Extended Abstracts of the 2015 International Conference on Solid State Devices and Materials, Sapporo, 2015, pp528-529

Shape-Controlled Preparation of $MAPbI_3$ Nanoparticles by Ionic Liquid-Assisted Simple Spin-coating Method with Tunable Optical Absorption

Md. Shahiduzzaman, Kohei Yamamoto, Yoshikazu Furumoto, Takayuki Kuwabara, Kohshin Takahashi and Tetsuya Taima

Kanazawa Univ.,
Kakuma, Kanazawa 920-1192, Japan
Phone: +81-76-264-6279 E-mail: sohel_doc@stu.kanazawa-u.ac.jp; taima@se.kanazawa-u.ac.jp

Abstract

In this work, we have prepared $MAPbI_3$ based nanoparticles (NPs) on the TiO_x/indium tin oxide glass substrates with tunable optical absorption properties by controlling the size and shape of NPs using varying weight percent of 1-hexyl-3-methylimidazolium chloride (HMImCl) ionic liquid (IL) in conjunction with a simple spin-coating approach. 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 ($MAPbI_3$) 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 work, we have reported the varying concentration effect of ILs on the morphology of perovskite ($MAPbI_3$) film using spin-coating method.

2. Materials and method

Preparation of Perovskite ($MAPbI_3$) NCs Using a Simple Spin-Coating Technique

The PbI_2 (0.144 g) and MAI (0.05 g) were mixed in anhydrous DMF solvent (615 µl) at 2.89:1 molar ratio by shaking at room temperature (RT) for 30 min to produce a clear $MAPbI_3$ solution with concentration of 25 wt%. Lead iodide (PbI_2) was dehydrated in vacuum at 450 °C for 3h. Methylamonium lead Iodide was synthesized in our laboratory. A compact-TiO_x layer (30 nm) was deposited on an indium tin oxide (ITO) coated glass using CBD method. A DMF solution of $MAPbI_3$ (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 $MAPbI_3$ film is produced. All the preparation process was performed in an N_2 filled glove box.

Preparation of Perovskite ($MAPbI_3$) NPs by Simple Spin-Coating Technique

$MAPbI_3$ NPs were prepared using the same spin-coating technique as that described in preparation of $MAPbI_3$ NCs, except that varying wt% of 1-hexyl-3-methylimidazolium chloride (HMImCl) was also included in the 25 wt% $MAPbI_3$ solution in DMF.

3. Results and Discussion

The Fig. 1a shows the AFM image of TiO_x (30 nm) amorphous film. The Fig. 1b shows that the films processed without IL additive have incomplete surface coverage and are composed of non-uniform large crystal ribbon-like shape morphology. The observation is similar to that of Xiao et al [4], which confirms that the non-uniformity in the perovskite film was due to the rapid evaporation of DMF solvent during the spin casting process. On the other hand, a highly uniform $MAPbI_3$ NPs having a well-controlled spherical shape has been observed while even varying weight percent of IL was added to the solution system (Fig. 1c–f).

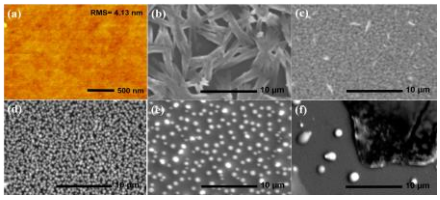

Fig. 1. The AFM image of (a) TiO_x film; The SEM images of the $MAPbI_3$ NPs prepared in the presence of varying wt% of IL: (b) 0, (c) 1, (d) 3, (e) 7, and (f) 10.

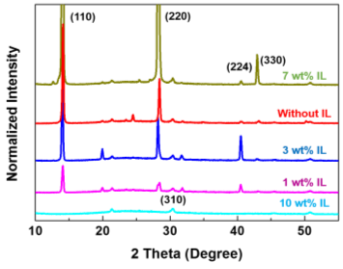

Fig. 2. The XRD patterns of $MAPbI_3$ films processed without and with varying wt% of IL.

