A high-quality polycrystalline SnO$_2$ electron-transfer layer is synthesized through an in situ, low-temperature, and unique butanol–water solvent-assisted process. By choosing a mixture of butanol and water as a solvent, the crystallinity is enhanced and the crystallization temperature is lowered to 130 °C, making the process fully compatible with flexible plastic substrates. The best solar cells fabricated using these layers achieve an efficiency of 20.52% (average 19.02%) which is among the best in the class of planar n–i–p-type perovskite (MAPbI$_3$) solar cells. The strongly reduced crystallization temperature of the materials allows their use on a flexible substrate, with a resulting device efficiency of 18%.

1. Introduction

Lead halide perovskite solar cells (PSCs) have attracted great attention due to simplicity, and low cost of fabrication, with rapidly improving power conversion efficiency, recently reported as high as 23.3%. This rapid progress has been mainly due to the extensive studies of perovskite films, electron transfer layers (ETL), as well as the hole transport layers (HTL). The main goal was to obtain better crystallinity of the perovskite films, higher charge transport efficiencies, better film morphologies, and enhanced interfacial quality. The n-i-p type PSCs, with the configuration FTO/ TiO$_2$/n-TiO$_2$/CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$)/spiro-OMeTAD/Ag, have been widely studied, mostly because of the maturity of its fabrication procedure. In those devices TiO$_2$ is commonly used as an ETL, which can provide good energy level matching and a fair electron mobility (10$^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$). However, its high-temperature sintering process (≥450 °C) is not compatible with low-cost flexible substrates and roll-to-roll processing. Meanwhile, there have been efforts to develop simpler devices even without the mesoporous layer, which however suffer from lower efficiency.

SnO$_2$ is an excellent alternative to TiO$_2$, which has a wide optical bandgap (3.6–4.0 eV), and a much higher electron mobility (up to 240 cm$^2$ V$^{-1}$ s$^{-1}$). In addition, it can be pro-cessed at low-temperature, and has a good chemical and optical stability. Low-temperature atomic layer deposition (ALD) at 120 °C has been used to deposit a layer of SnO$_2$ as ETL, with the PCE above 18%, whereas this film is generally amorphous and limits its electron mobility.

Despite, plasma-assisted ALD enhanced the crystallinity of SnO$_2$, the necessary fabrication temperature was as high as 200 °C. In another attempt, sol-gels of SnCl$_2$·2H$_2$O, or SnCl$_4$·5H$_2$O was spin-coated, followed by approximately 180 °C anneal. This process produced a high-quality conductive film, but the relatively high annealing temperature made this process incompatible with most of plastic substrates. Moreover, the influence of thermal annealing temperature on the flexible substrates has been systematically investigated demonstrating that the processing temperature of 150 °C is still incompatible.
with commonly used PET substrates. Thus, using vacuum-free wet chemistry to synthesize high-quality SnO$_2$ nanocrystal (NC) and use as ETLs at a lower temperature is promising, but challenging.\textsuperscript{[15]} Along these lines, You and co-workers used commercialized SnO$_2$ NCs colloidal and annealed under 150 °C to obtain SnO$_2$ ETL, achieving a certified efficiency of 19.9%.\textsuperscript{[16]} In another work, the same annealing temperature was used to crystallize an ETL, made of room-temperature synthesized colloidal SnO$_2$ NCs, yielding the efficiency as high as 20.32%.\textsuperscript{[17]} It was also reported, that thermal annealing of the refluxed ethanol solution of SnCl$_2$·2H$_2$O at 150 °C yielded an efficiency of 19.20%.\textsuperscript{[18]}

Herein, we developed mixture of butanol and 5% water as crystallization solvent, which allowed the crystallization temperature of the SnO$_2$ ETL to be lowered to 130 °C, while achieving an efficiency as high as 20.52% (averaged 19.02%) of the resulting n-i-p planar PSCs (based on the CH$_3$NH$_3$PbI$_3$). This annealing temperature is acceptable for a whole class of inexpensive plastic, flexible substrates.

2. Results and Discussion
2.1. Crystallization and Morphology of SnO$_2$ ETLs

To obtain highly crystallized SnO$_2$ ETLs, the solvent used is of great importance for the hydrolysis process due to its direct and fundamental influence on the quality of SnO$_2$ NCs and the following thermal annealing process. Hence, four types of alcohol are selected with the consideration of their increasing boiling point following thermal annealing process. Hence, four types of alcohol are selected with the consideration of their increasing boiling point.

