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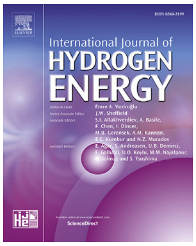

Study of carbon-based hole-conductor-free perovskite solar cells

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ABSTRACT

In this paper, the perovskite solar cells (PSCs) with the structure of FTO glass/compact TiO_2/mesoporous TiO_2/$CH_3NH_3PbI_3$/carbon electrode were designed and fabricated. The $CH_3NH_3PbI_3$ absorption layers were prepared using one-step solvent-engineering method. The effects of volume ratios of dimethyl sulfoxide (DMSO) to N, N-dimethylformamide (DMF) and molar ratios of PbI_2 to CH_3NH_3I (MAI) on structure and morphology of $CH_3NH_3PbI_3$ absorption layers, as well as photovoltaic performance of PSCs were studied. The results show that the PSCs based on a specific ratio of PbI_2:MAI = 1:1.4 and DMSO:DMF = 1:3 exhibited an optimal photovoltaic performance, yielding an open-circuit voltage (V_{oc}) of 0.72 V, short-circuit current density (J_{sc}) of 25.98 mA/cm^2, fill factor (FF) of 0.46, and power conversion efficiency (PCE) of 8.45%. And the incident photon-to-electron conversion efficiency (IPCE) is close to 85% between 400 and 600 nm visible region.

Introduction

Organic-inorganic hybrid perovskites, which were applied in photovoltaic devices for the first time in 2009, are a kind of material with very promising photovoltaic performance. In a few years after the first application, the power conversion efficiency (PCE) of perovskite solar cells (PSCs) have increased rapidly from 3.8% [1] to 22.1% [2]. Compared with other solar cells, the efficiency of PSCs has significantly been improved in a short time, with the most important reason that perovskites have a large absorption coefficient, high carrier mobility, direct band gap, long charge transmission distance and bipolar transmission characteristics of carriers (electrons or holes) [3,4]. Since the carrier lifetime of the perovskite is much longer than that of the first and the second generation of solar cells, PSCs also have the potential to further increase the power conversion efficiency (PCE). Initially, the low coverage and poor crystallinity of the perovskite films limited the PCE enhancement. Thus, to obtain high-quality PSCs, the most effective ways is to generate high-quality perovskite films. It means to control the crystal morphology, improve coverage and reduce pinholes of the perovskite films. The charge separation efficiency, charge transfer and diffusion length and other factors also depend on the crystallization quality of the

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films [5–13]. Recently, Shi et al. have reported interesting results for the single crystal growth of $MAPbX_3$ using an anti-solvent vapor-assisted crystallization (AVC) technique [14]. The single crystals were grown very slowly by the vapor-phase diffusion of the anti-solvent into $MAPbX_3$ precursor solutions. In this way, they successfully fabricated high-quality $MAPbX_3$ single crystals with low trap density and long carrier diffusion length. This excellent study inspired us to develop a less costly and less operationally complex solution approach.

A typical PSCs consist of electron transport materials, perovskite layer, hole transport materials (HTMs) and noble metal electrode. Most devices use gold (Au) as a back contact, in conjunction with organic hole conductors acting as electron-blocking layers. Hole conductors such as the widely used arylamine spiro-OMeTAD not only expensive but also limit the long-term stability of the device [15,16], which surely hinders the commercialization of PSCs in the future. Fortunately, it was found that HTM-free PSCs could also operate efficiently since the unique ambipolar property of the perovskite allows it to serve not only as a light harvester but also as a hole conductor [15]. Hole-conductor–free perovskite photovoltaic devices were first reported by Etgar et al. [17]. With Au electrode, the power conversion efficiency of the PCSs already exceeded 10% by improving the perovskite film deposition and back contact, showing the promising prospect of HTM-free PSCs [18,19]. However, the noble metal Au electrode is also costly, and the thermal evaporation process under high vacuum condition is required. Therefore, it is necessary to develop low-cost materials to replace the costly noble metal electrode (Au or Ag). Carbon materials, especially graphite and carbon black, are low cost, are abundantly available and have been applied in dye-sensitized solar cells. Carbon-based HTM-free PSCs are very promising for practical applications because of their high stability and low prices [20–22]. However, the PCE of carbon-based HTM-free PSCs are still relatively low in comparison with the organic HTM-based PSCs. For example, Ma and Sun et al. directly deposited commercial conductive carbon pastes onto the perovskite layers of HTM-free devices, achieving the PCE of 8–9%, respectively [23,24]. Meng et al. reported that the carbon films are directly hot-pressed onto perovskite film to be used as the counter electrode for HTM-free PSCs, and power conversion efficiency of 13.53% has been achieved [4].

