

Fabrication, Characterization and Photovoltaic Properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoparticles

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Abstract

In this contribution, we have prepared $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoparticles (NPs) on the compact- TiO_x /indium tin oxide glass substrates by a simple spin-coating technique to control the size and shape of NPs. The NPs were prepared from the solution of perovskite and ionic liquid (IL) 1-hexyl-3-methylimidazolium chloride in N,N-dimethylformamide (DMF). A varying concentration of IL has found to affect the sizes and morphologies of the NPs. The resultant NPs are spherical in shape, and were uniformly distributed on compact- TiO_x substrates.

1. Introduction

Perovskites have shown potential application in multiple fields, such as, photocatalysis [1], ferroelectric [2], etc. Hybrid organic/inorganic halide perovskite, e.g., methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) with direct bandgaps, high absorption coefficients, long excitons diffusion lengths, and excellent charge transport properties as light absorber and carrier conductors material for thin-film photovoltaic application [3]. The researchers are interested to develop thin-film perovskite materials through simple, cost-effective and precise techniques rather than chemical synthesis.

In this study, we have reported the effect of varying the weight percentage (wt %) of ILs on the morphology of perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) film using spin-coating method.

2. Materials and method

Preparation of Perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) NPs by employing a Simple Spin-Coating Technique

The PbI_2 (0.144 g) and methylammonium iodide (0.05 g) were mixed in anhydrous DMF (615 μL) at 2.89:1 molar ratio followed by shaking at room temperature (RT) for 30 min to prepare the $\text{CH}_3\text{NH}_3\text{PbI}_3$ solution (25 wt %). The IL was used as the additive at varying concentration in the 25 wt % $\text{CH}_3\text{NH}_3\text{PbI}_3$ solution in DMF. A compact- TiO_x layer (30 nm) was deposited on ITO coated glass using chemical bath deposition (CBD) method. A DMF solution of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (25wt %) were spun-cast on top of the amorphous compact- TiO_x layer at 3000 rpm. During spin-coating, the color of the films changed from transparent to peach. The films were left to dry at RT for 30 min, to allow slow solvent evaporation, followed by annealing on a

hot plate at 100 °C for 10 min. Finally, 200 nm $\text{CH}_3\text{NH}_3\text{PbI}_3$ film is produced. All the preparation process was performed in an N_2 filled glove box.

3. Results and Discussion

The Fig. 1a shows the AFM image of TiO_x (30 nm) amorphous film. $\text{CH}_3\text{NH}_3\text{PbI}_3$ NPs having spherical morphology, was formed as shown in Fig. 1 (c, d and e), in the presence of 1, 3 and 7 wt % IL with respective diameters of 540, 350 and 600 nm. In contrary, the addition of high concentration of 10 wt % IL has resulted in irregular aggregation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ blocks as shown in Fig. 1f. We observed unchanged shapes but changed morphology of NPs with varying wt % of IL to the solution. The observation was similar to a previous report by Duan *et al.*[4] which confirms that the sizes and morphologies of the crystals depended on the concentration of the ionic liquid.

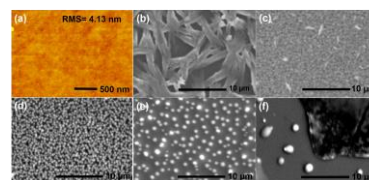


Fig. 1. The AFM image of (a) TiO_x film; The SEM images of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ NPs prepared in the presence of varying wt% of IL: (b) 0, (c) 1, (d) 3, (e) 7, and (f) 10.

The XRD patterns (Fig. 2) of perovskite films for NPs as prepared using varying wt% of ILs shows that all the peaks are similar to that of without IL. The diffraction peaks with and without IL were obtained at $2\theta = 14.01^\circ$, 28.40° and 40.44° , which are assigned respectively to the (110), (220) and (224) crystal planes. The peak positions confirm an orthorhombic crystalline structure [5]. There is a tiny peak at 12.65° , corresponding to a low-level impurity of PbI_2 at 7 wt % IL.

The UV-Vis spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films without and with varying wt% of IL cast on glass/ITO/ TiO_x substrates is shown in Fig. 3. The optical properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ NPs depend on the size and the shape of the particles. The absorption peaks were observed at around 493, 550, 520 and 525 nm for the system with 1, 3, 7 and 10 wt % IL, respectively, which corresponds to NPs in accordance with

the observation from Ayi, *et al.* [6]. The sharp absorption peaks for the spherical NPs also indicate a fairly uniform shape and size.

