Unraveling the roles of mesoporous TiO₂ framework in CH₃NH₃PbI₃ perovskite solar cells

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ABSTRACT Both of planar and mesoporous architectures prevail for perovskite solar cells (PSCs). However, it is still an open question how the architecture affects the performance of PSCs. The inconsistent results in the references often create confusion. In particular, the specific roles of mesoporous frameworks are yet to be well elaborated and require further clarification. In this study, we carefully compared the properties of perovskite films and the device performances for both architectures to unravel the roles of mesoporous TiO₂ frameworks in CH₃NH₃PbI₃ PSCs. The detailed characterizations of structural, microscopic, optical and electrical properties revealed that the presence of mesoporous TiO₂ framework contributed to enlarged perovskite crystal sizes, enhanced light harvesting, efficient electron extration and suppressed charge recombination. As a result, compared with the planar device, the mesoporous device yielded an improved power conversion efficiency of 18.18%, coupled with a reduced hysteresis. This study reveals the benefits of mesoporous TiO₂ framework in PSCs and provides the guidance for the design and optimization of architectures for high-performance devices.

Keywords: perovskite solar cells, CH₃NH₃PbI₃, device architecture, electron transporting layer, electron extraction

INTRODUCTION

Owing to the sustainable and renewable features of solar energy, photovoltaic devices that directly convert sunlight energy into electric energy have received much attention [1–3]. The particular aim of researchers is to construct solar cells with high efficiency, low cost and long-term stability [4,5]. To date, a number of light harvesting

materials have been explored for photovoltaic applications, such as conventional silicon (single-crystalline, poly-crystalline, and amorphous silicon), inorganic polycompound semiconductors (CdTe, Cu(In,Ga)Se₂, GaAs, etc.), organic dyes, polymers, quantum dots, as well as the emerging perovskite systems [1,6]. Specially, inorganic-organic halide hybrid perovskites afford superior optical and electronic features including strong light absorption, tunable bandgap, high carrier mobility, long intrinsic recombination lifetime and small exciton binding energy [7–10]. Combined with other merits of abundant raw materials, low cost and ease of manufacturing, perovskite solar cells (PSCs) become very promising in the photovoltaic community [11–13]. Recent years have witnessed unprecedented development of PSCs. At present, the record power conversion efficiency (PCE) has been pushed up to 25.2% [14], which manifests the enormous potential of this next-generation photovoltaic technology for practical application.

Current studies of PSCs are focusing on compositional tuning, interfacial engineering, band tailoring, solvent engineering, elemental doping, and functional additives, resulting in striking achievements [15–21]. Lots of efforts have also been devoted to improving the stability and large scale manufacturing of PSCs [22,23]. Nevertheless, the research related to the design and optimization of device architectures is rare. At present, the architectures of PSCs mainly fall into two types: planar structure and mesoporous structure [20,24]. Typically, a mesoporous architecture comprises conducting substrate, compact electron transporting layer (ETL), mesoporous ETL, perovskite absorber layer, hole transporting layer (HTL)

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and noble metal back electrode. When abandoning the mesoporous scaffold layer, it is the planar architecture. It is well known that the ETLs play a crucial role in transporting and collecting photogenerated electrons [25,26].

The previous studies have revealed that, in contrast to the planar architecture, the mesoporous counterpart delivers more than >20% efficiencies [27–29]. In mesoporous-type organic-inorganic halide PSCs, the commonly used mesoporous TiO_2 (m- TiO_2) framework has been demonstrated to serve as the porous support for subsequently deposited perovskite layer and benefit the infiltration of perovskite precursor solutions. However, some investigations also prove that the presence of m- TiO_2 layer increases the series resistance of devices, resulting in retarded charge transport in the mesoporous layer and inhibited growth of perovskite grains, which leads to poorer device performance in contrast to the planar devices [30,31]. Meanwhile, in the case of the mesoporous architecture, it often involves more difficulties in pore filling while there are no infiltration problems in the planar architecture [32]. Moreover, the *I-V* hysteresis has been shown to depend strongly on the presence or absence of m- TiO_2 [33]. Some studies demonstrate that the m- TiO_2 is beneficial to the suppression of *I-V* hysteresis [33–36], while others reach the opposite conclusion, revealing that the planar architecture delivers negligible hysteresis in inverted structures when organic ETLs/HTLs are employed [37–39].

At present, it is still an open question regarding which architecture affords better results. The contradictory results in the references often create confusion. A main reason responsible for the conflicting results is associated with the devices fabricated in different groups and with different procedures. It is well known that the photovoltaic performance depends strongly on the processing of various functional layers, while perovskite films with impurity phases and solar cells with poor efficiencies might not evaluate the real function of each component and reach a totally correct conclusion. Although both of planar and mesoporous architectures have been studied intensively, systematic comparisons of such popular architectures have seldom been reported. In particular, the specific role of mesoporous framework is yet to be well elaborated and still requires further clarification.

