Activating Old Materials with New Architecture: Boosting Performance of Perovskite Solar Cells with H₂O-Assisted Hierarchical Electron Transporting Layers

Fengyou Wang, Meifang Yang, Yuhong Zhang, Lili Yang,* Lin Fan, Shiquan Lv, Xiaoyan Liu, Donglai Han, and Jinghai Yang*

The breakthrough of organometal halide perovskite solar cells (PSCs) based on mesostructured composites is regarded as a viable member of next generation photovoltaics. In high efficiency PSCs, it is crucial to finely optimize the charge dynamics and optical properties matching between the perovskites and electron transporting materials to relax the trade-off between the optical and electrical requirements. Here, a simple antipolar route with H₂O as the additive is proposed to prepare hierarchical electron transporting layers to boost the efficiency of dopant-free PSCs. The photovoltaic performance of the PSCs is enhanced owing to increased light-scattering, improved Ostwald ripening, and photo-generated electron extraction. Optimization of the H₂O addition enables a valid power conversion efficiency of 19.9% (reverse scan: 20.02%) to be achieved. The device can retain more than 90% of its initial performance after storage in air for more than 30 days. These results are inspiring in that they present that a mesoporous transporting layer could be easily re-constructed to hierarchical architecture by the antipolar method to further improve the performance of PSCs.

1. Introduction

Inorganic–organic hybrid perovskite solar cells (PSCs) have attracted considerable attention owing to their unique characteristics such as the broad range in which they absorb sunlight, low exciton binding energy, long electron–hole diffusion length, tunable direct band gaps, and high extinction coefficient.¹–⁴ These cells, which have an n-i-p architecture, can be fabricated by using different hole transporting layers (HTLs) and electron transporting layers (ETLs) on the rear and front sides of the perovskite layer, respectively, to selectively extract the photo-generated carriers to an external circuit. The highest power conversion efficiency (PCE) of (FAPbI₃)₀.₉₅(MAPbBr₃)₀.₀₅ solar cells is 23.2%.⁵ The preparation process and the dose of each cation used as dopant need to be sophisticatedly controlled with the view of achieving ideal crystallization and good chemical stability. Therefore, it is difficult to maintain a high level of reproducibility. In contrast, the reproducibility of robustly fabricated dopant-free MAPbI₃-based solar cells is easier to control. However, owing to their modest ability to extract photo-generated carriers extraction and their wider bandgap than FA-doped perovskite materials, which always result in a lower short circuit current density, the PCE of MAPbI₃-based solar cells is still not optimal and needs to be further improved.⁶ The ETL is important because it not only provides the path for electron extraction, but also has a significant impact on the light-scattering characteristics and chemical nucleation of the perovskite layers. Therefore, it is necessary to consider the optical and electrical, as well as the chemical and physical stability of ETLs simultaneously to realize a high-performance device. Previously, materials such as TiO₂, PCBM, SnO₂, or ZnO were widely adopted into PSCs to enhance electron extraction and transport. Among all these alternative ETLs,
mesoporous TiO2 (m-TiO2) is the most commonly used n-type semiconductor and acts as scaffold layer for a large portion of PSCs, owing to its favorable band-edge positions, superior chemical stability, and low cost. However, a major drawback of planar m-TiO2 ETLs, which renders them unsuitable for application as PSCs, is that their interfacial charge extraction is insufficiently rapid. The charge accumulation at the TiO2/perovskite interface induced by ion migration in the perovskite layer is known to cause hysteresis, thereby causing the performance of the device to deteriorate.\[7,8\] To solve this problem, we previously modified planar TiO2 ETLs with a thin PC61BM buffer layer, and found that the elastic nature of the PC61BM could facilitate the formation of high-quality perovskite films and improve the TiO2/perovskite interfacial properties.\[9\] Considering the modest efficiency of these solar cells and the high cost of the PC61BM, it is still essential as well as vital to explore a more comprehensive way to boost the charge extraction and performance of these solar cells. Enlarging the TiO2/perovskite interfacial area may effectively release the accumulated electrons at the heterointerface because this would increase the probability of electron extraction by the ETL.\[10,11\] This suggests that suitably shaping the architecture of ETLs may be an alternative approach to optimize the charge dynamics at the TiO2/perovskite heterointerface to improve the performance of the PSCs.

