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Lead-free, air-stable ultrathin $Cs_3Bi_2I_9$ perovskite nanosheets for solar cells

Fan Bai[a,1], Yonghong Hu[b,1], Yanqiang Hu[a], Ting Qiu[a], Xiaoliang Miao[a], Shufang Zhang[a,*]

[a] College of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China
[b] School of Nuclear Technology and Chemistry & Biology, Hubei University of Science and Technology, Xianning 437100, China

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ABSTRACT

Organometallic halide perovskite materials have attracted great attention in the past few years owing to their excellent optical properties and solution-processable fabrication. However, the further development of these lead-based materials is restricted by the toxic heavy-metal element Pb. Herein, we present a dissolution-recrystallization method to fabricate high-quality lead-free $Cs_3Bi_2I_9$ perovskite nanosheets film and further explore its potential application in solar cells with three different kinds of hole transport materials. The solar cells based on ultrathin $Cs_3Bi_2I_9$ nanosheets show remarkable improvement in the photovoltaic performance and a high power conversion efficiency of 3.20% has been achieved in the solar cell with CuI as the hole transport material, which is the highest efficiency value of Bi-based perovskite solar cells that has been reported so far. The $Cs_3Bi_2I_9$ nanosheets based solar cell with CuI also showed a long-term stability in ambient air. These encouraging results of our work demonstrate the possibility of further improvement of the performance of lead-free perovskite solar cells.

1. Introduction

Hybrid organic – inorganic metal halide perovskites have attracted increasing research interests as novel light absorber materials in next generation high-efficiency thin film solar cells owing to their excellent optical properties, such as tunable band-gap, unique ambipolar charge-carriers transport and very long charger carrier diffusion lengths [1–4]. Over the last few years, the power conversion efficiency (PCE) of the conventional lead-based perovskite (e.g. $MAPbI_3$) solar cells has exceeded 22% [5–12]. Although these lead-based perovskite materials have showed excellent photovoltaic properties, the further development of these lead-based materials is restricted by the heavy-metal element Pb, which is rather toxic [13]. In order to solve this problem, it has been found that Sn and Ge, also as the members of group-14 metals, could replace Pb to form the less toxic perovskite structure [14–17]. Nevertheless, Sn^{2+} and Ge^{2+} are not as stable as Pb^{2+} in air, which are easily and quickly oxidized into a more stable Sn^{4+} and Ge^{4+} under the oxidizing atmosphere, and will cause quick destruction of the perovskite structure. To avoid such problem, all process including material preparation and device performance testing have to be performed in inertia gas atmosphere, which greatly increases the difficulty and cost of operation.

Recently, Bi-based halide perovskites with the chemical formula of $A_3Bi_2X_9$ (A refers to a monovalent cation, such as Na^+, K^+, Rb^+, Cs^+ and $CH_3NH_3{}^+$; X refers to a halogen atom), have gained much attention due to solving the stability and toxic problems related to lead-based perovskite materials [18–27]. These Bi-based halide perovskite materials have been reported for a long time, but most of the studies only focused on the crystal structures, phase transitions, *et.al.* Very recently, a few practical applications of $A_3Bi_2I_9$ in solar cells were reported [28–37]. So far, the highest power conversion efficiency of the $A_3Bi_2I_9$-based solar cells is as low as 1.64% [37]. The low power conversion efficiency may be caused by the poor quality films prepared by the conventional spin-coating method, as our group previously reported [38]. Thus poor film morphology usually arose from slow crystallization mainly owing to the high boiling point of the commonly used solvent N, N-dimethylformamide (DMF, 153 °C). Hence, it is important to develop a faster, facile solution-processing technique to further improve the film quality as well as the device performance.

In this work, we introduce a dissolution-recrystallization process to fabricate high-quality Bi-based halide $Cs_3Bi_2I_9$ film containing ultrathin $Cs_3Bi_2I_9$ nanosheets and explore its potential application in solar cells as light-absorbing material. The as-prepared ultrathin $Cs_3Bi_2I_9$ nanosheets formed uniform and compact $Cs_3Bi_2I_9$ film and exhibited a typical bilayer structure with a thickness of about 4.3 nm. We further fabricated the ultrathin $Cs_3Bi_2I_9$ nanosheets based planar heterojunction structured solar cells with three different kinds of materials as the hole transport materials (HTMs): CuI, 2,2′,7,7′-tetrakis(N,N-di-p-

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* Corresponding author.
E-mail address: zhangshufang@njust.edu.cn (S. Zhang).

