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Interfacial charge-transfer engineering by ionic liquid for high performance planar $CH_3NH_3PbBr_3$ solar cells

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ABSTRACT

The energy barrier at the $CH_3NH_3PbBr_3/TiO_2$ interface hinders the electron transfer from $CH_3NH_3PbBr_3$ to compact TiO_2 (cp-TiO_2). Ionic liquid (IL), that forms dipoles pointing away from TiO_2, can adjust the work function of TiO_2 resulting in suitable energy level for charge transfer from $CH_3NH_3PbBr_3$ to TiO_2. The time-resolved photoluminescence spectroscopy (TRPL) measurements confirm faster electron transfer from the $CH_3NH_3PbBr_3$ film to TiO_2 after modification by IL. Solar cells based on IL modified cp-TiO_2 demonstrate efficiency of ~6%, much higher than the devices (0.2%) fabricated using untreated cp-TiO_2 as the electron transport layer.

1. Introduction

The organic–inorganic hybrid perovskite $CH_3NH_3PbX_3$ (X = Cl, Br, I) has emerged as a promising candidate in photovoltaic and optoelectronic applications due to its high absorption coefficient, direct band-gap, long carrier lifetime, and large electron/hole diffusion length [1–4]. In addition to these characteristics, the precursor compounds are abundant and inexpensive, and thin films can be easily synthesized by both solution and vacuum-based techniques [5–8]. Owing to these reasons, perovskite solar cells (PSCs) are projected to be cost-effective alternatives. $CH_3NH_3PbBr_3$ has a cubic structure, which is more compact and stable compared to the tetragonal phase of $CH_3NH_3PbI_3$ [9,10]. Another advantage of $CH_3NH_3PbBr_3$ is its wide band gap, which can be tuned by composition engineering to a lower value without transforming the cubic structure [11]. PSCs using compact TiO_2 (cp-TiO_2) as the electron transport layer possess relatively simple device structure and good compatibility with low temperature fabrication process, such as sputtering, e-beam deposition, spin coating and chemical base deposition. However, unlike the mesoporous TiO_2 (mp-TiO_2), it has been found that the poor charger transfer between $CH_3NH_3PbBr_3$ and compact TiO_2 leads to a low J_{sc}, and thereby deteriorates the performance of PSCs (lower than 0.5%) [9,12]. This indicates that an energy barrier exists at the $CH_3NH_3PbBr_3/TiO_2$ interface, which can hinder the electron collection by TiO_2.

Interface plays crucial role in governing performance of photovoltaic (PV) devices. Systematic interface engineering can reduce the contact barrier and thereby enhance the charge transport properties while minimizing the energy loss [13,14]. Ionic liquids (ILs) are salt possessing high electrochemical and thermal stability, good optical transmittance and environment-friendly nature. Their ability to adjust the work function through formation of interface dipoles along with their low temperature synthesis makes them excellent interfacial layers for solar cells [15–19]. In this study, 1-butyl-3-methylimidazolium tetrafluoroborate ($[BMIM]BF_4$) is chosen as the interfacial layer for modifying the work function of cp-TiO_2. The interface dipole formed by $[BMIM]BF_4$ can reduce the energy gap between TiO_2 and $CH_3NH_3PbBr_3$, and thereby promote the electron transfer from $CH_3NH_3PbBr_3$ to TiO_2. This will improve the charge collection efficiency in PV device. PSCs based on $[BMIM]BF_4$ modified TiO_2 possess an efficiency of ~6%, much higher than the untreated TiO_2 based PSCs (0.21%).

2. Experimental

2.1. Materials preparation

Synthesis of $CH_3NH_3PbBr_3$ perovskite solution: CH_3NH_3Br powders (Lumtec) and $PbBr_2$ (Sigma-Aldrich) were added to a mixture of *N,N*-dimethylformamide (DMF) and dimethylsulphoxide (DMSO) (7:3 v/v) for forming 1.2 M solution. The resulting $CH_3NH_3PbBr_3$

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precursor solution was stirred overnight before using it for further processing.

