

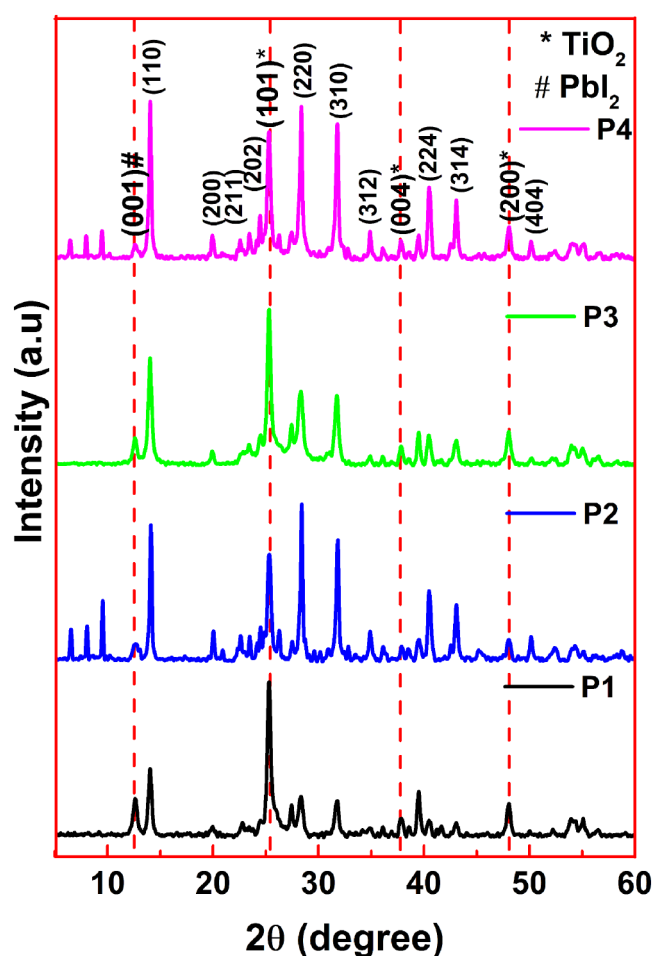


FIG. 4. XRD patterns of one-step spin-coated MAPbI_3 films showing tetragonal phase structure.

in the cubic crystal system shown in Fig. 5(b) (enlarged view). In the growth process, crystal ions interact with the Pb via intermolecular hydrogen bonding of the NH_3^+ group, which predominantly reduces the surface energy of organic-inorganic interfaces.

Figure 6 shows the field emission scanning electron microscope (FESEM) images of MAPbI_3 grown on the TiO_2 mesoporous structure revealing the formation of uniform monodispersed micro-crystals of different morphologies (sheaf and hexagonal). It was also observed that a large number of crystallites with various nucleation centers that were completely projecting out at both sides showed good surface coverage. 2D MAPbI_3 perovskites with well-aligned sheaf like hyperbranched bundles and hexagonal rods were grown along the c axis, which is clearly visible. Hyperbranched nanoarchitectures were composed of nanospindle which appear like “paper fan” morphology. Furthermore, we observed hyperbranched sheaflike structures, which were distributed from the center and split into a hexagonal shape, which was clearly seen at the end of

