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Research paper

Solvent control of the morphology of the hole transport layer for high-performance perovskite solar cells

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ABSTRACT

We investigated the effect of the morphology of 2,2′,7,7′-tetrakis-(*N*,*N*-di-*p*-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD) prepared using chlorobenzene (CB) and 1,2-dichlorobenzene (DCB) on the performance of perovskite solar cells (PSCs). We find that a more uniform and smoother spiro-OMeTAD layer was obtained using DCB than CB. The PSCs prepared using DCB exhibited a higher power conversion efficiency (PCE = 16.2%) than those obtained using CB (PCE = 14.5%). The hysteresis was reduced from 4.8% to 0.6%, with improved stability. The highest PCE of PSCs prepared using DCB was 16.6%, indicating that the use of DCB for spiro-OMeTAD processing enables the fabrication of high-performance PSCs.

1. Introduction

Following the first application of methylammonium lead halide perovskites ($CH_3NH_3PbX_3$, X = Cl, Br, or I) in solar cells by Miyasaka and coworkers in 2009 [1], the development of perovskite solar cells (PSCs) has been very rapid, because of their excellent performances and simple fabrication process. A record power conversion efficiency (PCE) of 22.1% was recently reported for a single PSC [2], highlighting the great potential of these systems for future commercialization [2–6].

Common PSCs have a typical *p-i-n* structure, with the perovskite sandwiched between the hole and electron transport layers [3–7]. A mesoporous TiO_2 layer is usually deposited onto a compact thin TiO_2 layer, fabricated on a fluorine-doped tin oxide (FTO)-coated glass substrate, to form the *n*-type electron transport layer [3–7]. In the case of the hole transport layer, 2,2′,7,7′-tetrakis-(*N*,*N*-di-*p*-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD) is widely used for extracting holes from the perovskite layers and transporting them to the metal electrode [3–7]. Besides the specific materials used as perovskite absorbers and electron/-hole transporters, the morphology of each layer plays a very important role in the device performance [8–17]. For examples, the morphology of the perovskite layer may affect its light harvesting and charge generation capabilities [8], whereas the morphology of the electron and hole transport layers has a strong influence on the charge transport, dissociation, and collection processes [9–17]. Recent investigations of the effect of the TiO_2 morphology on the performance of PSCs have led to the use of a mesoporous TiO_2 layer, a compact TiO_2 layer, and TiO_2 nanomaterials of different size as the electron transport layer in high-performance PSCs [3–7,10,13–15]. On the other hand, in the case of the hole transport layer, doping with organic and/or inorganic materials is a widely used strategy to improve the hole transport properties of spiro-OMeTAD [3–7,16,17]. The preparation of the spiro-OMeTAD layer usually involves dissolving spiro-OMeTAD in chlorobenzene (CB) [3–7,16,17]. In addition, ethyl acetate has been used for spiro-OMeTAD preparation, which resulted in a high PCE of 19.4% [18]. However, other solvents have not been widely used for spiro-OMeTAD layer preparation. Furthermore, the control of the morphology of the spiro-OMeTAD layer has not been thoroughly investigated so far. Solvent engineering is a widely used strategy to control the morphology of organic layers [11,12], which highlights the importance of investigating the effect of solvent-related changes in the morphology of the spiro-OMeTAD layer on the performance of PSCs.

In this work, we investigate the effect of the spiro-OMeTAD morphology on the performance of PSCs by using CB and

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1,2-dichlorobenzene (DCB) for the deposition of the spiro-OMeTAD layer. The analysis shows that DCB leads to a smoother spiro-OMeTAD layer compared with CB. This finding is attributed to the high boiling point and low vapor pressure of DCB, which considerably reduces the solvent evaporation rate during the formation of the spiro-OMeTAD layer by solidification. The improved morphology of the spiro-OMeTAD layer enhances its contact with the perovskite and the metal electrode. As a result, the PCE of PSCs based on a DCB-processed spiro-OMeTAD layer increased from 14.5% to 16.2%, with a simultaneous enhancement in the open circuit voltage (V_{oc}), short circuit current density (J_{sc}), and fill factor (FF) characteristics. Furthermore, the DCB-processed spiro-OMeTAD layer led to significantly reduced hysteresis (from 4.8% to 0.6%) and improved stability. The best PSC prepared using the DCB-processed spiro-OMeTAD layer showed a PCE as high as 16.6%. The present results indicate that using DCB for processing spiro-OMeTAD represents a simple and effective strategy for fabricating high-efficiency, low-hysteresis, and stable PSCs.

