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Photovoltaic performance and stability of fullerene/cerium oxide double electron transport layer superior to single one in *p-i-n* perovskite solar cells

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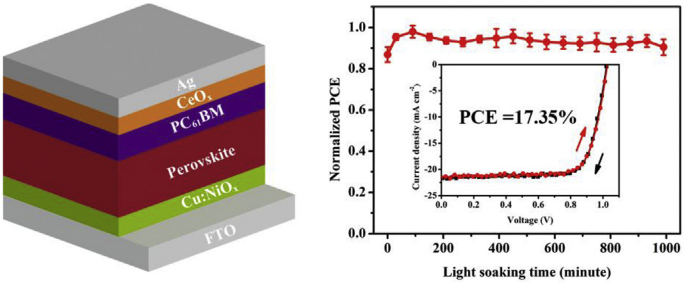
HIGHLIGHTS

- CeO_x and $PC_{61}BM$ were applied as double ETLs by low-temperature solution process.
- The J_{sc} and stability of devices were enhanced by applying $PC_{61}BM/CeO_x$ double ETLs.
- The devices based on $PC_{61}BM/CeO_x$ double ETLs show negligible hysteresis.

GRAPHICAL ABSTRACT



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ABSTRACT

Interface engineering that involves in the metal cathodes and the electron transport layers (ETLs) facilitates the simultaneous improvement of device performances and stability in perovskite solar cells (PSCs). Herein, low-temperature solution-processed cerium oxide (CeO_x) films are prepared by a facile sol-gel method and employed as the interface layers between [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) and an Ag back contact to form $PC_{61}BM/CeO_x$ double ETLs. The introduction of CeO_x enables electron extraction to the Ag electrode and protects the underlying perovskite layer and thus improves the device performance and stability of the *p-i-n* PSCs. The *p-i-n* PSCs with double $PC_{61}BM/CeO_x$ ETLs demonstrate a maximum power conversion efficiency (PCE) of 17.35%, which is superior to those of the devices with either $PC_{61}BM$ or CeO_x single ETLs. Moreover, $PC_{61}BM/CeO_x$ devices exhibit excellent stability in light soaking, which is mainly due to the chemically stable CeO_x interlayer. The results indicate that CeO_x is a promising interface modification layer for stable high-efficiency PSCs.

1. Introduction

Organic-inorganic hybrid perovskite solar cells (PSCs) have generated considerable interest as a promising alternative to traditional inorganic photovoltaic devices because of their potential to achieve a high efficiency at competitive costs [1–4]. The power conversion

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efficiencies (PCEs) of PSCs have risen steadily from ~3% [5] to 22.1% [6] in recent years, which can rival that of traditional solar cells such as those based on crystalline silicon, cadmium telluride (CdTe), and copper indium gallium diselenide (CIGS). Most of the best device efficiencies have been achieved on mesoporous and planar device structures using TiO_2 as the electron transport layer (ETL). However, high-temperature (~500 °C) annealing is usually required for the TiO_2 scaffold in a mesoporous structure, which is not compatible with flexible substrates. The regular structure (i.e., n-i-p structure) based on TiO_2 not only requires a high-temperature sintering process but also suffers from an anomalous current density-voltage (*J-V*) hysteresis [7,8]. To address these issues, a new device structure, referred to as an "inverted" planar structure (*p-i-n* structure), has attracted much attention because of its high efficiencies, low-temperature processing, and negligible *J-V* hysteresis effects [9–12].

For inverted structure (*p-i-n*) PSCs, the commonly used hole transport layer (HTL) and ETL are poly(3,4-ethylenedioxythiophene):poly (styrenesulfonic acid) (PEDOT: PSS) and the fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$), respectively [11–14]. However, the acidic and hygroscopic nature of PEDOT: PSS limits the long-term stability of perovskite solar cells. To improve the stability of *p-i-n* PSCs, various inorganic HTLs such as NiO_x [15–18], CuO_x [19], CuI [20], CuSCN [21], and CoO_x [22] have been introduced into *p-i-n* PSCs to replace PEDOT: PSS. Apart from HTLs, ETLs also have a significant impact on the long-term stability of *p-i-n* PSCs. To design efficient and stable ETLs for *p-i-n* PSCs, criterion are usually considered in terms of high electron mobility and conductivity [23], high oxygen, ambient and chemical stability [24,25], matched energy levels and wide band gaps for enhancing the charge extraction and suppressing charge recombination [26], optimal nanostructure and morphology [12,27], low-temperature solution processing and low cost [28], and good solubility [29,30] etc. For instance, Chen et al. reported that inverted planar PSCs based on Mg-doped NiO HTL and Nb-doped TiO_x ETL exhibited a high stability [15]. Yang et al. employed ZnO nanoparticles instead of fullerene as the ETL to improve the air stability of *p-i-n* PSCs [18]. Choulis et al. reported that *p-i-n* PSCs incorporating aluminum-doped zinc oxide (AZO) as the ETL and Au as the top electrode maintained 100% of the initial PCE for over 1000 h of exposure in air [31]. Jen et al. prepared crystalline Zn_2SnO_4 nanoparticles via the hydrothermal method and applied them as the ETL to create inverted and flexible PSCs [32]. Chueh et al. used highly crystalline SnO_2 nanocrystals as ETL to simultaneously enhance the device performance and stability [33]. He et al. adopted titanium, zirconium, and hafnium acetylacetonate as the ETLs to create high-performance and stable planar PSCs with a PCE over 16% on a 1 cm^2 scale [34]. These ETLs have enhanced the device efficiency and improved the device stability of *p-i-n* PSCs. Nevertheless, these electron transport materials must be doped, or fabricated into nanoparticles using complicated fabrication processes, which hinders the utilization of PSCs. Furthermore, little is known about the stability under continuous light soaking of the devices based on those ETLs. Therefore, it is highly desirable to develop an undoped, air- and light-stable ETL that can be fabricated by a facile, low-cost, and low-temperature solution-processed approach.

