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Effects of organic solvents for the phenyl-C61-butyric acid methyl ester layer on the performance of inverted perovskite solar cells

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ABSTRACT

We fabricated inverted perovskite solar cells (PSCs) using different organic solvents, including chloroform, chlorobenzene, and 1,2-dichlorobenzene, to prepare the phenyl-C61-butyric acid methyl ester (PCBM) layer. We found that using 1,2-dichlorobenzene resulted in smoother PCBM morphology compared to the chloroform- and chlorobenzene-based solvents; this would be beneficial for improving charge transport between the perovskite and cathode. In accordance with the morphologies, the average power conversion efficiency (PCE) of 1,2-dichlorobenzene-processed PSCs was 17.5%, which was higher than those of chlorobenzene- and chloroform-processed PSCs (16.7% and 11.0%, respectively) The best-performing cell was fabricated using 1,2-dichlorobenzene, showing PCEs of 17.9% and 18.2% in forward and reverse scans, respectively. We found that the conductivity and the PCBM surface roughness showed good linear dependence on the evaporation rate of the solvent, which could be an important factor for identifying new good organic solvents.

1. Introduction

Organic–inorganic hybrid methylammonium lead halide perovskite solar cells (PSCs) have attracted increasing attention because of their good performance, low cost, and simple processing properties [1–4]. Since they were first reported in 2009, the maximum power conversion efficiency (PCE) of PSCs has been improved to 22.1% [5], which promises a bright future for PSC commercialization [1–5].

Methylammonium lead halide-based PSCs have a typical p-i-n structure with the perovskite ($CH_3NH_3PbX_3$, where X is Cl, Br, or I) sandwiched between the hole and electron transport layers [1–4,6,7]. For conventional-structure PSCs, TiO_2 is typically employed as the electron transport material. However, the high processing temperature (*ca.* 500 °C) for TiO_2 sintering would possibly increase the production cost in future commercialization and limit its application on flexible substrates [1–3,8–10]. To overcome this problem, inverted-structure PSCs have been rapidly developed, which usually use an organic material (phenyl-C61-butyric acid methyl ester, PCBM) for electron transport [8–13]. Recently, the PCEs of inverted PSCs have improved beyond 18%, and are already comparable to those of TiO_2-based conventional PSCs [14–16]. However, the processing temperature has dramatically reduced from 500 °C to approximately 140 °C [8–16], which is more suitable for large-scale and roll-to-roll production [8–16].

In addition to finding new materials, the morphologies of the perovskite and charge transport layers play critical roles in the performance of PSCs [16–25]. For example, the morphology of perovskites is highly related to the light-harvesting and charge-generation properties of PSCs [18,19]. Recently, techniques such as thermal annealing, solvent vapor annealing, and solvent engineering have been developed to control the morphology of the perovskite layers for boosting the performance of PSCs [17–21]. However, the morphology of the charge transport layers is a critical factor for charge separation and collection in the PSCs [16–25]. In the case of inverted PSCs, recently, morphology control of the PCBM layers has been actively investigated to improve their performance [16,22–25]. For example, poly(methylmethacrylate) was used as an additive to decrease the aggregation of PCBM, leading to an improvement in PCE from 18.02 to 18.72% [16]. Thermal annealing and solvent vapor annealing were performed to improve the morphologies of PCBM films, with the PSCs showing high PCEs of 16.3–19.4% [22,23]. A high-boiling-point 1,8-diiodoctane was adopted as a solvent additive, and a smoothed PCBM morphology and improved device performance (from 11.01 to 12.73%) were obtained [24]. A combination of PCBM solution- and vapor-processing techniques was developed

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to obtain a smooth morphology, improving the PCE to 12.2% [25]. In these studies, either chlorobenzene (CB) or 1,2-dichlorobenzene (DCB) was used as the solvent for PCBM dissolution and deposition [11–16,22–25]. However, the effects of the different solvents could not be compared directly because of the distinct experimental conditions of each study. In addition, chloroform (CF), which is also widely used for PCBM-based bulk-heterojunction solar cells [26], has not been frequently used for PSCs using PCBM.

For bulk-heterojunction organic solar cells based on PCBM, the effects of organic solvents on performance have been extensively studied. It was found that active-layer morphologies including PCBM were significantly affected by the choice of the organic solvent [26–28]. Depending on the donor materials, in some cases (such as poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b′] dithiophene-*co*-3-fluorothieno[3,4-b]thiophene-2-carboxylate]), using DCB leads to the best active-layer morphology, resulting in the best PCE, whereas in other cases (such as poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-*b*']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno [3,4-*b*]thiophenediyl]]), using CB is better than DCB for the organic solar cell performance [27]. Furthermore, sometimes, for poly(3-hexylthiophene)-based organic solar cells, using CF resulted in better active-layer morphology than CB [28]. The best organic solvent for the PCBM layer in inverted PSCs cannot be simply guessed from studies on organic solar cells, because the materials and structures of PSCs are significantly different from those of organic solar cells. Hence, a systematic study investigating the effects of organic solvents on the PCBM layer in inverted PSCs is highly desired for obtaining optimum performance.

In this work, we systematically investigated the morphology dependence of PCBM layers on different organic solvents (CF, CB, and DCB) and its effect on the performance of the relevant inverted PSCs. CF, CB, and DCB were tested as solvents for processing PCBM layers in our PSCs; these solvents are those most widely used for PCBM-based organic solar cells [26]. We found that the surface morphology of PCBM became smoother as the organic solvent was changed from CF through CB to DCB. The uniform and smoothed PCBM layer is advantageous for charge extraction from the perovskite and collection by the electrode. Consistent with the morphologies, the PCEs obtained using CF, CB, and DCB were 11.0, 16.7, and 17.5%, respectively. Our results show that using DCB for PCBM processing leads to the best PCE performance and long-term stability of PSCs. The best sample was obtained using DCB; it exhibited a high PCE of 17.9% (by forward scan), without significant hysteresis (18.2% by reverse scan). The conductivity and root-mean-square (RMS) roughness of the PCBM layer showed good linear dependences on the evaporation rate of the solvent. We discuss how the evaporation rate possibly affects the PCBM morphology.

