Graphical Abstract

Solution-processed CuO_x as an efficient hole-extraction layer for inverted planar heterojunction perovskite solar cells

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A high power conversion efficiency of 17.43% is achieved by integrating a solution-processed CuO_x film as the hole-transporting layer for inverted planar heterojunction perovskite solar cells.

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Original article

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ABSTRACT

A solution-processed CuO_x film has been successfully integrated as the hole-transporting layer (HTL) for inverted planar heterojunction perovskite solar cells (PVSCs). The CuO_x layer is fabricated by simply spin-coating a copper acetylacetonate (Cu(acac)₃) chloroform solution onto ITO glass with high transparency in the visible range. The compact and pinhole-free perovskite film with large grain domains is grown on the CuO_x film. The inverted PVSCs with the structure of ITO/CuO_x/MAPbI₃/PC₆₁BM/ZnO/Al are fabricated and show a best PCE of 17.43% under standard AM 1.5G simulated solar irradiation with a V_{OC} of 1.03 V, a J_{SC} of 22.42 mA cm⁻², and a fill factor of 0.76, which is significantly higher and more stable than that fabricated from the often used hole-transporting material PEDOT:PSS (11.98%) under the same experimental conditions. The enhanced performance is attributed to the efficient hole extraction through the CuO_x layer as well as the high-quality CH₃NH₃PbI₃ films grown on the CuO_x. Our results indicate that low-cost and solution-processed CuO_x film is a promising HTL for high performance PVSCs with better stability.

1. Introduction

Perovskite solar cells (PVSCs) based on methylammonium (CH₃NH₃PbI₃, denoted as MAPbI₃) have been paid tremendous attentions as a promising next-generation solar cell technology due to the intense broadband absorption, high charge carrier mobility, low-cost precursor materials and simple solution processing of the perovskite films [1-6]. Recently, the power conversion efficiency (PCE) for the PVSCs has quickly increased to a certified value of 22.1% due to the development of composition engineering [7], interface engineering [8, 9] and processing methods [10]. However, most of the high efficiency PVSCs are usually fabricated in conventional mesoscopic architectures, which usually sandwich the perovskite layer between compact and mesoporous TiO₂ layers and a hole-transporting layer (HTL) such as 2,2',7,7'-tetrakis(N,N-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) [11, 12]. These mesoscopic devices suffer from the issue of device processing due to the high sintering temperature for mesoporous and compact TiO₂ layers. Thus there are growing interests in inverted planar heterojunction (PHJ) PVSCs with a simpler architecture of ITO/ poly(3,4-ethylenedioxythiophene): polystyrenesulfonate (PEDOT:PSS)/MAPbI₃/[6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM)/cathode, because of the low temperature processing procedure and small hysteresis [13-15]. The PCEs over 18% have been achieved for this type of devices with small device areas [16, 17] and a certified PCE of 15% with large size (1 cm²) [18]. However, the widely used PEDOT:PSS is not an ideal HTL due to the insufficient electron-blocking capability and relatively low work function (-5.0 eV) which lead to low open-circuit voltage (V_{OC}) (0.95-1.0 V). On the other hand, the hydrophilic and acidic nature of PEDOT:PSS is inferior to the device stability. Organic and inorganic materials with high work function and good chemical stability are tried to replace PEDOT:PSS [19-21]. For example, poly(bis(4-phenyl)(2,4,6-trimethylphenyl)amine) (PTAA) is one of the most efficient organic HTL which improves the V_{OC} to 1.05-1.09 V from 0.92 V for PEDOT:PSS [22, 23]. The improvement is attributed to its high work function (-5.4 eV) which aligns well with the valance band (VB) of MAPbI₃, forming ohmic contact at the HTL/MAPbI₃ interface and thus reducing V_{OC} loss. Also the hydrophobic surface of PTAA suppresses heterogeneous nucleation of perovskite, leading to large grain boundary and better crystallinity. In comparison with the organic transporting materials, transition metal oxides with high work function, such as MoO₃ [24, 25], V₂O₅ [26], NiO [27] and WO₃ [28], usually show high hole mobility, high optical transmittance, high

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chemical stability and low cost, which could be good candidates to replace PEDOT:PSS and have already been introduced into organic solar cells [29]. Among them, NiO [30], Mg-doped NiO ($\text{Ni}_x\text{Mg}_{1-x}\text{O}$) [18], Cu-doped NiO [31], CuSCN [32], and CuS [33] were demonstrated as excellent hole-transporting materials for inverted planar PVSCs with PCEs of 14.42%, 18.4%, 15.4%, 16.0%, and 16.2% respectively. However, the processing of these materials is relatively complicate, for example, high temperature is needed for NiO and $\text{Ni}_x\text{Mg}_{1-x}\text{O}$, which makes the device processing costly.

