Efficient planar perovskite solar cells using solution-processed amorphous WO$_x$/fullerene C$_{60}$ as electron extraction layers

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In perovskite solar cells (PSCs), an electron extraction layer (EEL) plays a crucial role in extracting electrons from the perovskite layer and blocking the holes in it from recombining with the electrons in the fluorine-doped tin oxide (FTO). Amorphous tungsten oxide (WO$_x$) has been successfully employed as EEL in PSCs. However, the WO$_x$ device suffers from inherent charge recombination, resulting in low open circuit voltage (V_{oc}) and fill factor (FF). Here, we report that WO$_x$/fullerene C$_{60}$ can work coactively to further enhance the performance of PSCs. PSC with WO$_x$/C$_{60}$ EELs showed a power conversion efficiency of 16.07% with an open circuit voltage of 0.93 V, a short-circuit current density of 22.15 mA/cm^2, and a fill factor of 0.78, which were higher than those of PSCs with pristine WO$_x$ EEL. Our results suggest that using WO$_x$/C$_{60}$ as EELs offer a simple and effective approach for fabricating high-performance and low-temperature PSCs.

1. Introduction

Organic—inorganic methylammonium lead halide perovskites (e.g., CH$_3$NH$_3$PbX$_3$; X = Cl, Br or I) have been widely reported to be excellent light-absorbing materials for photovoltaic applications because of their tunable bandgaps, large absorption coefficients, high charge carrier mobility, long exciton diffusion length, solution processability, low cost and impressive power conversion efficiencies (PCEs) [1—6]. In 2009, Kojima and co-workers achieved a PCE of 3.8% using CH$_3$NH$_3$PbX$_3$ perovskite as a light-absorbing material in dye-sensitized solar cells (DSCs) [7]. Since then, the PCEs of solar cells based on methylammonium lead halide (MAPbI$_3$) perovskites have surpassed 20% [8]. Several research groups have demonstrated various architectures [4,9—11], among which the planar n-i-p and p-i-n (n, i, p refers to electron transporting layer, light-absorber layer, and hole transporting layer, respectively) perovskite solar cells (PSCs) have attracted increased interest from the photovoltaic community because of their high efficiencies and simpler fabrication method [12—14].

In both n-i-p and p-i-n PSCs, the charge selective contacts play a crucial role in an attempt to further improve the performance of the

solar cells [15,16]. Several robust and stable metal oxide-based electron extraction layer (EELs) such as titanium oxide (TiO$_2$) [9,10], zinc oxide (ZnO) [17,18], tin oxide (SnO$_2$) [19], and indium oxide (In$_2$O$_3$) [20], have been used successfully in the n-i-p-type PSCs. Among the metal oxides, TiO$_2$ has been widely used as EELs. However, high-temperature (>450 °C) treatment of TiO$_2$ EEL is apparently required to obtain a highly compact and crystallized structure for efficient PSCs [21]. High-temperature treatment tends to be unfavorable when considering the production cost and energy payback time of PSCs. Low-temperature TiO$_2$ has been introduced as an EEL in PSCs, but its low electron conductivity and mobility usually results in charge accumulation in the TiO$_2$ layer [22—24]. Tungsten trioxides (WO$_3$) are chemically stable metal oxide semiconductors with bandgaps in the range of 2—3 eV and high electron mobility (10—20 cm^2. V^{-1}. s^{-1}) [25—28]. WO$_3$ has also received significant attention as a very interesting material for electrochromic devices [29,30], gas sensing [31,32], photocatalysis [33], polymer and DSCs [27,28,34,35]. Mahmood et al. were the first to employ WO$_3$ as an EEL in PSCs and achieved impressive PCEs [36]. Following their pioneering work, Wang et al. showed that low-temperature amorphous tungsten oxide (WO$_x$) could be used as EEL in PSCs [37]. It was found that WO$_x$ based PSCs suffer from severe charge recombination at the perovskite/WO$_x$ interface, resulting in an unsatisfied open-circuit voltage (V_{oc}) and fill factor (FF). Chen et al. modified the perovskite/WO$_3$ interface with cesium