Compared with traditional planar m-TiO2 ETLs, the hierarchical structure of TiO2 consists of particles of different sizes that could provide a larger interfacial area for charge extraction and more flexible architecture for light-scattering. In addition, as the substrate of perovskite layer, morphological properties of hierarchical structure TiO2 (size, distribution, and structure, etc.) can be modulated efficiently; hence, conceptually TiO2 is a more likely candidate for controlling the nucleation of the perovskite. Thus, in principle, hierarchical TiO2 could be an effective solution for improving the performance of the device.\[12–14\] Previously, hierarchically structured TiO2, which is synthesized by a two-step hydrothermal procedure, was used as the ETL in liquid state dye-sensitized solar cells to enhance the performance of the device.\[15\] Nevertheless, for PSCs, owing to the lack of appropriate architectural modulation, introducing a substrate with hierarchical architecture usually reduces the crystallinity of the perovskite films, which increases the density of defects and TiO2/perovskite interfacial recombination. Therefore, the use of hierarchically structured TiO2 to enhance the performance of PSCs beyond that of T-m-TiO2-based PSCs has not yet been reported.

Accordingly, in this work, we propose a tri-functional hierarchical m-TiO2 (H-m-TiO2) ETLs, which is first fabricated using H2O as an additive to shape the architecture and balance the light-trapping, crystallization, and charge extraction properties. The MAPbI3 solar cells with the n-i-p structure and H-m-TiO2 ETLs show a high efficiency of 20.02% (reverse scan) and are almost free of hysteresis. The enhanced performance is attributable to the unique H-m-TiO2 ETLs, which improves the light-scattering behavior and crystallization of the perovskite layer, and accelerates charge extraction. This work not only demonstrates a simple route for preparing hierarchical carrier transporting layers, but also paves the way for the possible application of hierarchical ETLs in extensive optoelectronic devices.

### 2. Results and Discussion

First, we examine the morphological changes upon H2O addition (Figure 1a–d). Top-view scanning electron microscopy (SEM) images of m-TiO2 films with 0, 5, 15, and 25% v/v of added H2O are shown in Figure 1a–d, respectively. The traditional m-TiO2 (T-m-TiO2) film without H2O addition shows a flat porous structure, which coincides with the state-of-the-art results that were previously reported.\[16–18\] As the addition of H2O increase to 15%, the roughness of the surfaces of the PC61BM is facilitated, which leads to the state-of-the-art results that were previously reported.\[16–18\] As the addition of H2O increase to 15%, the roughness of the surfaces of the H-m-TiO2 film increases and some microscale pits on the original m-TiO2 are created (H-m-TiO2). This can be ascribed to the large differences in polarity between the H2O and the solvent of the TiO2 colloid (ethanol), which provides sufficient surface tension to allow assembling of the TiO2 particles. Large amounts of TiO2 nanoparticles are accumulated to form the clusters, whereas particles in other areas become thinly spread as a consequence. Increasing the addition of H2O even further

Figure 1. Schematic diagrams and SEM images of m-TiO2 films with different H2O addition: a) 0%, b) 5%, c) 15%, and d) 25%. The white dash circles show the areas without m-TiO2.
to 25% causes too many TiO₂ particles to wash out during the spin-coating process, resulting in the exposure of large areas of the compact TiO₂ films.

Empirically, different morphological characteristics are likely to affect the optical properties of the ETLs. As the window layer of n-i-p type PSCs, surface texturization is the preferable configuration to ensure effective light-trapping over a wide wavelength range.[19–21] We examined the optical properties of the ETLs, including their vertical transmittance (VT) and total transmittance (TT) by UV–Vis–NIR spectrophotometry (Figure S1, Supporting Information). Increasing of H₂O addition from 0 to 15% causes the VT to reduce, whereas the TT almost remains unchanged (Figure S2a,b, Supporting Information), indicating that the surface light-scattering properties of the surface are promoted. However, when the addition of H₂O is promoted to 25%, the VT only increases slightly because the TiO₂ films are partially washed out (as shown in Figure 1d).