Recently, cerium oxide (CeO_x) has been used in organic solar cells [35] and *n-i-p* PSCs [36] because of its outstanding properties, such as a wide band gap, a large dielectric constant, high ionic conductivity, and high thermal and chemical stability [36]. However, its applications in *p-i-n* PSCs are rarely reported. Herein, we have successfully prepared a low-temperature solution-processed CeO_x film via a facile sol-gel method and employed it as the interface layer between $PC_{61}BM$ and an Ag back contact to form a $PC_{61}BM/CeO_x$ double ETL. The introduction of CeO_x facilitates electron extraction to the Ag electrode and protects the underlying perovskite $CH_3NH_3PbI_3$ ($MAPbI_3$) layer, thus simultaneously improving the device performance and stability. The *p-i-n* PSCs with double $PC_{61}BM/CeO_x$ ETL demonstrated a PCE of 17.35%, which is much higher than that of devices based on either a $PC_{61}BM$ or CeO_x single ETL. The enhancement in PCE mainly comes from the optical spacer effect and the hole-blocking nature of the CeO_x interlayer, which improves the charge extraction efficiency and enhances light harvesting. Moreover, with the double $PC_{61}BM/CeO_x$ ETL, the stability of the *p-i-n* PSCs was dramatically improved, which maintained over 90% of the initial PCE after 1000 min light soaking in the air. This improved stability clearly illustrates the advantage of CeO_x interlayer as a chemically stable protecting layer for the underlying perovskite layer. This work indicates that high-efficient and stable perovskite solar cells can be obtained by employing $PC_{61}BM/CeO_x$ double ETLs. More importantly, our work opens up a new and promising interfacial modification strategy using double ETLs for achieving efficient and stable perovskite solar cells. We believe that interface engineering using double ETLs will make great contribution to the future development of perovskite solar cells towards commercialization.

2. Experimental

2.1. Materials

Nickel (II) acetylacetonate (96%), copper (II) acetylacetonate (98%), lead (II) iodide (PbI_2, 99.9985%), and cerium (III) 2,4-pentanedionate hydrate ($Ce(acac)_3 \cdot xH_2O$) were purchased from Alfa-Aesar. *N*,*N*-dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.8%), acetonitrile (99.8%), chlorobenzene (99.8%), di-isopropyl ether (99.8%) were received from Sigma-Aldrich. Fluorine-doped tin oxide coated glass substrates (FTO, 14 Ω sq^{-1}) were purchased from Wuhan Ge'ao Co., Ltd. $PC_{61}BM$ was obtained from American Dye Source Inc. PEDOT: PSS (Baytron P VP AI 4083) was purchased from HC Stark. Methylammonium iodide (CH_3NH_3I, 99.5%) was purchased from Lumtec Corp. All reagents and chemicals were used without further purification unless otherwise noted.

2.2. Device fabrication and characterization

Patterned FTO glass substrate was cleaned by sequential ultrasonic treatments in a detergent, deionized water, acetone, and isopropyl alcohol for 15 min, followed by being dried in an oven at 80 °C. The FTO glass substrate was treated in a UV ozone chamber for 10 min prior to spin-coating the HTL. The Cu-doped NiO (Cu:NiO_x) HTL was fabricated according to the previously described methods with minor modifications. A 0.06 M acetonitrile/ethanol (with 95:5 vol ratio) solution of nickel acetylaceonate (95 mol%) and copper acetylacetonate (5 mol%) was spin-coated on top of the FTO substrate at 3000 rpm for 30 s. The FTO/Cu:NiO_x substrate was further treated at 500 °C for 30 min in the air and moved into a glove box filled with N_2 after cooling. The perovskite precursor solution was prepared by mixing 461 mg of PbI_2, 159 mg of CH_3NH_3I, and 78 mg of DMSO in 600 mg of the DMF solution at room temperature and stirring for 1 h. The completely dissolved solution was spin-coated on the HTL layer at 4000 rpm for 25 s and 1 mL di-isopropyl ether was dripped on the rotating substrate within 10 s. The transparent precursor film was heated at 100 °C for 10 min to obtain a dense perovskite film. After cooling down to room temperature, the $PC_{61}BM$ was deposited on the top of the perovskite layer by spin-coating a solution of 20 mg mL^{-1} in chlorobenzene at 2000 rpm for 20 s. To prepare the CeO_x film, cerium (III) 2,4-pentanedionate hydrate was dissolved in 2-propanol with various concentrations, and then was treated in a ultrasonic bath for 30 min to prepare the $Ce(acac)_3$ precursor solution. The precursor solution was spin-coated on top of the $PC_{61}BM$ layer at 6000 rpm for 30 s and was followed by thermal annealing at 100 °C for 10 min. Finally, an Ag electrode (~70 nm) was thermally deposited under a base pressure of $\sim 2 \times 10^{-4}$ Pa to complete the device.

All the devices were characterized in the ambient conditions. The photovoltaic performances were characterized under the illumination of AM 1.5 G, 100 mW cm^{-2} using a 300 W xenon solar simulator