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Electrochemical deposition of PbI_2 for perovskite solar cells

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ABSTRACT

In this work, PbI_2 is coated on the TiO_2 films via the cost-effective electrochemical deposition method and a $MAPbI_3$ layer is formed by exposing the deposited PbI_2 to CH_3NH_3I subsequently. The structure, composition and morphology of the deposits are characterized in detail by the measurements of X-ray diffraction, scanning electron microscopy, and energy dispersion spectroscopy, respectively. The results suggest that a high coverage and uniform perovskite layer has been fabricated by virtue of the electrochemical deposition method. The influence of the deposition time in the morphology of the obtained perovskite is investigated and the optical properties of the prepared PbI_2 and $CH_3NH_3PbI_3$ are studied as well. As a result, the assembled perovskite solar cells exhibited a maximum PCE of 6.62% with the corresponding photocurrent of 12.5 mA cm^{-2} and open-circuit voltage of 0.957 V at AM 1.5 solar light of 100 mW cm^{-2}, thus demonstrating the feasible application of electrochemical deposition in perovskite solar cells.

1. Introduction

The growing interests and intense study in organic-lead halide perovskite solar cells boost their power conversion efficiency (PCE) over 21% in recent years (Saliba et al., 2016). Methylammonium lead iodide ($CH_3NH_3PbI_3$) as a promising material in photovoltaic application exhibits superior properties including favorable band gap, high absorption coefficient, long hole-electron diffusion length, and excellent carrier transport properties (Eperon et al., 2014; Jeon et al., 2014; Ryu et al., 2015; Hodes, 2013). A typical perovskite solar cell employs an n-i-p architecture, which comprises the sequential combination of a mesoporous TiO_2/perovskite ($MAPbI_3$) material/hole-transport material (HTM) (Jeon et al., 2015; Chen et al., 2014). In view of the perovskite plays a critical role in light absorption and carrier transportation, the structure, composition and morphology of it closely affect the photovoltaic performance of the solar cell (Nie et al., 2015; de Quilettes et al., 2015; Bi et al., 2016; Wu et al., 2014; Li et al., 2017). Yi et al. (2016) added Cs^+ cations to $FAPbI_3$ to stabilize the perovskite phase of $FAPbI_3$ and obtained the desired black perovskite with the corresponding solar cell yielding high average PCEs over 17%. In the aspect of morphology, Li et al. (2015) adopted an intermolecular self-assembly approach to retard the crystallization of PbI_2 in dimethylformamide (DMF) by adding dimethylsulfoxide (DMSO) thus obtaining an ultraflat and dense thin film of $MAPbI_3$.

Generally speaking, there are two routes to synthesis perovskite: single step and sequential deposition methods (Laban and Etgar L, 2013; Dualeh et al., 2014; Im et al., 2014). For the former one, a mixture of PbX_2 and CH_3NH_3X in a common solvent is deposited onto a mesoporous metal oxide film to form the perovskite compound. However, the uncontrollable precipitation of the perovskite often results in large morphological variation, thus hampering the reproducibility and improvement of photovoltaic performance (Bi et al., 2016). In this occasion, the sequential deposition method is developed with PbI_2 being introduced from solution into metal oxide films firstly and subsequent conversion into perovskite by exposing to a CH_3NH_3I solution, which exhibits better control over the perovskite morphology (Burschka et al., 2013). Nowadays, substantial efforts have been made to control the crystal growth and improve the quality of perovskite films (Xie et al., 2015; Streltsov et al., 1998; Kim et al., 2015). Xie et al. (2015) optimized the sequential deposition method by introducing CH_3NH_3I in PbI_2 precursor solution in the first step, which can affect the crystallization and composition of PbI_2 raw films. The efficiency of the resulted perovskite solar cells was improved from 11.13% to 13.37%. Although the photovoltaic performance of perovskite solar cells has

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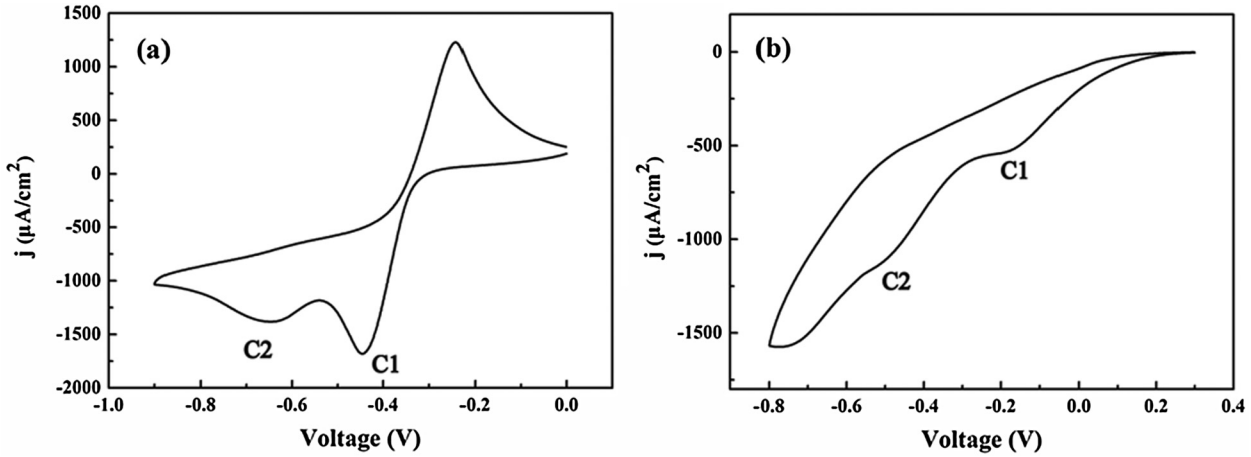

Fig. 1. Cyclic voltammograms for the TiO_2 electrode in a solution of (a) 0.01 M $Pb(NO_3)_2$ + 0.1 M $NaNO_3$, adjusting pH to 2 with HNO_3; (b) 0.02 M I_2 + 0.1 M $NaNO_3$, adjusting pH to 2 with HNO_3.