The haze factor is one of the major roles to evaluate the light-scattering ability of the substrate. We calculated the haze factor from the variation between VT and TT (Equation (1)) as follows:[22]

\[
\text{Haze} = \left( \frac{\text{TT} - \text{VT}}{\text{TT}} \right) \times 100
\]

Without the addition of H₂O, T-m-TiO₂ films could not produce an adequate light-scattering effect in the wavelength region of 400–800 nm owing to the small feature size of mesoporous structure. This means that much of the light is transmitted directly by the substrate without changing its orientation. After constructing the hierarchical structure, large TiO₂ clusters were able to effectively scatter the incident light, thereby resulting in an increased haze factor (Figure 1c). Optical simulations of the PSCs prepared on T-m-TiO₂ and H-m-TiO₂ ETLs were carried out to ascertain their light harvesting capability. The shape parameters that were used for the optical simulation are exhibited in Figure S3 in the Supporting Information. Figure 2b shows the 2D optical intensity distribution of electric fields in the perovskite layer. Detailed information of the simulation is included in Note S1 in the Supporting Information. Incident light with a wavelength of 600 nm incident from the fluorine-doped tin oxide (FTO) side was used for the simulation, and the color scale bars illustrating the absorption intensity were confined to the same range. It shows that for perovskite films on T-m-TiO₂ ETLs, a hierarchical electric field which originated from the forward- and reverse-propagating light waves exists in perovskite absorber layer, indicating moderate light-scattering. In comparison, strong light-scattering, owing to the larger surface roughness of the H-m-TiO₂ ETLs, is found in perovskite films, which results in more intense absorption. Figure 2c shows images of the perovskite thin films grown on T-m-TiO₂ ETLs and H-m-TiO₂ ETLs, respectively. Obviously, the H-m-TiO₂ ETLs sample exhibits a darker color, indicating stronger absorption than the T-m-TiO₂ ETLs sample. The light paths are schematically depicted in Figure 2d to visually illustrate benefits of this light-trapping effect for PSCs. Once the incident light approaches the H-m-TiO₂ ETLs, the stronger light-scattering effect (higher haze factor) between the H-m-TiO₂ and MAPbI₃ films prolongs the light path. Consequently, compared with T-m-TiO₂ ETLs, MAPbI₃ films based on H-m-TiO₂ are expected to achieve stronger light absorption (Figure S4, Supporting Information). In addition, for full cells with spiro-OMeTAD and Au layers on top, the absorption of the cell could be further
enhanced due to the subsequent larger reflection angle at the interfaces of MAPbI3/spiro-OMeTAD/Au.

Except for the optical behavior, the crystallization of perovskite films based on various substrates was investigated. Cuboid MAPbI3 crystals between 210 and 500 nm are formed on the pristine T-m-TiO2 ETLs (Figure 3a). For the substrates evolving from T-m-TiO2 to H-m-TiO2, as the addition of H2O increases from 0% to 15%, this also causes the grain size of MAPbI3 films to increase (Figure 2b,c). However, some pinholes and small grains are formed in the MAPbI3 films, thereby further escalating the H2O addition of the m-TiO2 substrates. The X-ray diffraction (XRD) patterns of the MAPbI3 films also verify the crystallization features (Figure 3e,f). All compositions exhibit a typical perovskite peak at \( \approx 14^\circ \), which corresponds to the (110) orientation of the photoactive black phase of MAPbI3. Compared with the other samples, the films grown on the H-m-TiO2 achieve the highest diffraction intensity and lowest full width at half maximum (FWHM), which also indicates improved crystallization. All these results imply that the crystallization characteristics of perovskite films seem to be greatly affected by the architecture of the substrates.

Here, we introduce the Ostwald ripening model to unravel the coarsening of the perovskite particles. During the nucleation process, precursors with different particle sizes are initially formed on the H-m-TiO2 surface. The relationship between the chemical potential and particles radius can be depicted as follows:\(^{[23]}\)

\[
\mu = \mu_0 + \frac{2\beta V}{r}
\]  

where \( \mu \) is the chemical potential of the surface, \( \beta \) is the surface energy, \( \mu_0 \) is the chemical potential for a flat surface, \( r \) is the radius of a particle, and \( V \) is mole volume of a particle. Hence, a smaller particle is energetically less stable than a larger particle owing to higher chemical potentials. This means small grains are easily dissolved than large grains if there is a sufficient amount of solvent present. The dissolved components between large grain and small grain will lead to a concentration gradient, causing the mass transportation from small grain to large grain according to Fick's first law.\(^{[24]}\) Therefore, as the period of annealing is elongated, the small grains vanish and the size of the large grains increases because of the mass transportation of the dissolved component. In this case, compared with the flat T-m-TiO2 layer, the H-m-TiO2 layer, which consists of small nanoscale mesoporous and large microscale holes, would require less solvent (DMF and DMSO) after the spin coating process. During the heating procedure, the H-m-TiO2 layer would inevitably delay the extraction of solvent, and prolong the ripening of the MAPbI3 precursor to form larger columnar crystals. Hence, the large perovskite grains finally coarsen by absorbing surrounding small grains via mass transportation (Figure 3g). In contrast, for the T-m-TiO2 layer or the non-optimized layers (with 5% or 25% H2O added), due to its flatter architecture, the solvent molecules are extracted more easily from the precursor films, which leave less time for Ostwald ripening process.