Copper oxides (CuO_x), including cuprous oxide (Cu_2O) and cupric oxide (CuO), are typical p-type semiconductors. Their advantages of earth-abundant source, low cost, and simplicity of preparation make them promising candidates for photovoltaic applications. In our previous work, we have successfully applied this material for organic solar cells as an efficient HTL, achieving a higher PCE and better stability than the ones using PEDOT:PSS as HTL [34]. Recently, copper oxides have also been employed as efficient HTL in PVSCs due to its proper energy levels that match those of MAPbI_3 [35-38]. For instance, Hamid *et al.* have demonstrated the cuprous oxide by reactive magnetron sputtering as an efficient HTL and a PCE of 8.93% was achieved for conventional PHJ PVSCs [35]. Amlan *et al.* have prepared Cu_2O through a successive ionic layer deposition and reaction (SILAR) method and the PCE for inverted PHJ PVSCs was 8.23% [36]. Wu *et al.* reported that the thermal oxidized ultrathin Cu_2O film can serve as an efficient HTM, and a PCE of 11.03% was obtained for inverted PHJ PVSCs [37]. However, the magnetron sputtering based method, SILAR method, and thermal oxidized method are complicated, costly and incompatible with the roll to roll techniques. Quite recently, Cu_2O and CuO films prepared via in situ conversion of CuI film in aqueous NaOH solution were used as HTLs in inverted PHJ PVSCs with PCEs of 13.35% and 12.16%, respectively [38]. Even though these works validated the potential of using CuO_x as efficient HTLs for PVSCs, facile and effective fabrication methods for CuO_x film are still needed.

In this work, we demonstrated the facile solution-processed CuO_x film can be applied to the inverted PHJ PVSCs with a PCE up to 17.43% as well as good stability. The CuO_x film with high work function is simply spin-coated from a copper acetylacetonate precursor solution. Larger crystalline $\text{CH}_3\text{NH}_3\text{PbI}_3$ domains are grown on the CuO_x film. These results indicate that low-cost, simple-preparation and solution-processed CuO_x is a promising HTM applicable in the high performance inverted PHJ perovskite solar cells.

2. Experimental

2.1 Materials

Unless stated otherwise, all materials were purchased from Sigma-Aldrich and used as received. PC_{61}BM was purchased from American Dyes Source, Inc. $\text{CH}_3\text{NH}_3\text{I}$ (MAI) was purchased from Shanghai Materwin New Materials Co., Ltd. ZnO nanoparticles were synthesized by a sol-gel process using Zn acetate and tetramethylammonium hydroxide (TMAH), and dispersed in anhydrous ethanol with a concentration of 20 mg mL^{-1} [39].

2.2 Device fabrication and testing.

Prior to fabrication, the substrates were cleaned by sonication using detergent, deionized water, acetone, and isopropanol sequentially for every 15 min followed by 15 min of ultraviolet ozone (UV-ozone) treatment. PEDOT:PSS (Baytron P AI4083) was spin-coated on the ITO substrate to form a 35 nm film and baked at 140°C for 20 min. The substrates were transferred to a glovebox. CuO_x was fabricated by spin-coating a $\text{Cu}(\text{acac})_2$ chloroform solution with different concentrations ($1, 2, 4$, and 8 mg mL^{-1}) on the ITO substrate and then annealed at 120°C for 20 min in glove-box. Afterwards, the CuO_x films were washed by methanol and followed by 15 min UV-Ozone treatment.