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carbonate (Cs_2CO_3)/phenyl-C_{61}-butyric acid methyl ester (PCBM) to further improve the performance of the device and achieved a PCE of 10.0% [38]. Wang et al. used WO_x –TiO_x composite thin films as EELs in PSCs. The WO_x–TiO_x composite EELs enabled a strong light transmittance, efficient charge transport, and dissociation, and as well as inhibition of the charge recombination, which notably increases the performance of the PSCs [39]. Wang et al. also demonstrated that amorphous niobium-modified tungsten oxide (W(Nb)O_x) could be used as EELs for efficient, flexible PSCs [40].

In this work, we propose the use of a low-temperature solution processed WO_x/fullerene C_{60} as excellent EELs for efficient planar PSCs. Fullerenes, such as C_{60} and PCBM have been used as excellent acceptors in organic solar cells [41–43], and EELs in PSCs [44–51]. According to previous reports, C_{60} and PCBM are excellent passivation materials for perovskite, which can effectively passivate the grain boundaries in the perovskite and reduce the density of trap states as well as reduce hysteresis of PSCs [52–54]. Moreover, fullerene C_{60} is a low-cost material that exhibits superior electron mobility (1.6 cm^2 V s^{-1}) and conductivity (2.3 $\times$ 10^{-3} S cm^{-1}) than that of PCBM (6.1 $\times$ 10^{-2} cm^2 V s^{-1} and 3.2 $\times$ 10^{-4} S cm^{-1}, respectively) [45]. Here, we incorporated C_{60} as an interface modifier for WO_x-based PSCs [47]. The WO_x/C_{60} EELs was found to work synergistically to further enhance the performance of PSCs. The best-performing planar PSCs using WO_x/C_{60} achieved PCEs of 16.07% and 14.11% when measured under reverse and forward voltage scans, respectively. Such enhancement is mainly attributed to the improved V_{oc} and FF, benefiting from the better electron transfer and less charge recombination. This work shows that low-cost and high-performance PSCs can be achieved using WO_x/C_{60} EELs.

2. Material and methods

2.1. Materials and reagents

Methylammonium iodide (MAI) was synthesized in accordance with the reported procedures [9]. Fluorine-doped tin oxide (FTO) glass substrates (sheet resistance: 12 Ω/sq.) were purchased from Asahi Glass. Semico-Clean, acetone, isopropanol, tungsten hexachloride (WCl_6; $\geq$99.9%, Sigma-Aldrich), titanium (IV) isopropoxide (99.0%), ethanol, acetonitrile, dichlorobenzene, N-methyl-2-pyrrolidone (NMP; >99%, Sigma-Aldrich), γ-butyrolactone (GBL; >98.5%, Sigma-Aldrich), anhydrous diethyl ether (DEE; >99.0%, Sigma-Aldrich), dimethyl sulfoxide (DMSO; 99.0%, Wako), Fullerene C_{60} (>99%, Jilin OLED Material), 2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene (Spiro-OMeTAD), and PbI_2 (99.0%, Sigma-Aldrich) were used without further treatment.

2.2. Device fabrication

FTO-coated glass substrates were patterned by etching with hydrochloric acid (HCl) and zinc (Zn) powder and sequentially cleaned with Semico-Clean, ultrahigh purified water, acetone, and isopropanol. The substrates were then treated with ultraviolet ozone cleaner for 15 min. The WO_x EELs were prepared by a low-temperature solution process described in a previous report [37]. 0.1 g/ml WCl_6 was dissolved in ethanol and stirred at 50 °C. The WO_x solution was spin-coated on clean FTO substrates in air at a spin rate of 3000 rpm for 30 s. The films were subsequently annealed on a hot plate in the atmosphere at 150 °C for 10 min. The thickness of the WO_x EELs is about 50 nm. WO_x/C_{60} EELs were prepared by spin-coating C_{60} dichlorobenzene solutions (15 mg/ml) on WO_x films at a spin rate of 2500 rpm for 30 s and then annealed on a hot plate at 60 °C for 2 s. The thicknesses of C_{60} films were controlled by varying the concentration of C_{60} in dichlorobenzene.

