Fabrication of Lead-free $(CH_3NH_3)_3Bi_2I_9$ Solar Cell Using Anti-Solvent Engineering Treatment

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1. Introduction

Solar cell is one of the favorite issues in renewable energy research. Among of them, the lead-based perovskite solar cells (PSCs) has been considered as one of the most promising photovoltaic technology due to its advantages, including high efficiency, simple process, low cost, and the rapid growth of power conversion efficiency (PCE), which achieved to 22.7% in 2018 [1]. However, the toxicity of lead and poor stability hamper the commercialization of PSCs. As a result, the development of lead-free perovskite solar cells and improving the stability are bound to be the main issue for future research. Initially, the tin (Sn) has been used to replace the lead ion in perovskite materials owing to their similar valence state [2, 3]. However, the tin-based PSCs are easily oxidized which results in low stability and efficiency. To substitute lead ion and improve stability, bismuth has become a potential candidate due to its toxic-free and radioactivity-free. Bismuth also has similar properties to lead, and it could form a perovskite-like structure of $A_3Bi_2I_9$, where A is an organic cation, X is a halogen. Also, spin-coating is one of the film production method, which is widely used in solution-processed PSCs. Generally, the morphology of solution-processed perovskite films is determined by the nucleation and crystallization rate. Anti-solvent dripping is considered as an effective method to improve nucleation process. Here, we synthesize lead-free perovskite photovoltaic devices by one-step solution spin-coating method. We further investigated the crystal structure, morphology and PCE of PSCs fabricated with the anti-solvent treatment, which could promote crystallinity and improve morphologies of perovskite films.

2. General Instructions

For the synthesis of $(CH_3NH_3)_3Bi_2I_9$ ($MA_3Bi_2I_9$) precursors, methylammonium iodide (MAI) and bismuth triiodide (BiI_3) were dissolved in dimethylformamide (DMF)/dimethyl sulfoxide (DMSO) solvent mixture (v:v=13:1) with continuous stirring overnight. The molar ratio for MAI and BiI_3 was fixed at a molar ratio of 1:1. For solar cell fabrication, a TiO_2 compact layer (cp-TiO_2) was deposited on FTO glass by spray pyrolysis at 450 °C. A mesoporous TiO_2 film (mp-TiO_2) was screen printed onto the FTO glass/cp-TiO_2 substrate using diluted TiO_2 paste followed by a calcination process at 500 °C. The $MA_3Bi_2I_9$ solution was spin-coated onto the FTO glass/cp-TiO_2/mp-TiO_2 substrate. For anti-solvent dripping, toluene was further continuous dropped on the spinning substrate during the spin-coated process. The spiro-OMeTAD spin-coated on top of $MA_3Bi_2I_9$ film. Finally, a silver electrode was deposited by thermal evaporation.

The PSC based on the structure of FTO glass/cp-TiO_2/mp-TiO_2/$MA_3Bi_2I_9$/spiro-OMeTAD/Ag electrode is shown in **Fig. 1(a). Fig 1(b)** shows the *J-V* curves characteristics of PSCs with and without anti-solvent treatment. The short-circuit current density (J_{SC}) and open-circuit voltage (V_{OC}) of perovskite with anti-solvent treatment slightly increased from 0.32 to 0.51 mA/cm^2 and 0.55 to 0.66 V, respectively. The PCE of bismuth-based perovskite with anti-solvent treatment has improved from 0.07% to 0.24%, which is 70.83% higher than the PSCs without anti-solvent treatment.

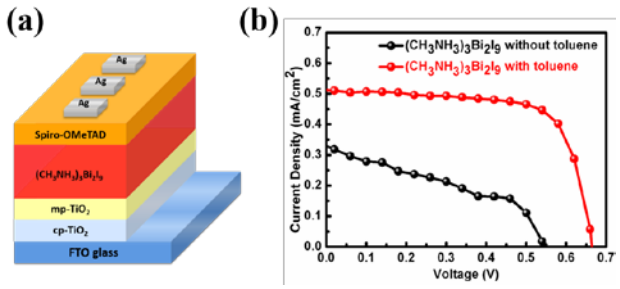

Fig. 1 **(a)** The schematic diagram of PSC structure, and **(b)** the *J-V* curves of the PSC with and without anti-solvent (toluene) treatment.

3. Conclusions

In summary, we use one-step solution spin-coating method to fabricate lead-free bismuth-based perovskite solar cells. After dripping anti-solvent, the power conversion efficiency improved from 0.07% to 0.24%, which is 70.83% higher than the PSCs without anti-solvent treatment. The bismuth-based perovskite shows the promising properties in the photovoltaic application, specifically in solar cells.

Acknowledgments

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