PbI_2 (1 mol L^{-1}) and DMSO (1 mol L^{-1}) were dissolved in DMF under stirring at 70°C . The solution was kept at 70°C during the whole procedure. The solution was then spin coated on the as-prepared CuO_x film at 6000 rpm for 60 s. Then a solution of MAI in 2-propanol (IPA) (50 mg mL^{-1}) was dropped and spin-coated at 6000 rpm for 60 s. Afterwards, the as prepared films were heated at 90°C for 15 min. After cooling down, a layer of [6,6]-phenyl- C_{61} -butyric acid methyl ester (PC_{61}BM , 20 mg mL^{-1} in chlorobenzene) was spin-coated at 2000 rpm for 45 s. A hole-blocking layer was deposited via spin-coating ZnO nanoparticles in ethanol at 4000 rpm for 30 s on the top of PC_{61}BM layer. Subsequently, samples were loaded into a vacuum deposition chamber (background pressure $\approx 5 \times 10^{-4} \text{ Pa}$) to deposit a 100 nm thick Al cathode with a shadow mask defining an active device area of 5.5 mm^2 .

The J-V characteristics were measured with Keithley 2400 measurement source units with the devices maintained at room temperature in air. The photovoltaic response was measured under a calibrated solar simulator (Abet 300 W) at 100 mW cm^{-2} , and the light intensity was calibrated with a standard photovoltaic reference cell. The EQE spectrum was measured using a Stanford Research System Model SR830 Lock-in Amplifier unit coupled with a monochromator and a 500W xenon lamp, and a calibrated Si photodiode with known spectral response was used as a reference.

2.3 Films characterization.

The X-ray diffraction (XRD) patterns were recorded at a scan rate of 5° min^{-1} on the Rigaku D/max-2550PC X-ray diffractometer with Cu $K\alpha$ radiation (1.5406 nm). X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectrum (UPS) measurements were conducted using an ESCALAB 250Xi (Thermo) system. The UV-visible absorption spectra were measured on a Varian CARY100 Bio spectrophotometer. The SEM data were scanned by S-4800 (Hitachi) field-emission scanning electron

microscope (FESEM). Atom force microscopy (AFM) images were obtained using a Veeco Multimode atomic force microscopy in the tapping mode. The photoluminescence (PL) spectra (both of steady-state and transient spectra) are measured using an FluoroMax-4 HORIBA Jobin Yvon spectrofluorometer.

3. Results and discussion

3.1 CuO_x film characterization

The CuO_x film is fabricated by simply spin-coating a copper acetylacetonate (Cu(acac)₂) chloroform solution on ITO and annealed at 120 °C for 20 min with UV-Ozone treatment for 15 min, which is modified from our previous work[34]. The chemical component of the as-prepared film was confirmed by X-ray photoelectron spectroscopy (XPS) with Cu²⁺/Cu⁺ ratio of about 3.2:1 (see Fig. S1a in Supporting information). Such solution-processed CuO_x thin film has a smooth surface with a RMS of 3.5 nm (Fig. S1b) and a high transparency similar to ITO in the visible range (Fig. S1c). The work function (WF) of CuO_x film was measured by ultraviolet photoelectron spectrum (UPS). As shown in Fig. 1, the WFs of bare ITO and ITO/PEDOT:PSS are 4.4 eV and 5.0 eV, respectively, which are close to the reported values [40, 41]. ITO/CuO_x however gives a higher WF of 5.4 eV, which aligns well with the valance band (VB) of MAPbI₃ for ohmic contact [38]. These results indicate that CuO_x could be potentially used as an excellent HTL in PVSCs.

3.2 Perovskite film characterization

The film formation and surface morphology of the perovskite layer is heavily dependent on the substrates and is crucial in determining the performance of solar cells [42-44], and thus the morphology of the perovskite films on various HTLs of CuO_x and PEDOT:PSS are characterized by scanning electron microscopy (SEM) (Fig. 2). The MAPbI₃ films are fabricated via two-step coating method. All films are compact and pinhole-free, and the perovskite film on top of CuO_x shows the largest grain domains and reduced grain boundaries. The film quality is further analyzed by X-ray diffraction (XRD), which is shown in Fig. 3a. Intense XRD signals are observed for the crystalline MAPbI₃ films on all substrates. The diffraction intensity of MAPbI₃ film on CuO_x is slightly stronger than that of perovskite films on bare ITO and PEDOT:PSS. The intensity ratio for peaks at 14.5° on bare ITO, PEDOT:PSS, and CuO_x is 1:1:1.2, indicating higher crystallinity for MAPbI₃ film on CuO_x. The higher crystallinity of MAPbI₃ film on CuO_x layer is also supported by its higher absorption as shown in Fig. 3b.