Considering that crystallization always determines the defects in perovskite films, we also investigated the trap state density and band tail state density in T-m-TiO2-based and
H-m-TiO2-based perovskite films. We studied the dark current–voltage characteristics and light-absorption characteristics for electron-only devices. Figure 4a,b illustrates the dark current–voltage characteristics of the solar cells, indicating linear ohmic response at low bias, a trap-filling regime, and a trap-free space charge limit current (SCLC) regime. The trap state density was determined by the trap-filled voltage as follows:[25]

\[ N_t = \frac{2\varepsilon \varepsilon_0 V_{TFL}}{q E} \]

where \( \varepsilon \) is the relative dielectric constant, \( \varepsilon_0 \) is the vacuum permittivity, \( V_{TFL} \) is the onset voltage of the trap-filled limit region, \( L \) is the thickness of the film, and \( q \) is the elemental charge. We found that the trap densities remarkably decrease from \( 1.5 \times 10^{-16} \) cm\(^{-3} \) to \( 9.2 \times 10^{-15} \) cm\(^{-3} \) for T-m-TiO2 ETLs and H-m-TiO2 ETLs, respectively. We also examined the Urbach energy (\( E_u \)) of the films, which probe the sharp onset of disorder in shallow energy level (Figure 3b). The \( E_u \) values for the H-m-TiO2 ETLs are lower, indicating a more disordered MAPbI3 films due to the enhanced crystallization.

Figure 3a–f and 4, introducing the H-m-TiO2 ETLs could enhance the crystallization of the MAPbI3 films and reduce the grain boundaries and trap-states density. To obtain deeper insights into the impact of different ETLs on the trap-states and charge-dynamics of the device, the influence of different ETLs on the trap-states and charge-dynamics of the device, the influence of different ETLs on the trap-states density. To obtain deeper insights into the impact of different ETLs on the trap-states and charge-dynamics of the device, the influence of different ETLs on the trap-states and charge-dynamics of the device, the influence of different ETLs on the trap-states density.

For the solar cells with T-m-TiO2 ETLs, the PCE of R-S and F-S are 16.0% (R-S: \( V_{oc} = 1.07 \) V, \( FF = 76.3\% \), \( J_{sc} = 19.6 \) mA cm\(^{-2} \)) and 15.04% (F-S: \( V_{oc} = 1.05 \) V, \( FF = 73.5\% \), \( J_{sc} = 19.5 \) mA cm\(^{-2} \)), respectively. The difference in the PCE between F-S and R-S is 0.96%. As expected, the champion cells based on H-m-TiO2 ETLs exhibit weaker hysteresis behavior. The PCE of R-S and F-S is 20.02% (R-S: \( V_{oc} = 1.13 \) V, \( FF = 80.2\% \), \( J_{sc} = 22.1 \) mA cm\(^{-2} \)) and 19.74% (F-S: \( V_{oc} = 1.13 \) V, \( FF = 79.8\% \), \( J_{sc} = 21.9 \) mA cm\(^{-2} \)), respectively. The PCE difference between F-S and R-S is 0.28%, which gives a valid PCE of 19.9%. To our best knowledge, this is a very high valid efficiency for dopant-free MAPbI3-based solar cells. Figure 4d shows the external quantum efficiency (EQE) and integrated current density of the solar cells. Apparently, the cells based on H-m-TiO2 have superior spectra response in the wavelength range from 350–800 nm. The integrated \( J_{sc} \) of the solar cells is 21.9 mA cm\(^{-2} \) (H-m-TiO2) and 19.6 mA cm\(^{-2} \) (T-m-TiO2), respectively. Furthermore, we also investigated the reproducibility of this technique. The photovoltaic parameters of 40 devices (20 cells based on H-m-TiO2, 20 cells based on T-m-TiO2) prepared in one batch are summarized in Figure S6 in the Supporting Information. The average PCE of 19.4% for these 20 H-m-TiO2 devices can be achieved, which is also higher than the devices based on T-m-TiO2 ETLs.