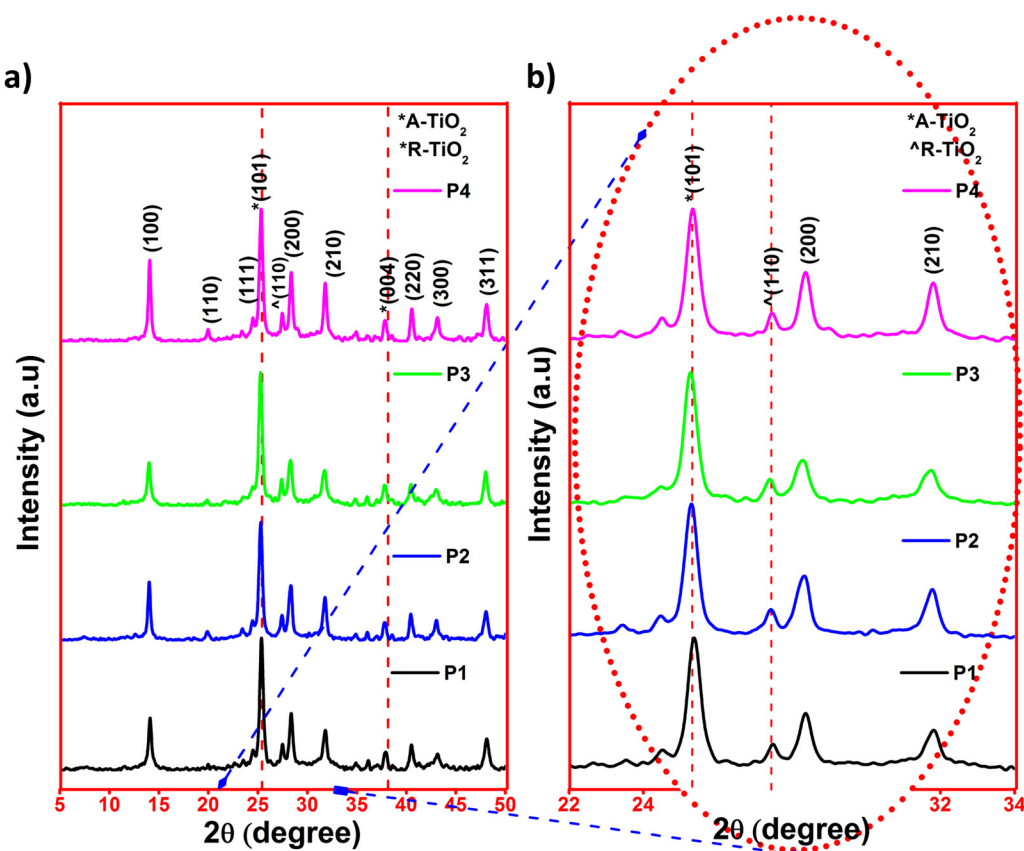


FIG. 5. (a) One-step spin-coated MAPbI₃ films grown at 150 °C on top of TiO₂ and (b) its enlarged view.

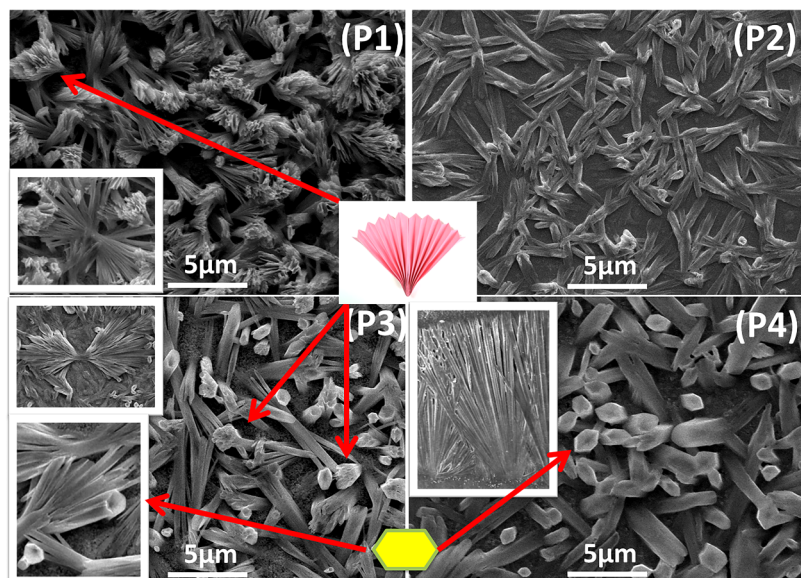


FIG. 6. FESEM images of MAPbI₃ films prepared by the one-step spin coating of P1–P4 inks.

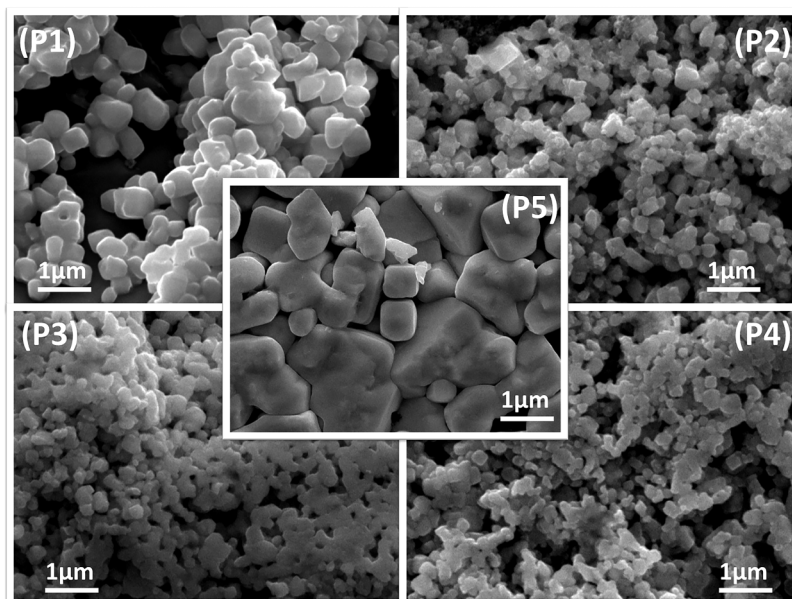


FIG. 7. FESEM images of MAPbI₃ films (using P1–P4 powders) grown at 150 °C. Inset (P5) shows the crystal grains of MAPbI₃ films prepared from standard perovskite solution (Ossilla-1101).

the rod for mechanosynthesized MAPbI₃. Micro rod crystals were grown along the crystallographic axis at different nucleation centers when the spin-coated films were grown at 100 °C. At the growth temperature of 150 °C, we observed tightly packed micrometer sized agglomerated crystal grains of size >500–1000 nm. It is evident from Fig. 7 that well defined crystals were observed at a higher annealing temperature. In Fig. 7, P5 shows the crystal grains

of MAPbI₃ perovskite standard solution that were deposited on ETL and grown at 150 °C.