The $MAPbI_3$ perovskite layers were prepared according to our previous reported method [14]. The perovskite films were prepared by spin-coating the precursor solution of PbI_2 (2 M), and MAI (2.39 M) dissolved in a mixed solvent of NMP (1 ml) and GBL (0.2 ml) and stirred at room temperature for 12 h to form the $MAPbI_3$ precursor solution. The precursor solution was dropped onto the WO_x and WO_x/C_{60} layers to prepare the $MAPbI_3$ films. The spin-coating process was performed at a constant rotation speed of 4500 rpm for 30 s without acceleration time. The obtained perovskite layer thickness is about 250 nm. The hole extraction layers (HELs) were prepared by spin-coating a solution of Spiro-OMeTAD on top of the perovskite film at a spin rate of 2000 rpm for 60 s in the air. The obtained Spiro-OMeTAD thickness is about 230 nm. The Spiro-OMeTAD solution was prepared by mixing 17.5 μl of lithium bis(trifluoromethane)sulfonimide (Li-TFSI) solution (520 mg of Li-TSFI in 1 ml of acetonitrile) and 28.8 μl of 4-tert-butylpyridine with 72.3 mg of Spiro-OMeTAD in 1 ml of chlorobenzene solution. The final devices were completed by vacuum evaporation of Au back contacts with a thickness of 80 nm at 3.4 $\times$ 10^{-4} Pa. For each solar cell, the active area defined by the electrode was 0.06 cm^2.

2.3. Characterization

The morphology of the perovskite layer was observed by field-emission scanning electron microscopy (FE-SEM; JEOL JSM-6335FM, acceleration voltage of 10 kV). Atomic force microscopy (AFM) images were obtained using a Keyence VN-8000 viewer and an analyzer. Current density–voltage (J–V) measurements were recorded by applying external potential biases to the cells and recording the output photocurrent with a digital source meter (Agilent B2901A). A 150 W xenon lamp (Bunkoukeiki Otento-SUN3 Xe-S150) was used as the light source, and the output irradiation intensity was adjusted to the AM 1.5 G condition (100 mW/cm^2). Before each measurement, the light intensity was calibrated using a silicon reference cell (Bunkoukeiki). The step voltage and delay time were 40 mV and 200 ms, respectively. Incident photon-to-electron conversion efficiency (IPCE) measurement was conducted in the wavelength range of 350–900 nm with a 300 W xenon light source and a monochromator (Asahi Spectra PVL 3300). Ultraviolet–visible (UV–vis) absorption spectra were measured using a UV–vis spectrophotometer (Shimadzu UV 2450). X-ray diffraction (XRD) patterns were recorded in the 2θ range of 5–60° using an X-ray diffractometer (Rigaku RINT2500V/PC) with Cu Kα radiation (40 kV, 100 mA). Photoluminescence (PL) spectra were measured using a Jasco NRS-5100PL laser Raman spectrophotometer. The excitation wavelength was 325.29 nm, and the detection range was 600–900 nm. For thickness testing, we used a thickness tester (Kosaka Laboratory Surfcorder ET200).

3. Results and discussion

Fig. 1a shows the XRD patterns of the WO_x films annealed at 150 °C and 500 °C (crystalline WO_3). The film annealed at 150 °C shows only a broad feature at about 25°, suggesting an amorphous structure. In contrast, the film annealed at a higher temperature exhibits sharp crystalline peaks corresponding to monoclinic WO_3 [55,56]. Fig. 1b shows the device architecture of a planar PSC, which consists of FTO/WO_x (50 nm)/C_{60} (27 nm)/$MAPbI_3$ (250 nm)/Spiro-OMeTAD (~230 nm)/Au (80 nm). The fullerene C_{60} was introduced as an interface modifier between the WO_x and perovskite layers. The energy band diagram is shown in Fig. 1c. The conduction band minimums (CBMs), valence band maximums (VBMs) of WO_x and $MAPbI_3$ together with the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels of C_{60} were selected based on previous reports [35,47]. The HOMO