These results indicate that the performance enhancements of the solar cells can be ascribed to the synergistic effect among different properties. First, the improved light-scattering characteristics via the hierarchical architecture could elevate the light absorption of the MAPbI3 films by extending the effective light path. Therefore, the spectra response of the solar cells based on H-m-TiO2 would be better in a large wavelength region (Figure 5d). Second, as shown in Figures 3a–f and 4, introducing the H-m-TiO2 ETLs could enhance the crystallization of the MAPbI3 films and reduce the grain boundaries and trap-states density. To obtain deeper insights into the impact of different ETLs on the trap-states and charge-dynamics of the device, the influence of the logarithm of light intensity \( P \) on the \( V_{oc} \) characteristics was investigated (Figure 5e). This logarithmic relationship is consistent with the fundamental relationship \( V_{oc} = nk_B T/q \).
\( \ln(P) \), where \( n \) is a constant referred as the ideality factor, \( k_B \) is Boltzmann's constant, \( T \) is the temperature, and \( q \) is the elementary charge.\(^{27,28}\) According to the literature, the \( P \) dependence of the \( V_{oc} \) can provide insights into the role of trap-assisted recombination versus bimolecular recombination at open circuit.\(^{29,30}\) The recombination processes always strongly determine the properties of solar cells at open circuit condition because there is no current extraction and all the photo-generated carriers recombine. It is generally recognized that the ideality factor should be equal to 1 if Langevin recombination dominates, whereas other involvements of the interfacial trap-assisted Shockley–Read–Hall recombination would result in \( n \) being larger than 1. In this case, the value of \( n \) obtained for T-m-TiO\(_2\) and H-m-TiO\(_2\) is 1.69 and 1.52, respectively. This implies that the trap-assisted Shockley–Read–Hall recombination is present in both devices. In addition, the smaller \( n \) of the H-m-TiO\(_2\)-based solar cells also suggests that improved crystallization reduces recombination and consequently leads to the improvement of the photovoltaic performance.

Moreover, as previously reported, a good electronic contact with faster extraction could reduce charge accumulation at the MAPbI\(_3\)/contact layer interface induced by ion migration, and could promote carrier transportation.\(^{9,31–33}\) Here, we suppose that the vertical architecture (with a large surface area) of the H-m-TiO\(_2\) may form an additional radial collection path for photo-generated charges (Figure 6a,b), which may accelerate the extraction of photo-generated charges (Figure 6c,d). To confirm the enhanced charge extraction by H-m-TiO\(_2\) ETLs, we characterized the devices by steady photoluminescence (PL) and time-resolved photoluminescence (TRPL) (Figure 6e,f). More intensive PL quenching and a shorter lifetime would indicate faster charge transfer at the H-m-TiO\(_2\)/MAPbI\(_3\) interface. This accelerating photo-generated electron

**Figure 5.** a) Architecture and b) energy bandgap diagrams of the MAPbI\(_3\) solar cells. Inset (a): the graph of the practical devices (aperture area: 0.1 cm\(^2\)). c) Illuminated J–V curves (F-S and R-S) and PCE of the solar cells. The open circles indicate reverse scan data, and the filled circles represent forward scan data. d) EQE and integrated current density of the MAPbI\(_3\) solar cells. e) Dependence of the \( V_{oc} \) of H-m-TiO\(_2\) and T-m-TiO\(_2\)-based solar cells on the light intensity. Lines show linear fits to the experimental data.
extraction could effectively reduce the accumulation of charge at the hetero-interface, separate the holes and electrons, eliminate the recombination, and suppress the hysteresis behavior of the device. To gain more insight on the charge transport and recombination at the interface, electrical impedance spectroscopy (EIS) measurements were also performed in the as-fabricated PSCs (Figure 6g). Nyquist plot of EIS spectra were measured under dark and open circuit conditions, in the frequency range from 0.1 MHz to 10 Hz. As shown in Figure 6e, the fitted equivalent circuit model is composed of a series resistance ($R_s$), charge transfer resistance ($R_{tr}$) at the ETLs/MAPbI$_3$ and the MAPbI$_3$/spiro-OMeTAD interfaces, and recombination resistance ($R_{rec}$) forming a parallel circuit with capacitors ($C_{tr}$ and $C_{rec}$). The fitted parameters of $R_s$, $R_{tr}$, and $R_{rec}$ are exhibited in Table S1 in the Supporting Information. The $R_s$ is obtained from the x-axis intercept of the high-frequency curve. $R_{tr}$ is ascribed to the high-frequency arc and $R_{rec}$ is assigned to low-frequency arc. The values of $R_s$ show little variation for these two devices, indicating that the hierarchical TiO$_2$ ETLs have no significant effect on the series resistance. The H-m-TiO$_2$-based device exhibits a lower value of $R_{tr}$, probably because the hierarchical architecture could extract the charge effectively. These results could be further verified by applying 0.8 V bias voltage to the device (Figure S7, Supporting Information). Thus, $n$ carriers could be more easily extracted to the external circuit because charges are not trapped in the trapping centers in the perovskite films. Therefore, the H-m-TiO$_2$ layer could not only improve the light-scattering behavior and crystallization of the MAPbI$_3$’s crystallization, but also enhance the extraction of photo-generated charges.