Synthesis of the compact TiO_2 layer solution: 369 µL of titanium isopropoxide (99.99% Sigma-Aldrich) was added to 2.53 mL ethanol, and at the same time 35 µL 2 M HCl solution was added to 2.53 mL ethanol in another vial. The second solution was then added dropwise to the first solution and stirred for 1 h. The mixture was filtered with a PTFE 0.2 µm filter. All materials were used as received without further purification.

2.2. Device fabrication

The solar cells were fabricated using anti-solvent assisted crystallization (ASAC) approach [9]. Briefly, the compact TiO_2 blocking layer was spin-coated on the FTO substrate at 2000 rpm for 20 s using a mildly acidic titanium isopropoxide solution and sintered at 500 °C for 15 min. After cooling to room temperature, $CH_3NH_3PbBr_3$ perovskite solution was coated onto the substrate by spin-coating process at 1000 rpm for 10 s and 4000 rpm for 30 s in glove box. The substrate was treated with 60 µL of toluene for 20 s before the second-step spin-coating. For PSCs using cp TiO_2-IL as the electron transport layer, $[BMIM]BF_4$ dissolved in methanol (0.3 wt%) was spin-coated on the cp-TiO_2 film at 4000 rpm and dried at 100 °C for 10 min before preparation of $CH_3NH_3PbBr_3$. After the $CH_3NH_3PbBr_3$ perovskite films were dried at room temperature for 10 min, the 2,2′,7,7′-tetrakis[*N*,*N*-di(4-methoxyphenyl)amino]-9,9′-spirobifluorene (spiro-OMeTAD) based HTM was deposited at 4000 rpm for 30 s. Finally, 80 nm of gold was thermally evaporated as the top electrode. The active area of each device was 0.1 cm^2.

2.3. Characterization

X-ray photoelectron spectroscopy (XPS) spectra were recorded by a scanning photoelectron spectrometer microprobe (PHI Quantera SXM) using Al K_α radiation at a power of 50 W. The binding energy was calibrated by C 1s peak at 284.8 eV. UV–vis absorption spectra were recorded using U4100, Hitachi UV–vis spectrophotometer. X-ray diffraction (XRD) measurement was performed at a scanning rate of 5 min^{-1} on a Philips Xpert Pro X-ray diffractometer (Almelo, Netherlands). Scanning electron microscopy images were obtained (SEM, Quanta 600 FEG, FEI Company) at an accelerating voltage of 5 kV. Atomic force microscopy (AFM) topography images were obtained using Bruker Metrology Nanoscope III-D system in tapping mode under atmospheric condition. The surface potential was measured in air using scanning Kelvin probe microscopy (SKPM) through Bruker Metrology Nanoscope III-D atomic force microscope. Conducting AFM tips (SCM-PIT/PtIr, Bruker, USA) were used for this study with a typical spring constant of 2.8 N m^{-1} and a resonance frequency of 75 kHz. Time-resolved photoluminescence spectra (TRPL) were recorded on an FLS920 fluorescence spectrometer (Edinburgh Instruments) in air at room temperature. A picosecond pulsed diode laser (406.8 nm) was used as the excitation source. Photovoltaic performance of solar cells was evaluated under one sun (AM 1.5G, 100 mW cm^{-2}) illumination using solar simulator (150 W Sol 2ATM, Oriel), and the current–voltage characteristics of each cell was recorded using Keithley digital source meter (model 2400).

3. Results and discussion

Fig. 1a describes the device architecture of PSCs, wherein the cp-TiO_2 or IL modified cp-TiO_2 (denoted as TiO_2-IL) is used as the ETL, spiro-OMeTAD as the hole transport material (HTM), and the gold layer as top electrode. The chemical structure of the IL, $[BMIM]BF_4$, is shown in Fig. 1b. To confirm the existence of IL on surface of TiO_2, X-ray photoelectron spectroscopy (XPS) spectra of TiO_2 and TiO_2-IL was obtained as shown in Fig. 1c. Compared to TiO_2, peaks related to B1s, F1s and N1s are presented in TiO_2-IL, indicating the successful deposition of IL on top of TiO_2. Fig. S1 provides transmission spectra of FTO, FTO-TiO_2 and FTO-TiO_2-IL films. The influence of TiO_2 or TiO_2-IL films on transmission of light is negligible. So, high optical transmittance of IL is favorable for photon flux to reach the $CH_3NH_3PbBr_3$ absorber, and generates charge carriers.