To investigate the hole-extraction ability of various HTLs, steady-state photoluminescence (PL) and time-resolved PL decay were conducted for MAPbI₃ films on different substrates. As illustrated in Fig. 3b, various levels of PL quenching were observed and the stronger PL quenching was found for MAPbI₃ on CuO_x than on PEDOT:PSS, indicating the better hole-extraction ability of CuO_x films. The time-resolved PL decays measured at the peak emission at 765 nm were shown in Fig. 3c. The MAPbI₃ only film exhibits an averaged decay time (Ave. τ) of 523 ns, while it decreased to 170 and 66 ns when it was applied on top of PEDOT:PSS and CuO_x, respectively. This indicates the improved hole extraction and the charge dissociation were achieved at the CuO_x/MAPbI₃ interface. These results demonstrate that CuO_x can be used as HTL replacing PEDOT:PSS for high performance PVSCs.

3.3 Photovoltaic performance of perovskite solar cells

According to the above results, we fabricated the inverted PHJ PVSCs in the structure of ITO/HTL/MAPbI₃/PC₆₁BM/ZnO/Al without and with different HTLs of CuO_x and PEDOT:PSS (Fig. 4a). The energy level diagram of the device with different HTLs is shown in Fig. 4b. The devices with CuO_x as HTL were optimized by adjusting the concentration of the CuO_x precursor. As shown in Table 1, the best devices were obtained with the concentration of 2 mg mL⁻¹. The current density-voltage (*J*-*V*) characteristics of the best devices with different HTLs measured under AM 1.5G conditions (100 mW cm⁻²) are presented in Fig. 4c and the relevant parameters are summarized in Table 2.

As expected, PVSCs without HTL show poor performance with low *V*_{OC}, *J*_{SC} and FF. After incorporating a layer of PEDOT:PSS as HTL, the *J*_{SC} increases from 13.73 mA cm⁻² to 16.85 mA cm⁻², FF increases from 0.60 to 0.75, *V*_{OC} increases slightly from 0.94 V to 0.95 V, and the PCE significantly improved to 11.98% from 7.72%. However, it is still low comparing to the state-of-art PVSCs. The reason is mainly due to the low *V*_{OC} and *J*_{SC} resulted from the low work function and the inability to block electrons efficiently of PEDOT:PSS, as well as the small crystalline grains of MAPbI₃ film on PEDOT:PSS. When CuO_x is used as alternative, the best PCE surges to 17.43% which substantially surpass the performance of PEDOT:PSS based device, with significantly enhanced *J*_{SC} of 22.42 mA cm⁻² and *V*_{OC} of 1.03 V. FF is slightly increased to 0.76 comparing to the one based on PEDOT:PSS. The enhanced *J*_{SC} can be interpreted as a consequence of the better charge-extraction ability of CuO_x and larger grain domains, reduced grain boundaries of the MAPbI₃ films. The higher *V*_{OC} is resulted from the higher WF of CuO_x which renders the ohmic contact at the CuO_x/MAPbI₃ interface and thus reducing *V*_{OC} loss. On the other hand, reduced charge recombination originating from the larger grain domains of MAPbI₃ film with reduced grain boundaries also attributes to the enhanced *V*_{OC}. The external quantum efficiency (EQE) spectra of PVSCs without and with different HTLs are shown in Fig. 4d. Using CuO_x as a HTL significantly improves the photocurrent in the region from 350 to 800 nm, which agrees well with the enhanced *J*_{SC}. In summary, the performance enhancement of the CuO_x-based device is attributed to the larger grain size, reduced recombination and more effective charge extraction described above.