[1] Fan Bai and Yonghong Hu contributed equally to this work.

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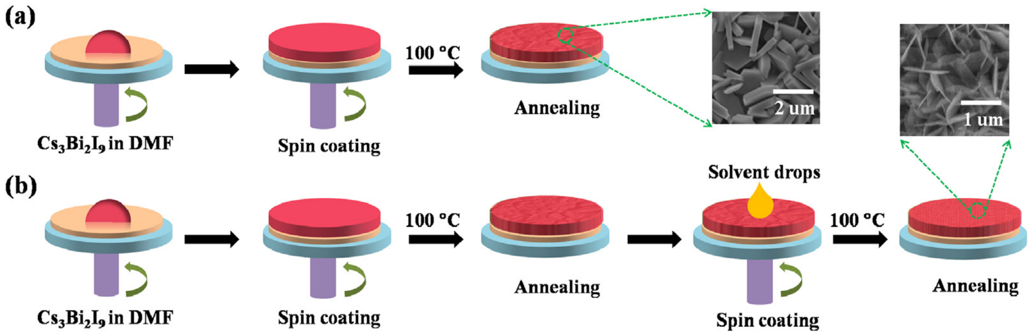

Fig. 1. Schematic illustration of the conventional spin-coating process (a) and the dissolution-recrystallization process (b) for preparing the $Cs_3Bi_2I_9$ films, respectively.

methoxyphenylamine) – 9,9′-spirobifluorene (spiro-OMeTAD) and poly-triarylamine (PTAA), respectively. The results were encouraging, a high PCE of 3.20% was achieved in the solar cell with CuI as the HTM. To the best of our knowledge, this is the highest PCE value of Bi-based perovskite solar cells so far. In addition, the highly performed device can remain over 57% of the initial PCE after 38 days in ambient condition (average RH = 45% and 25 °C).

2. Experimental

2.1. Chemicals and reagents

Bismuth iodide (BiI_3, 99%), Cesium iodide (CsI, 99.9%), *N,N*-dimethylformamide (DMF, anhydrous, 99.8%), titanium diisopropoxidebis (acetylacetonate) (75% in isopropanol) and CH_3OH (anhydrous, 99.8%) were purchased from Sigma-Aldrich. All salts and solvents were used as received without any further purification.

2.2. $Cs_3Bi_2I_9$ ultrathin nanosheets preparation

Firstly, a fluorine-doped tin oxide (FTO) conducting glass (sheet resistance < 15 Ω/square) was ultrasonically cleaned by detergent, deionized water, and acetone for 20 min sequentially, and treated by a UV/O_3 cleaner for 15 min. Then, a uniform dense TiO_2 layer was deposited on the substrate by spin coating 0.15 M titanium diisopropoxide bis (acetylacetonate) at 3500 rpm and repeating the process twice, and then sintered at 500 °C for 30 min. A precursor solution for $Cs_3Bi_2I_9$ was prepared by dissolving a mixture of BiI_3 (1.65 M) and CsI (2.475 M) in DMF and stirring for over 24 h at 70 °C. The thick $Cs_3Bi_2I_9$ polycrystalline film was deposited onto the TiO_2 film by spin coating of the precursor solution at 5000 rpm and followed by heating at 100 °C for 2 min. After cooling down, the sample was put back to the spin coater and the volatile polar organic solvent (the mixed solvent of DMF and CH_3OH) was dropwise added onto the $Cs_3Bi_2I_9$ film while it was spinning. Solvents with different DMF concentrations were prepared by adding 50, 100, 200, and 500 µL DMF in 1000 µL mixture of CH_3OH and DMF, respectively. Finally, the sample was annealing at 100 °C for 30 min and the ultrathin quasi-2D $Cs_3Bi_2I_9$ nanosheets were formed upon the evaporation of solvent.