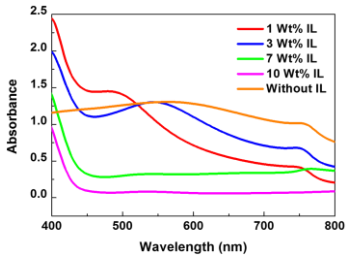

Fig. 3. The UV-Vis spectra of the $MAPbI_3$ films processed without and with varying wt% of IL.

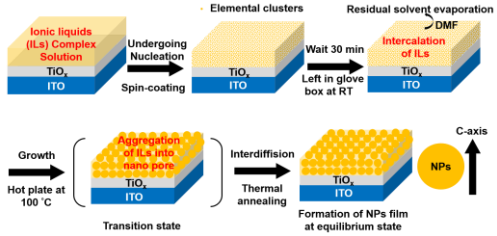

Fig. 4. Schematic view of $MAPbI_3$ NPs formation mechanism

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 2θ = 14.01, 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. It should be noted that aforementioned peak in the XRD patterns (with/without IL) indicates the complete consumption of PbI_2 within the process. The mean crystalline sizes for the perovskite crystals, with (1, 3, 7 wt% IL)/without IL, were 35.8, 38.0, 44.0 and 37.5 nm, respectively as estimated using the Scherer's formula from the full width at half-maximum of the (110) primary peak. The results indicate a similar crystallinity; nevertheless, the wt% of IL was varied.

The UV-Vis spectra of $MAPbI_3$ films without and with varying wt% of IL cast on glass/ITO/ TiO_x substrates is shown in Fig. 3. The optical properties of $MAPbI_3$ 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.

When the amount of IL was increased to 10 wt%, we obtained amorphous $MAPbI_3$ blocks formed by irregular aggregation of small particles (Figure 1e), 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:

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

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.

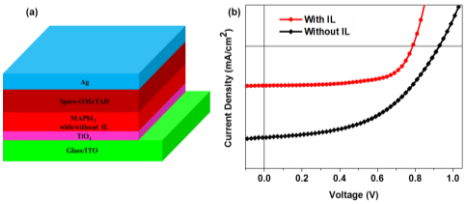

Fig. 5. (a) Device architecture of the planar structure $MAPbI_3$ solar cells; (b) I-V curves for a planar junction cell processed with/without IL.

The current density versus voltage (I-V) characteristics of $MAPbI_3$ films with/without IL measured at AM 1.5G illumination is shown in Fig. 5b. While the device without ILs shows a short-circuit current density (J_{sc}) of 11.90 $mAcm^2$ and values of V_{oc} = 0.92 V, FF = 0.49, and PCE = 5.10%, the device with IL displays values of J_{sc} = 4.84 $mAcm^2$, V_{oc} = 0.78, FF = 0.64, and PCE = 2.44%. The PCE is lower than the reference material, which might be due to the residual IL content coated within the $MAPbI_3$ NPs that hindered the device performances as well as impact on charge dissociation/transport/recombination. However, the performance of solar cells prepared with $MAPbI_3$ NPs is assumed to be improved if the content of residual IL is removed from the surface of NPs.

Conclusion

The preparation of $MAPbI_3$ 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 $MAPbI_3$ NPs (~350 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

[1] H. Kato and A. Kudo, J. Phys. Chem. B **105** (2001) 4285.
[2] P. M. Rørvik, T. Grande and M.-A. Einarsrud, Adv. Mater. **23** (2011) 4007.
[3] H. J. Snaith, The Journal of Physical Chemistry Letters **4** (2013) 3623.
[4] M. Xiao, F. Huang, W. Huang, Y. Dkhissi, Y. Zhu, J. Etheridge, A. Gray-Weale, U. Bach, Y.-B. Cheng and L. Spiccia, Angew. Chem. **53** (2014) 9898.
[5] Q. Chen, H. Zhou, Z. Hong, S. Luo, H.-S. Duan, H.-H. Wang, Y. Liu, G. Li and Y. Yang, J. Am. Chem. Soc. **136** (2013) 622.
[6] A. A. Ayi, C. A. Anyama and S. S. Etuk, J. Appl. Chem. **2** (2014) 26.
[7] L. Wu, J. Lian, G. Sun, X. Kong and W. Zheng, Eur. J. Inorg. Chem. **2009** (2009) 2897.