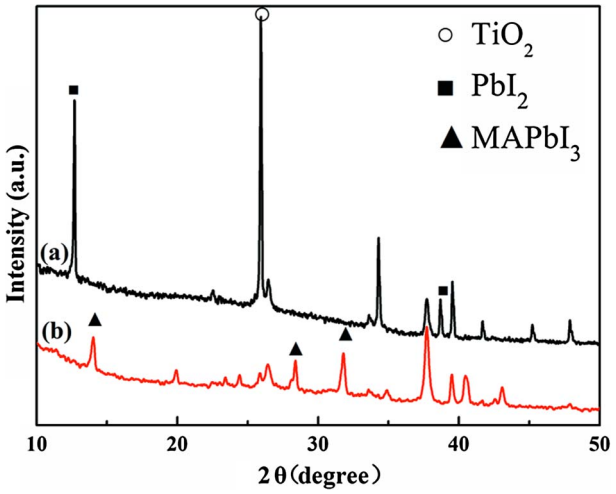

Fig. 2. XRD patterns of the electrodeposited of PbI_2 (a) and the resulted $CH_3NH_3PbI_3$ (b).

been improving continuously via modification of deposition method, less attention has been paid on the fabrication and microstructure regulation of the PbI_2 compound precursor yet, which is certainly very crucial to the resulted perovskite and the final photovoltaic performance, let alone most of the used PbI_2 is obtained by purchasing which is expensive.

As a cost-effective technique, electrochemical deposition method can realize depositing large area thin films (Streltsov et al., 1998). Accordingly, electrochemical deposition of semiconductor films has received intense attention due to their possible applications as photoelectrodes in solar cells (Li et al., 2016, 2014; Feng et al., 2012). For example, Sato et al. (2005) prepared SnS thin films by electrochemical deposition and adopted a pulse-form bias to optimize the morphology. By adjusting the deposition parameters, Lee et al. (2013) fabricated dense $CuInSe_2$ films with high crystallinity and uniformity on the In_2Se_3/ITO substrate via employing a single bath electrochemical deposition. However, few attempts have been reported on the electrochemical deposition of PbI_2 yet.

Given this issues, in this paper, electrochemical deposition method is employed to synthesize PbI_2 crystals and simplify the whole fabrication process of perovskite solar cells. After a series of detail characterization, the feasibility of electrochemical deposition method has been confirmed. Eventually, the resulted perovskite solar cells yield a maximum PCE of 6.62%, suggesting the promising application of electrochemical deposition method in perovskite solar cells.

2. Experimental section

2.1. Electrochemical deposition of PbI_2

TiO_2 compact layer was synthesized by adopting a solution containing 100 μL titanium (IV) acetylacetonate in 1 mL n-butyl alcohol and spraying on the cleaned FTO substrates which were placed on a hot plate with 450 °C. Then, commercial TiO_2 paste (20 nm) diluted with ethanol (1:3 wt ratio) was spin-coated on the TiO_2 compact layer to form mesoporous TiO_2 layer, followed by annealing at 500 °C for 30 min under an ambient atmosphere.

The obtained substrates were used to deposit PbI_2 with a three-electrode system including a Pt foil counter electrode and a saturated calomel electrode (SCE). The electrochemical deposition solution contains 10 mM lead nitrate, 20 mM iodine, and 100 mM sodium nitrate in deionized water/ethanol (1:2 by volume) with the pH of 2 adjusted by nitric acid. Subsequently, the mesoporous TiO_2 film as the working electrode, was dipping in the electrochemical deposition solution to deposit PbI_2.

2.2. Device fabrication

CH_3NH_3I was prepared according to the literature (Christians et al., 2014). Then the substrate deposited with PbI_2 was dipped into a beaker containing 10 mg ml^{-1} CH_3NH_3I solution (dissolved in isopropanol) as our previous work (Li et al., 2017). The spiro-OMeTAD is used as hole transporting layer with 80 nm gold vacuum-deposited on the top of it. The cells were characterized under an Air Mass 1.5 Global (AM 1.5 G) solar simulator with an irradiation intensity of 100 mW cm^{-2}. The resulted active area was 0.1 cm^2.

2.3. Characterization

The structure and morphology analysis were obtained using a Philip X'pert X-ray diffractometer equipped with Cu Kα radiation source (λ = 1.5406 Å) and a Nova NanoSEM 450 field emission scanning electron microscope (FE-SEM), respectively. UV–vis light absorption spectra were measured with a Lambda 35 (Perkin Elmer) ultraviolet visible (UV–vis) spectrophotometer. The photoluminescence (PL) spectra were carried by employing a LabRAM HR800 spectrometer. The cycle voltammogram curves and photovoltaic measurements of the PSCs were performed via a CHI604D electrochemical workstation under a simulated sunlight (Chang Tuo, incident light intensity 100 mW cm^{-2}).