In this work, we introduced an easy anti-solvent technique in fabricating the perovskite films to improve the morphology and crystallinity of the perovskite films and obtain high performance hybrid perovskite solar cells. Ethyl acetate was used as the anti-solvent because it allowed the solute to rapidly precipitate. As a result, controlling the rate of perovskite crystallization could obtain the high-quality perovskite film. By using low-cost carbon material instead of Au to prepare counter electrode, PSCs with the structure of FTO/compact TiO_2/mesoporous TiO_2/$MAPbI_3$/carbon electrode were fabricated and its photovoltaic performance was studied. The morphology and structure of the $MAPbI_3$ as well as the photovoltaic performance of PCSs were controlled by tuning the volume ratios of DMSO to DMF and the molar ratios of PbI_2 to MAI in the precursor solution.

Experimental details

Starting materials

Lead iodide (PbI_2, 99.9%), dimethyl sulfoxide (DMSO, 99.9%) and N, N-dimethylformamide (DMF, 99.9%) were purchased from Shanghai Aladdin Reagent Company. Methyl amine iodide (MAI, Dyesol, 99%) and TiO_2 spin-coating solution (OPV-18NR-T) were provided by Dalian Yingkou OPVTech Technology Company. Bis (pentane-2, 4-dionato-O, O′) bis (propan-2-olato) titanium (75% Isopropyl alcohol) solution purchased in Shanghai McLean Biochemical Technology Company. Commercial carbon paste (JUJO, CH-8 MOD) purchased from Guangzhou Kongtaifu Trade Company. Anhydrous ethanol (analytical reagent, 99.8%) and ethyl acetate (analytical reagent, 99.9%) were produced by Shanghai Sinopharm Company. All the reagents were analytical grade and they were used without any further purification.

Preparation of the compact TiO_2 layer and the mesoporous TiO_2 layer

The specification of the FTO (15 Ω/□, OPVTech Technology Company) used in this experiment is 2.0 cm × 1.5 cm, and the conductive surface is etched into two parts by utilizing a laser. The FTO substrates were cleaned by ultrasonic sequentially in acetone, alcohol and deionized water for 15 min each and were finally dried in air.

The compact TiO_2 layer was prepared onto the FTO substrates using spin-coating. In a typical synthesis process, the precursor solution was prepared by dissolving the bis (pentane-2, 4-dionato-O, O′) bis (propan-2-olato) titanium solution in n-butanol (mass ratio of 1: 10.3). The well-cleaned FTO substrates were pre-heated on a hot plate at 100 °C for 5 min. After that, the precursor solution was coated onto the pre-heated FTO substrate by spin coating at speed of 2500 rpm for 30 s, and then dried for 10 min at 100 °C. This spin coating procedure (coating and drying) was repeated twice to get the compact TiO_2 layer with thicknesses of approximately 80 nm. The compact TiO_2 layer was sintered at 500 °C for 30 min. The mesoporous TiO_2 layer was deposited by spin coating TiO_2 spin-coating solution (OPV-18NR-T) at speed of 5000 rpm for 30 s, and then sintered at 500 °C for 30 min. The thickness of the mesoporous TiO_2 layer is approximately of 500 nm.

Preparation of $CH_3NH_3PbI_3$ absorption layer

As the core part of the PSCs, the quality of the $CH_3NH_3PbI_3$ absorption layer is particularly important for the photovoltaic performance of PSCs. The $CH_3NH_3PbI_3$ layers were prepared by using the one-step solvent-engineering method in the air at room temperature. Typically, the $MAPbI_3$ precursor solutions were prepared by using 576 mg of PbI_2 and 199 mg of MAI as solute, 200 μl of DMSO and 800 μl of DMF as solvent. And the anti-solvent was ethyl acetate. Firstly, the substrates were pre-heated on a hot plate at 100 °C for 5 min. Secondly, the $MAPbI_3$ precursor solutions were spin-coated on the TiO_2 mesoporous layer, while, the anti-solvent ethyl acetate had to be added before the film was turbid during spin coating. The

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