High absorbance was observed in the UV region for MAPbI₃ films deposited on the TiO₂ layer (Fig. 8). It is noteworthy that the recorded UV-Visible spectra for 150 °C grown MAPbI₃ films [Fig. 8(b)] exhibited wide spectral response in the entire visible region as compared to 100 °C grown films [Fig. 8(a)], which in

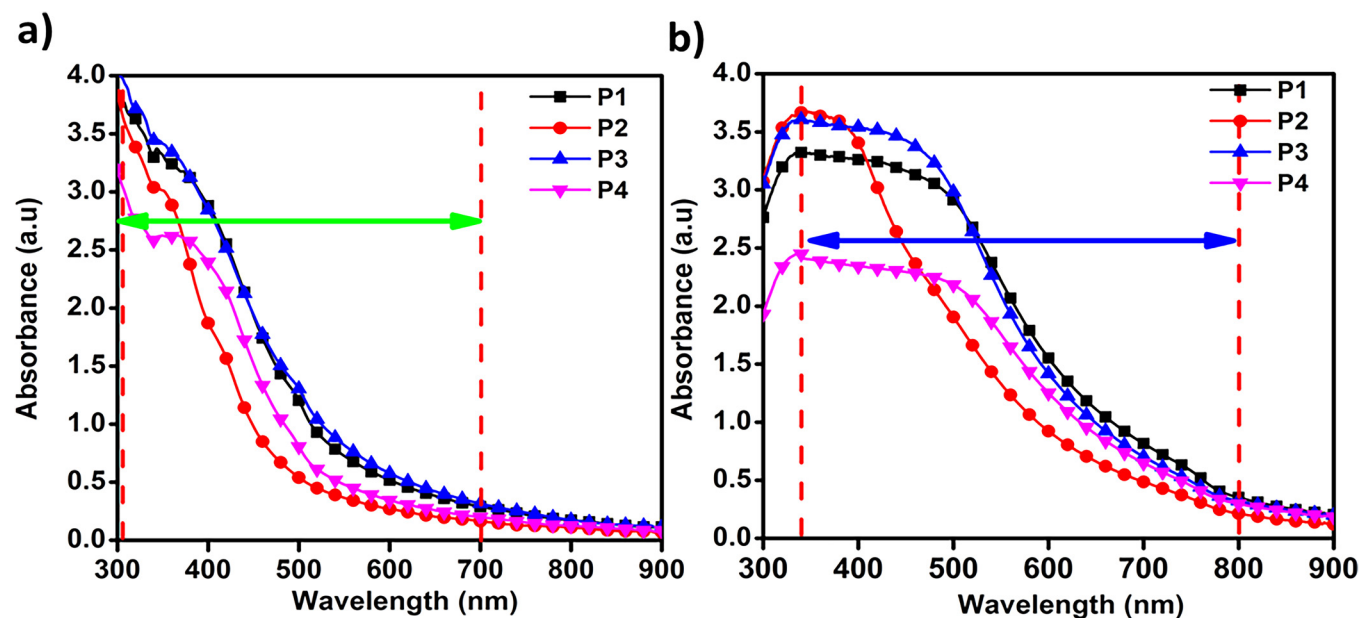


FIG. 8. UV-Visible absorption spectra of MAPbI₃ (P1–P4) grown at (a) 100 °C and (b) 150 °C.

turn could improve the efficiency of the solar cells. Moreover, we observed absorption toward the longer wavelength region, which reduced optical bandgap energy with respect to the single-step deposition because of the increased grain size of the grown materials. The optical bandgap was estimated to be 1.56 eV for the MAPbI₃ perovskite film, which is consistent with the reported values.²⁶

IV. CONCLUSIONS

MAPbI₃ films were successfully grown on top of transparent ETL by the one-step process from solvent intervened as well as mechanochemically synthesized perovskites. Tetragonal phase structures of bulk powders as well as spin-coated films were confirmed through XRD patterns. Annealing temperature induces the phase transition of MAPbI₃ films from tetragonal to cubic at 150 °C. The absence of PbI₂/PbCl₂ peaks for solvent free mechanochemically synthesized perovskites revealed the potential of this method along with the surface morphology and stability. Highly ordered, sheaflike, hyperbranched, and stable microarchitectures were obtained for MAPbI₃ films using the one-step synthesis route. Observed optical bandgap of MAPbI₃ perovskite films of 1.5–1.6 eV suggests that the material could be used as an effective solar absorber in perovskite solar cells.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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