SnO$_2$ NCs were synthesized with a hydrolysis reaction in solvent through refluxing at 110 °C.\textsuperscript{[18]} Then the SnO$_2$ ETLs were obtained by spin-coating the as-obtained SnO$_2$ NCs solution on FTO substrate, followed by 1 h of thermal annealing at 130 °C.\textsuperscript{[18]} This thermal annealing temperature was chosen based on our preliminary evaluations described in the Sup-porting Information. Figure 1a–e show high-resolution transmission electron microscopy (HRTEM) images of the corresponding films. Insets show corresponding electron diffraction patterns. For single nanocrystal (NC) and uniform, continuous, and compact morphology, as well as high contrast, B-SnO$_2$ ETLs were characterized with scanning electron microscopy (SEM) images, shown in Figure 2a. Support Figure S1a, Supporting Information, shows the presence of O and Sn. The peaks at binding energies of 487.20, 487.23, 487.25 eV belongs to Sn 3d$_{5/2}$ and of 495.60, 495.62, 495.62 eV are contributed by Sn 3d$_{3/2}$, respectively, corresponding to E-SnO$_2$, B-SnO$_2$, and WB-SnO$_2$ (Figure S1b, Supporting Information). More...
5% v/v of deionized (DI) water into the butanol. A series of water quantities, 5%, 10%, and 15% (water and butanol are no longer mutual soluble above the ration of 15%), has been investigated as shown in Figure S2. Supporting Information, demonstrating the limited influence of water quantity on the PCE of the PSCs. The volume percentage of 5% was chosen on account that this quantity is enough for the reaction, and thus the basicity of the final mixed solvent would be barely influenced. With extra water dissolved in butanol, the hydrolysis reaction rate was increased with reaction time shortened from 13 to 4 h. The crystallinity of SnO2 was further improved as illustrated by the TEM in Figure 1e and XRD in Figure 1j. Moreover, the added water improved the quality of SnO2 ETL (WB-SnO2), to a uniform, pinhole-free morphology (Figure 2e). As shown in Figure 2, SnO2 with butanol solvent shows the best morphology. Therefore, in the following sections, E-SnO2, B-SnO2, and WB-SnO2 were selected as the prototypes to discuss the influence of solvent and the extra water on the optoelectronic properties. The morphology of bare FTO as reference was shown in Figure 2f.

2.2. Charge Transfer Properties and Optical Transmittance

Electronic structures of the valence bands were measured using UV photoelectron spectrometer (UPS) (Figure 3a). The Fermi Levels (EF) of -4.37, -4.25, and -4.25 eV for E-SnO2, B-SnO2, and WB-SnO2, respectively were estimated from the intercept of the higher binding energy with incident photon energy, while the corresponding valence band maximum (CBM) are located at -3.92, -3.82, -3.84 eV for E-SnO2, B-SnO2, and WB-SnO2, respectively (Figure S3a, Supporting Information). Thus, it is obvious that B-SnO2 and WB-SnO2 are not only well matched to the perovskite layer but also expected to favor a higher Voc (Figure S3b, Supporting Information). The electron mobility is another key factor for ETLs, which was assessed by the space-charge limited current (SCLC), achieving 9.45 \( \Omega \)0\(^{-5} \), 2.99 \( \Omega \)0\(^{-4} \), 6.02 \( \Omega \)0\(^{-4} \) cm\(^2\) V\(^{-1}\) s\(^{-1}\) for E-SnO2, B-SnO2, WB-SnO2, respectively (Figure 3b), which are consistent with results from literature.\(^\text{[21]}\) The optical transmittance of different SnO2 is also measured (Figure S4, Supporting Information). There is no different in transmittance for all of those SnO2, which is consistent with optical absorption (shown in Figure S3a, Supporting Information).

The charge transfer efficiency between perovskite absorber and the SnO2-based ETL was investigated by steady-state photoluminescence spectroscopy (PL) and time-resolved photoluminescence (TRPL) on the films of perovskite, E-SnO2/perovskite, B-SnO2/perovskite, and WB-SnO2/perovskite deposited on quartz (Figure 3c,d). The emission peak at 770 nm originates from the MAPbI3, which is significantly quenched with WB-SnO2 ETL. It demonstrates the fast electron extraction and transportation from perovskite layer, agreed well with its higher electron mobility (Figure 3b). TRPL has further confirmed this higher electron transfer efficiency with the reduced PL decay time (\( \tau_1 \) and \( \tau_2 \)) shown in Table S1, Supporting Information. \( \tau_1 \) reveals a higher and homogeneous surface potential profile of the WB-SnO2 film (686.15 mV) than those of E-SnO2 (419.77 mV) and B-SnO2 (575.25 mV). This fact means a lower work function and shallower Femi level...
for WB-SnO$_2$\cite{25}, which agrees well with the $E_F$ from UPS. The conductive atomic force microscopy (CFM) was also performed on the SnO$_2$ films. As shown in Figure 4d–f, the average currents are counted to be 732 pA, 6 nA, and 12 nA for E-SnO$_2$, B-SnO$_2$, and WB-SnO$_2$ ETLs, respectively, which shows that the conductivity of WB-SnO$_2$ is the best\cite{26}.