2. Experimental

2.1. Device fabrication

Lead acetate trihydrate ($PbAc_2{\cdot}3H_2O$), PCBM, and methylammonium iodide (MAI) were purchased from Sigma-Aldrich (USA), Nano-C (USA), and Xi'an Polymer Light Technology Corp. (China), respectively. All solvents (CF, CB, DCB, isopropanol, and *N,N*-dimethylformamide) used in this study were purchased from Sigma-Aldrich (USA). The perovskite precursor solution was prepared by dissolving MAI and $PbAc_2{\cdot}3H_2O$ (3:1 M ratio) in anhydrous *N,N*-dimethylformamide with a total concentration of 40 wt%. Before device fabrication, indium-tin oxide (ITO)-coated glass substrates were washed using a bath sonicator with water, acetone, and isopropanol, sequentially. As shown in Fig. 1(a), the PSCs were fabricated on ITO substrates using an inverted structure of ITO/PEDOT:PSS/perovskite/PCBM/BCP/Ag. Here, PEDOT:PSS and BCP stand for poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate) and bathocuproine, respectively. First, a thin layer of PEDOT:PSS (40 nm, Clevios P VP AI 4083) was spin-coated on the prewashed ITO substrates and then baked at 140 °C for 15 min in air to remove the remaining solvent. After that, the perovskite precursor solution was spin-coated onto the PEDOT:PSS layer and annealed at 95 °C for 10 min in a glove box filled with Ar gas. Then, 20 mg mL^{-1} PCBM in CF, CB, and DCB solutions were respectively spin-coated onto the perovskite layers at 1000 rpm for 60 s. After annealing at 40 °C for 30 min, BCP (Sigma-Aldrich, USA) in isopropanol (0.5 mg mL^{-1}) was spin-coated onto the PCBM layers. Finally, the device fabrication was completed by thermally evaporating 100 nm Ag onto the PCBM/BCP layers under a high vacuum of 5×10^{-6} Torr. The effective device working area was 0.09 cm^2, as determined by a shadow mask. For X-ray diffraction (XRD) measurement of the PCBM layers, we fabricated devices with a glass/ITO/PEDOT:PSS/PCBM structure, where the PCBM layer was casted using CF, CB, or DCB as the solvent.

2.2. Characterization

The surface morphologies of the PCBM layers were measured by atomic force microscopy (AFM; Veeco, USA). Ultraviolet–visible (UV–vis) absorption spectra were acquired by spectroscopy (Perkin Elmer Lambda 750, USA). The perovskite surface and PSC cross-section were measured by scanning electron microscopy (SEM; JEOL, Japan) with an acceleration voltage of 15 kV. XRD analysis was performed with an X-ray diffractometer (PANalytical, Netherlands). Photoluminescence (PL) spectra were acquired using a spectrometer (FLS920, Edinburgh Instruments, UK). Electrochemical impendence spectroscopy (EIS) analysis was performed in dark conditions using an SP-240 potentiostat (Bio-Logic, France) over the frequency range of 0.1 Hz–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, AM1.5). The incident photon-to-current efficiency (IPCE) was measured using a Solar Cell IPCE measurement system (Solar Cell Scan 100, Zolix, China).

3. Results and discussion

As summarized in Table 1, the solvent parameters indicate that the solvent evaporation rate may decrease in the sequence of CF, CB, and DCB [29–32]. The quality of the perovskite layer was characterized using UV–vis, XRD, and SEM measurements, immediately after the perovskite layer was deposited on the PEDOT:PSS layer. The UV–vis spectrum in Fig. 1(b) shows a high absorption coefficient of the perovskite layers for wavelengths in the 400–800 nm range, indicating a good light-harvesting ability of the perovskite layers [19,33]. The XRD pattern in Fig. 1(c) indicates a tetragonal perovskite structure with the lattice parameters $\mathbf{a} = \mathbf{b} = 8.85$ Å and $\mathbf{c} = 12.64$ Å, similar to other high-quality perovskites in previous studies [33,34]. The SEM image in Fig. 1(d) shows the full surface coverage of the perovskite, with particles of 100–300 nm in diameter, again, consistent with other high-quality perovskites in previous studies [19,33]. The presented UV–vis absorption, XRD, and SEM results indicate that the perovskite layer in this study was well prepared, and is the basis for the *J–V* performance of the PSCs. Fig. S1 shows cross-section SEM images of the PSCs, which indicate a dense layer-by-layer structure of the PSCs, where CF, CB, or DCB was used as the solvent for PCBM. The thickness of the perovskite layers was approximately 400 nm, and the thickness of the PCBM layers prepared from CF, CB, and DCB were 96, 92, and 90 nm, respectively. A previous study indicated that such a small difference in PCBM thickness has a negligible effect on the performance of PSCs [35].

The forward-scan *J–V* performances of the PSCs are shown in Fig. 2(a). The device parameters and deviations are summarized in Table 2 and Fig. S2. In the case of using CF for the PCBM processing, the PSC showed a low PCE of 11.0%, with an open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill factor (FF) of 0.99 V, 17.8 mA cm^{-2}, and 62.3%, respectively. By using CB for PCBM processing, the V_{oc}, J_{sc}, and FF values of the PSCs were greatly improved to 1.05 V, 21.0 mA cm^{-2}, and 75.7%, respectively, yielding an improved