The device hysteresis behavior and stabilized power output of the best device are provided in Fig. 5a and Fig. 5b, respectively. We can see that no apparent hysteresis is detected with forward and reverse scans. The photocurrent density and PCE as a function of time at the maximum power point (0.86 V) were performed to further confirm the accuracy of our PCE. As shown in Fig. 5b, both the photocurrent and PCE remain stable within 300 s, and a stable PCE over 15% is demonstrated. Fig. 5c shows the statistic histogram of device parameters. The device performance of PVSC with CuO_x as HTL ranges from 12.80% to 17.43%, with the averaged value of

14.61%. In comparison, with PEDOT:PSS as HTL, a range from 8.51% to 11.98% and a much lower averaged PCE of 10.58% were obtained. In spite of the high photovoltaic efficiency, the long-term stability of PVSCs is of vital importance for practical applications. We therefore monitored the stabilities of different types of devices with various HTLs. Devices were tested without encapsulation in an ambient environment at 20 °C and with 20%-30% humidity. As shown in Fig. 5c, the PCEs of the CuO_x-based devices maintain 90% of its initial efficiency after 650 hours, while the PEDOT:PSS-based devices degrade to about 70% of the initial PCE. The degradation is mainly resulted from the reduced FF (Fig. S2 in Supporting information). These results indicate that CuO_x is a promising hole-extraction material for highly efficient PVSCs with good stability.

4. Conclusion

In conclusion, solution-processed CuO_x films with high optical transmittance, high work function, proper surface properties and excellent hole-extraction ability are fabricated at low temperature and applied to PHJ PVSCs as efficient HTL. The high work function of the CuO_x renders the ohmic contact at the MAPbI₃/CuO_x interface, reducing V_{OC} loss. While compact and pinhole-free perovskite films with large grain domains are formed due to the proper surface properties, leading to the reduced carrier recombination and thus obtaining high J_{SC} and V_{OC} . Combining the excellent hole-extraction ability of the CuO_x, high performance PHJ PVSCs with PCE up to 17.43% were demonstrated which is much higher than the ones of 11.98% based on PEDOT:PSS. The CuO_x-based devices also show good stability in an ambient environment at room temperature with low humidity. Our work reveals the promising applicability of low-cost solution-processed CuO_x in invert PHJ PVSCs with high performance and good stability.

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Fig. 1. UPS spectra of the various HTLs on ITO and the bare ITO.

Fig. 2. Top view (a, b, c) and cross-sectional (d, e, f) SEM images of perovskite films fabricated on top of bare ITO (a, d), PEDOT:PSS (b, e), and CuO_x (c, f).

Fig. 3. (a) XRD patterns of ITO/Perovskite, ITO/PEDOT:PSS/Perovskite and ITO/CuO_x/Perovskite on glass substrate. The star marked peaks belong to ITO. (b) UV-vis absorption and steady photoluminescence (PL) spectra of the optimized perovskite films on different HTLs. (c) Time-resolved PL measurements taken at the peak emission wavelength (765 nm) of the various HTLs. A 5 mW picosecond pulsed diode laser at 638.8 nm excited on the surface sided of films.

Fig. 4. Schematic of the device structure (a) and the energy-level diagram of the corresponding device (b). J-V curves (c) and EQE spectra (d) of the PVSCs without or with different HTLs.

Table 1. Device parameters of PVSCs fabricated from CuO_x precursors with different concentrations.

Concentration (mg mL ⁻¹)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)	
				best	average
8	1.03	12.25	0.72	9.15	7.89
4	0.99	16.87	0.73	12.06	11.19
2	1.03	22.42	0.76	17.43	14.61
1	1.08	19.32	0.71	14.85	12.71

Fig. 5. (a) J-V curves of the best PVSCs measured by forward and reverse scans, fabricated using CuO_x as HTL. (b) Stabilized photocurrent measurement of the best CuO_x based PVSCs under 1 sun illumination. (c) Efficiency histograms of 65 PVSCs with CuO_x as HTL and 45 PVSCs with PEDOT:PSS as HTL. (d) Normalized PCE as a function of storage time in air.

Table 2. Summarized solar cell parameters without and with different HTLs.

HTL	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)	
				best	average
w/o	0.94	13.73	0.60	7.72	6.28 ^a
PEDOT:PSS	0.95	16.85	0.75	11.98	10.58 ^a
CuO_x	1.03	22.42	0.76	17.43	14.61 ^b

^a Averaged from 45 devices; ^b Averaged from 65 devices.