Fig. 2a shows the topography images of TiO_2 and TiO_2-IL, measured using tapping mode AFM. The TiO_2 layer with thickness ~60 nm is deposited on FTO with a root mean square (RMS) roughness of 5.01 nm. After modification with the IL layer, $[BMIM]BF_4$, the RMS roughness changes to 5.19 nm. The surface morphology changes at the same time, from a film comprising of small nanoparticles to larger ones, which may be result of the coverage of IL on the surface of TiO_2. To verify the role of the IL on work function (WF) of TiO_2, the WF of TiO_2 and TiO_2-IL films were characterized by scanning Kelvin probe microscopy (SKPM, Fig. 2b). The deposition of the IL layer on TiO_2 effectively decreases the average surface potential of TiO_2, resulting in the reduction of WF from 4.47 eV to 3.97 eV. According to Li's work [15], the BF_4^- anions prefer the TiO_2 interface, while cations composed of organic fragments prefer the perovskite interface. The dipoles point away from TiO_2 can create an internal polarization field that shift up vacuum levels due to the electric field across this layer [20,21]. The WF and the band edge of the TiO_2 are changed by ΔV, where ΔV is the magnitude of surface potential change, and can be calculated through Poisson's equation [22]:

$$\Delta V = \frac{N_s \mu \cos\theta}{\varepsilon_r \varepsilon_0} \tag{1}$$

where N_s is the dipole concentration, μ is the dipole moment, θ is the angle between dipole direction and the surface normal, ε_r is the dielectric constant, and ε_0 is the permittivity of vacuum. The conduction band (E_c) of TiO_2 becomes closer to the vacuum level of perovskite layer, which should be beneficial for charge extraction.

In order to investigate the influence of IL on photovoltaic properties of $CH_3NH_3PbBr_3$ PSCs, devices were fabricated using our previously reported ASAC approach [9]. The XRD pattern for $CH_3NH_3PbBr_3$ thin film shown in Fig. S2 has a number of diffraction peaks at 15.2°, 30.4° and 45.6°, that can be indexed to the (1 0 0), (2 0 0) and (3 0 0) plane of $CH_3NH_3PbBr_3$ cubic phase. This highly preferred orientation in the (1 0 0) direction for $CH_3NH_3PbBr_3$ film consists with our prior results [9]. Fig. S3 presents the SEM images of the $CH_3NH_3PbBr_3$ film on TiO_2 substrate; the entire film is composed of a homogeneous, smooth, pinhole free perovskite layer. No morphology change has been found after the IL modification. Fig. 3a shows the cross-sectional view of planar $CH_3NH_3PbBr_3$ device. A continuous, flat, and dense TiO_2 layer is fully covered on the FTO substrate. On top of the TiO_2 layer, ~600 nm $CH_3NH_3PbBr_3$ light absorb layer is fabricated. Planar PSCs employing TiO_2-IL is also fabricated using the same fabrication process, other than an IL methanol solution treatment of the TiO_2 before the deposition of $CH_3NH_3PbBr_3$.The energy levels of TiO_2, $CH_3NH_3PbBr_3$, and spiro-OMeTAD are shown in Fig. 3b. The band structure of $CH_3NH_3PbBr_3$ is measured by XPS and SKPM, more details can be found in our prior work [23]. The WF of TiO_2 is −4.47 eV, which is too large to collect the photo-generated electrons in $CH_3NH_3PbBr_3$, while TiO_2-IL (−3.97 eV) can provide a more suitable energy level to promote the charge transfer from E_c of $CH_3NH_3PbBr_3$ (−3.38 eV) to TiO_2.

The current density–voltage (J–V) curves and the corresponding stabilized power conversion efficiency (PCE) and current density at the maximum power point as a function of time under simulated

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