Figure 3. Characterization and charge transfer properties of the ETLs. a) UPS of SnO$_2$ deposited on quartz. b) SCLC of FTO/ETLs/Ag. c) Steady-state PL and d) TRPL of FTO/ETL/MAPbI$_3$.

Figure 4. SKPM and CFM images of the ETLs. a–c) SKPM and d–f) CFM images of a,d) E-SnO$_2$, b,e) B-SnO$_2$, and c,f) WB- SnO$_2$. 

It is reported that the mixture of crystalline and amorphous SnO\(_2\) leads to oxygen-vacancy-related defects, which could capture electrons and cause recombination at the SnO\(_2\)/perovskite interface.\(^{[16]}\) Thus, the observed better electron mobility, conductivity, and transfer efficiency of WB-SnO\(_2\) is reasonably attributed to its continuous, crystalline, and uniform morphology.

### 2.3. Perovskite Solar Cells

A series of n-i-p type planar PSCs based on various SnO\(_2\) ETLs, with configuration of FTO/SnO\(_2\)/MAPbI\(_3\)/spiro-OMeTAD/Ag was fabricated, as shown in cross-sectional SEM image in Figure 5a. To exclude possible processing variations, the devices were fabricated in the same batch, with the exactly identical procedures and parameters. The thickness of SnO\(_2\), perovskite, spiro-OMeTAD, and Ag electrode was about 40, 400, 200, and 70 nm, respectively. Meanwhile, the thickness of E-SnO\(_2\), B-SnO\(_2\), and WB-SnO\(_2\) were controlled to be nearly equal, \(\approx 40\) nm. The morphologies of perovskite films deposited on top of the SnO\(_2\) are shown in SEM images in Figure 5b and Figure S5, Supporting Information. It is clear, B-SnO\(_2\) and WB-SnO\(_2\) based perovskite layers are pinhole-free, while those cells based on E-SnO\(_2\) are full of pinholes and vacancies.

The \(J-V\) curves with the parameters of the best devices are shown in Figure 5c. The E-SnO\(_2\) based device had a power conversion efficiency (PCE) of 14.26\% with open-circuit voltage (\(V_{OC}\)) of 1.08 V, short-circuit current density (\(J_{SC}\)) of 21.30 mA cm\(^{-2}\), and fill factor (FF) of 61.89\%. This is slightly improved by the application of iP-SnO\(_2\) and iB-SnO\(_2\) ETLs (Figure S6, Supporting Information). However, a significant improvement is achieved when B-SnO\(_2\) is adopted, showing PCE of 19.70\% (\(V_{OC}\) of 1.09 V, \(J_{SC}\) of 22.85 mA cm\(^{-2}\), FF of 79.16\%). As expected, the record high a PCE of 20.52\% (\(V_{OC}\) as high as 1.10 V, \(J_{SC}\) of 22.98 mA cm\(^{-2}\), and FF of 81.27\%) was achieved with the WB-SnO\(_2\) ETL. The external quantum efficiency (EQE) spectra shown in Figure 5d are consistent with the above results.

Figure 6a shows the steady-state PCE and current density of our PSCs under the constant bias voltages, at the maximum power output points (\(V_{mp}\), 0.76, 0.89, 0.93 V) in \(J-V\) curves. The stabilized PCEs are 14.93\%, 18.40\%, and 19.62\% with the current density of 19.52, 20.75, and 21.10 mA cm\(^{-2}\) based on E-SnO\(_2\), B-SnO\(_2\), and WB-SnO\(_2\), respectively, which agrees well with the highest PCEs data. Their response time was measured to be 15.96, 10.92, and 7.80 s, indicative of the reduced defect of WB-SnO\(_2\) ETL. The \(J-V\) curves of PSCs based on WB-SnO\(_2\) ETL from forward and reverse scan are shown in Figure S7, Supporting Information. Around 1\% PCE difference could be observed, which is probably related to the interfacial charge accumulations, ion migration in perovskite, ferroelectric polarization, etc.\(^{[27]}\) Whereas, the steady state PCE presenting short response time is merely ascribed to the relieved charge accumulation at the ETL/perovskite interface. Additionally, the \(J_{SC}\) estimated from \(J-V\) curve is in agreement with \(J_{SC}\) calculated from EQE, further supporting the reliable performances of our Perovskite solar cells.\(^{[28]}\)

To study the reproducibility of the devices, 24 PSCs for each ETL were fabricated and characterized. The parameter distribution histograms of cell performance are shown in Figure 6b, Figure S8 and Tables S2–S4, Supporting Information.