2. Experimental section

2.1. Device fabrication

Lead iodide (PbI_2), spiro-OMeTAD, and methylammonium iodide (MAI) were purchased from Sigma-Aldrich (USA), Nano-C (USA), and Xi'an Polymer Light Technology Corp. (China), respectively. All the solvents (CB, DCB, ethanol, 1-butanol, isopropanol, and *N,N*-dimethylformamide) used in this work were purchased from Sigma-Aldrich (USA). The perovskite precursor solution was prepared by dissolving MAI and PbI_2 (1:1 M ratio) in anhydrous *N,N*-dimethylformamide with a total concentration of 45 wt%. As shown in Fig. 1(a), the PSCs were fabricated in a FTO/TiO_2/perovskite/spiro-OMeTAD/Au configuration. First, a 20 nm-thick compact TiO_2 layer was coated on the cleaned FTO substrates by aerosol spray deposition of titanium diisopropoxide bis(acetylacetonate) (Sigma-Aldrich, USA) in 1-butanol solution. Then, a commercial TiO_2 paste (18NRT, Dyesol) diluted in ethanol was spin-coated on the compact TiO_2 layer. The TiO_2-coated substrates were annealed at 500 °C for 30 min, following which the $CH_3NH_3PbI_3$ perovskite precursor solution was spin-coated on the FTO/TiO_2 substrate at 5000 rpm in a N_2-filled glove box. During the spin-coating process, 120 μL CB was quickly added on the surface of the substrate after a specific delay time of 6 s to form a smooth and pinhole-free perovskite layer. The hole transport material was prepared by dissolving 75 mg mL^{-1} spiro-OMeTAD, 28 μL 4-*tert*-butylpyridine, and 18 μL of a solution of bis(trifluoromethane) sulfonamide lithium salt (520 mg in 1 mL acetonitrile) in 1 mL CB or DCB. Then, the solutions were separately spin-cast onto the perovskite film at 3000 rpm for 30 s. Finally, an Au anode of 100 nm was deposited on the devices under a vacuum of 10^{-4} Pa. The effective working area of the PSCs, determined by a shadow mask, was 0.1 cm^2.

2.2. Characterization

The surface morphology of the perovskite and spiro-OMeTAD layers was inspected by atomic force microscopy (AFM, Veeco, USA). Ultraviolet–visible (UV–vis) absorption spectra were measured by a Lambda 750 (Perkin Elmer, USA) spectrometer. The photoluminescence (PL) spectra were measured using a spectrometer (FLS920, Edinburgh Instruments, UK). Cross-section scanning electron microscopy (SEM) images were acquired using a microscope (Hatachi, Japan) operated at an acceleration voltage of 12 kV. Electrochemical impedance spectroscopy (EIS) analysis was performed in dark conditions using a SP-240 potentiostat (Bio-Logic, France) in the frequency range of 0.1 Hz to 7 MHz. The current density–voltage (*J–V*) characteristics of the PSCs were measured under an irradiation intensity of 100 mW cm^{-2} (1 sun, AM 1.5). The incident photon-to-current efficiency (IPCE) was measured using a Solar Cell IPCE measurement system (Solar Cell Scan 100, Zolix, China).

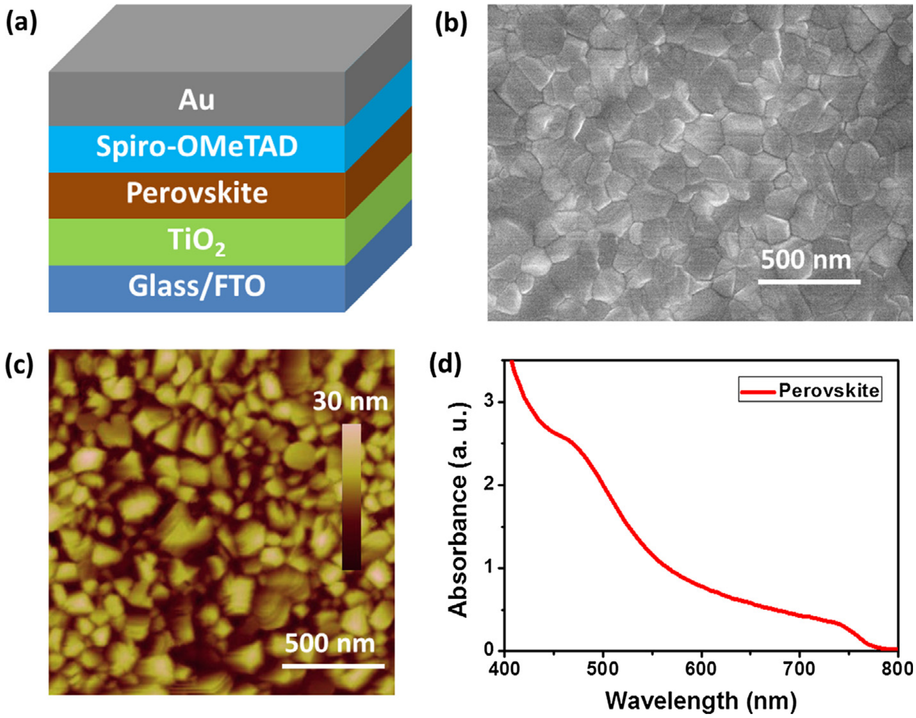

Fig. 1. (a) Schematic illustration of the PSCs investigated in this work; (b) SEM image of the prepared perovskite layer; (c) AFM height image of the prepared perovskite layer; (d) UV–vis absorption spectrum of the prepared perovskite layer.