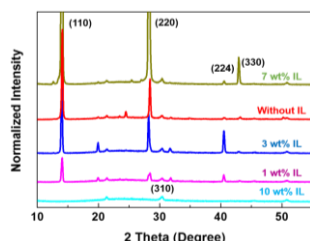


Fig. 2. The XRD patterns of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films processed without and with varying wt % of IL.

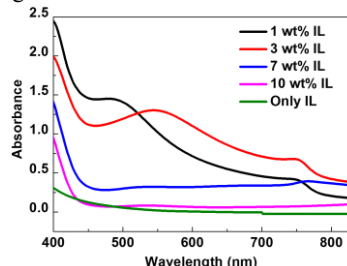


Fig. 3. The UV-Vis spectra of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films processed with varying wt % of IL.

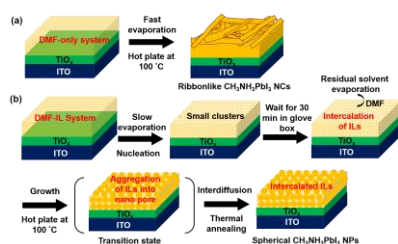


Fig. 4. Schematic view of $\text{CH}_3\text{NH}_3\text{PbI}_3$ NPs formation mechanism

When the amount of IL was increased to 10 wt %, we obtained amorphous $\text{CH}_3\text{NH}_3\text{PbI}_3$ blocks formed by irregular aggregation of small particles (Figure 1f), which can be attributed to the viscosity of the IL-DMF medium. A similar observation for IL-water medium was reported by Wu *et al.* [7], and the exponential expression used to express such characteristics were modified to fit into our system:

$$\eta = \eta_{\text{IL}} \cdot \exp[x_c/a]$$

Where, x_c is the mole fraction of DMF, a is a characteristic constant of the mixture, and η_{IL} is the viscosity of the pure IL. The empirical equation point out that the viscosity of IL-DMF mixtures is increased exponentially when the mole fraction of DMF (x_c) is decreased. When the amount of IL is increased, the viscosity of the system increases and the diffusion of the resulting complexes hindered.

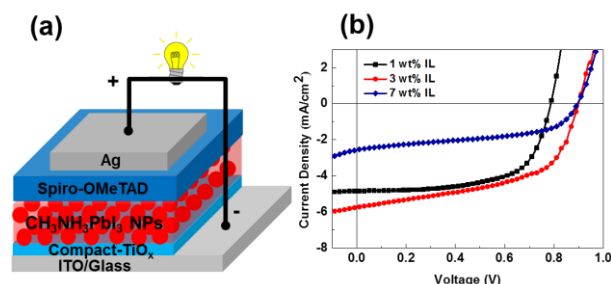


Fig. 5. (a) Device architecture of the planar structure $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells; (b) I-V curves for a planar junction cell processed with IL.

Figure 5a showed the device configuration of solar cells based on $\text{CH}_3\text{NH}_3\text{PbI}_3$ NPs. The $J-V$ characteristics of $\text{CH}_3\text{NH}_3\text{PbI}_3$ NPs based solar cells as obtained by using the varying concentration of IL (1, 3 and 7 wt %) and were measured at AM 1.5G illuminations are shown in Figure 5b. The photovoltaic devices prepared with 1 wt % IL-doped $\text{CH}_3\text{NH}_3\text{PbI}_3$ NPs showed a J_{sc} of 4.84 mA/cm^2 . An increase in the J_{sc} value to 5.74 mA/cm^2 was observed for the photovoltaic device prepared using 3 wt % IL-doped $\text{CH}_3\text{NH}_3\text{PbI}_3$ NPs, while the J_{sc} value is decreased to 2.56 mA/cm^2 for 7 wt % doping of IL. The PCE is also followed the similar trend of the J_{sc} values, showing a higher PCE of 2.81% for the photovoltaic device of 3 wt % IL-doped $\text{CH}_3\text{NH}_3\text{PbI}_3$ NPs. The low PCE, might be due to the residual IL content coated within the $\text{CH}_3\text{NH}_3\text{PbI}_3$ NPs that hindered the device performances as well as impact on charge dissociation/transport/recombination. However, the performance of solar cells prepared with $\text{CH}_3\text{NH}_3\text{PbI}_3$ NPs is assumed to be improved if the content of residual IL is removed from the surface of NPs.

Conclusions

The preparation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ NPs using a simple spin-coating method by introducing an ILs of varying wt % is reported. It has been observed that the size and shape of NPs can be controlled or modified by varying wt % of IL as additive in the solvent medium. The small-sized $\text{CH}_3\text{NH}_3\text{PbI}_3$ NPs ($\sim 350 \text{ nm}$) with superior optical absorption properties have been obtained with 3 wt % of IL in the medium, than the other evaluated IL concentrations (wt %) were 1, 7 and 10.

References

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