In addition, as an emerging technique for PSCs, it is necessary to evaluate the device stability to assess the application potential. PSCs are known to be sensitive to humid conditions. Furthermore, the heat produced by light illumination cannot be quickly and effectively spread out generally in the encapsulated PSCs, which could be an alternative reason for the instability of inorganic–organic perovskite materials. We, therefore, examined the stability of the PSCs (30 days, under ambient conditions, 50% humidity) based on both T-m-TiO$_2$ ETLs and H-m-TiO$_2$ ESLs (Figure 7a). The performance (90% of the pristine PCE) of the devices based on H-m-TiO$_2$ ETLs was superior. We attribute this to the enhanced crystallization of the MAPbI$_3$ films, which resist the moisture penetration during the aging process. Figure 7b shows the stabilized outputs of PSCs at the voltage of maximum power point ($V_{mpp}$) under continuous irradiation. Both current and PCE of the champion cell change very little after soaking under one-sun for 250 s, which demonstrates the good irradiation stability of the devices.
fore, the tri-functional H-m-TiO₂ ETLs can provide respectable H-m-TiO₂ layers. These H-m-TiO₂ layers were first dried at 135 °C for 10 min and then sintered at 500 °C for 30 min in air atmosphere. More details about the materials and PSCs fabrication procedure are demonstrated in Notes S2–S4, Supporting Information.

3. Conclusion

In summary, we successfully demonstrated solution-processed H-m-TiO₂ ETLs for high-performance MAPbI₃ solar cells. The resultant H-m-TiO₂ ETLs, which were prepared by a H₂O-assisted method, are highly textured, and confer efficient light-trapping properties upon the PSCs. Benefiting from its unique architecture, the crystallization of MAPbI₃ is improved owing to the enhanced Ostwald ripening process. Photo-generated charge extraction from MAPbI₃ is also promoted due to the additional radial collection induced by H-m-TiO₂ ETLs. Therefore, the tri-functional H-m-TiO₂ ETLs can provide respectable photoelectrical enhancement to yield a high valid PCE of 19.9% (R-S: 20.02%, F-S: 19.74%) in the derived devices. In addition, a compact and stable protecting layer for device is spontaneously formed to enhance the ambient stability of the derived PSCs. About 90% of its initial PCE can be retained after 30-day exposure in ambient conditions with ~50% relative humidity. These H-m-TiO₂ ETLs with hierarchical architecture not only provide a simple way to improve the performance and stability of PSCs, but also shows the great advantages in further development of efficient optoelectronic devices.

4. Experimental Section

Fabrication of H-m-TiO₂ ETLs: FTO glass substrates in the dimension of 2 × 2 cm² were patterned by etching with zinc powder and 2 m hydrochloric acid. The substrates were in sequence washed by ultrasonication with soap (5% Hellmanex in water), absolute alcohol, acetone, and deionized water for 20 min, and then cleaned by UV-ozone for 20 min. A 30 nm-thick layer of dense compact TiO₂ was coated onto the FTO-glass by spin-coating at 2000 rpm for 30 s and then annealed at 135 °C for 10 min. The TiO₂ paste (Dyesol 18NR-T) was diluted with ethanol with weight ratio of 1:7. Then, different volume ratios (0%–25%) of deionized water were dripped in the mixed solution. The solution was stirred in room temperature for 1 h. The as-prepared solution was spin-coated onto the TiO₂ compact film at 5000 rpm for 30 s to fabricate H-m-TiO₂ layers. These H-m-TiO₂ layers were first dried at 135 °C for 10 min and then sintered at 500 °C for 30 min in air atmosphere.

More details about the materials and PSCs fabrication procedure are demonstrated in Notes S2–S4, Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Figure 7. Stability of the PSCs with different ETLs. a) Device performances as a function of storage time in an ambient environment (~50% humidity, T = 25°C). b) Stabilized maximum power point voltage, current density, and PCE.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords
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