2.3. Perovskite solar cell fabrication

The film with $Cs_3Bi_2I_9$ ultrathin nanosheets was prepared according to the procedure mentioned above. The hole transporter spiro-OMeTAD was dissolved in chlorobenzene and Li-bis (trifluoromethanesulfonyl) imide (LiTFSI) and tert-butylpyridine (TBP) were used as additives (0.167 g spiro-OMeTAD, 0.0298 g TBP, .0103 g in 1.00 mL chlorobenzene), then the solution was deposited by spin-coating at 5500 rpm for 30 s. The 0.1 M CuI solution was prepared by dissolving copper iodide in 1:39 di-n-propyl sulfide to chlorobenzene and stirring for 12 h. The CuI solution was then coated on top of the perovskite layer at 5500 rpm for 30 s, which was similar as reported by Jeffrey A. Christians [43]. A PTAA/toluene (15 mg/1 mL) solution adding 13.6 mL LiTFSI/acetonitrile (28.3 mg/1 mL) and 6.8 mL TBP was spin-coated on the perovskite layer at 5500 rpm for 30 s. Finally, a 100-nm thick Au layer was deposited on top of the device by thermal evaporation under ca. 1×10^{-6} Torr vacuum condition.

2.4. Measurement and characterization

The surface and cross morphology and elemental compositions of the $Cs_3Bi_2I_9$ films were observed by field-emission scanning electron microscopy (FE-SEM; Quanta 250FEG) with energy dispersive X-ray spectroscopy (EDS). The $Cs_3Bi_2I_9$ ultrathin nanosheets were analyzed by atom force microscopy (AFM; Brook Multimode 8). Powder X-ray diffraction (XRD) patterns of the $Cs_3Bi_2I_9$ films were recorded by a Bruker D8 diffractometer with Cu Kα radiation (λ = 1.5406 Å). Absorption spectra of the prepared films were measured with a UV–vis–NIR spectrophotometer (UV-3600, Shimadzu). The current-voltage characteristic curves of the fabricated PSCs were measured under standard AM 1.5 sunlight (100 mW/cm^2, WXS-90L2, Wacom). The effective area of the cell was defined as 1.0 cm^2 using a non-reflective metal mask.

3. Results and discussion

A dissolution-recrystallization method for preparing the ultrathin $Cs_3Bi_2I_9$ nanosheets is shown in Fig. 1. First of all, a uniform dense TiO_2 layer was deposited on a FTO glass by spin-coating. Then, a precursor solution with the mixture of CsI and BiI_3 in DMF was spin-coated on the TiO_2 layer and heated to form the $Cs_3Bi_2I_9$ polycrystalline film. Subsequently, the dissolution-recrystallization process was performed by spin-coating a small amount of polar organic solvent (the mixture of DMF and CH_3OH) onto the $Cs_3Bi_2I_9$ polycrystalline film [39]. Finally, the sample was subjected to annealing at 100 °C for 30 min to remove the residual solvent, and ultrathin $Cs_3Bi_2I_9$ nanosheets were formed in the thin film (see details in the Experimental Section).

The DMF in the mixed polar organic solvent (DMF/CH_3OH) can thoroughly dissolve the $Cs_3Bi_2I_9$ polycrystalline film, and the fast evaporation of solvent (due to the very low boiling point of CH_3OH) can make the $Cs_3Bi_2I_9$ form nucleation rapidly and grow into the ultrathin crystals. Combined with the intrinsic layered feature of $Cs_3Bi_2I_9$, it is easily for $Cs_3Bi_2I_9$ polycrystalline film to transfered into high-quality ultrathin nanosheets (Fig. 1b). In contrast, in a conventional spin-coating process without the mixed polar organic solvent, the obtained $Cs_3Bi_2I_9$ grains were larger than 1 µm and the films were in relatively poor quality with very big grains and voids (Fig. 1a). In addition, the elemental compositions of the conventionally prepared $Cs_3Bi_2I_9$ film and the ultrathin $Cs_3Bi_2I_9$ nanosheet films were almost identical (Fig. 2), confirming that the dissolution-recrystallization was happened