In this study, the dependance of performance on planar and mesoporous architectures has been investigated on the basis of a case study of MAPbI_3 (MA = CH_3NH_3) PSCs. According to the systematic comparison of the properties of perovskite films and the performances of PSCs for both architectures, the mesoporous architecture

is likely to involve the preparation of high-quality perovskite films and the construction of high-performance PSCs. In particular, the careful assessments of electron extraction and charge recombination demonstrate that the presence of m- TiO_2 framework facilitates the efficient electron extration from perovskites to ETLs and suppresses the interfacial charge recombination in the devices. The mesoporous architecture also yields enhanced PCE with reduced hysteresis.

EXPERIMENT SECTION

Device fabrication

Transparent conducting fluorine-doped tin oxide glass (FTO, sheet resistance $\sim 15 \Omega \text{ sq}^{-1}$) was patterned by etching with zinc (Zn) powder and 6 mol L^{-1} hydrochloric acid (HCl) diluted in deionized (DI) water before being used as the substrate ($1.5 \times 2 \text{ cm}^2$). The etched substrate was then successively cleaned with a detergent solution, DI water, acetone, ethanol, and isopropanol for 15 min, respectively, and dried with N_2 flow. The cleaned substrate underwent a UV ozone treatment for 20 min prior to spin coating of compact TiO_2 (hereinafter referred to as c- TiO_2). A thin layer of 20–25 nm thick c- TiO_2 layer was formed *via* spin coating of 0.15 mol L^{-1} titanium diisopropoxide bis(acetylacetonate) diluted in *n*-butyl alcohol, followed by thermal treatment on a hot plate set at 135°C for 10 min and annealing at 500°C in air for 30 min. In the case of the mesoporous architecture, a 200 nm thick m- TiO_2 layer was further deposited on c- TiO_2 by spin coating a commercially available TiO_2 paste (Dyesol 18NR-T) diluted in anhydrous ethanol at 1:10 by weight at 4000 rpm for 30 s, further sintered under air at 500°C for 30 min. The as-obtained FTO/c- TiO_2 and FTO/c- TiO_2 /m- TiO_2 substrates further underwent a UV ozone treatment for 20 min prior to the deposition of perovskite films.

The MAPbI_3 perovskite films were fabricated through the following steps: 461 mg of PbI_2 , 159 mg of MAI, and 78 mg dimethylsulfoxide (DMSO) (with the molar ratio of 1:1:1) were dissolved in 600 mg of *N,N'*-dimethylformamide (DMF) at the ambient temperature, and the mixture solution was stirred for 1 h in glove box under nitrogen atmosphere. Particularly, 50 μL of perovskite precursor solution was dispensed dropwise onto the surface of FTO/c- TiO_2 or FTO/c- TiO_2 /m- TiO_2 , followed by spin-coating at 4000 rpm for 25 s, in which one drop (100 μL) of antisolvent ethyl acetate was dropped on the spinning substrate after 7 s. This process allowed a quick crystallization of the MAPbI_3 perovskite. The

coated films were thermally treated on a hot plate set at 105°C for 10 min. During the drying procedure at 105°C, the film changed color from light yellow to dark brown, indicating the formation of perovskite films. 1 mL of a chlorobenzene solution containing 72.3 mg of spiro-OMeTAD, 28.8 μL of *tert*-butylpyridine (TBP), and 17.5 μL of lithium bis(trifluoromethylsulfonyl)imide salt dissolved in acetonitrile (0.52 g mL⁻¹) was cast onto the perovskite surface and spun at a rate of 3000 rpm for 30 s to form the HTL layer. The as-obtained samples were left under dark in air overnight prior to performing thermal evaporation of Ag electrode to complete the fabrication of PSCs. The active area of the devices was 0.12 cm².

Characterization of materials and devices

X-ray diffraction (XRD) was performed on an X'Pert PRO MPD diffractometer (Panalytical B. V.) by using a monochromatic Cu K α source as the irradiation ($\lambda = 1.54056 \text{ \AA}$). Scanning electron microscopy (SEM) measurements were conducted by a field emission scanning electron microscope (JSM-6700F, JEOL). The contact angles were obtained by using a contact angle meter (OCA 15EC, DataPhysics Instruments GmbH). Optical absorption spectra were recorded on a UV-vis-NIR spectrophotometer (CARY 5000, Agilent) fitted with an integrating sphere accessory. The photoluminescence (PL) spectra of perovskite films were recorded with a charge-coupled device (CCD, Andor DU401A-BVF) mounted on a monochromator (Zolix Omni- λ 5028i), excited by a 473 nm solid state laser. The decay curves were recorded with a PZ-FLIM-110 Piezo Scanning fluorescence-lifetime imaging microscopy (FLIM) system using the time-correlated single photon counting (TCSPC) technique, under the excitation of 405 nm, 20 MHz picosecond diode laser with a pulse width of 70 ps in ambient conditions. The film samples were excited from both perovskite and glass sides. The current density-voltage (*J-V*) curves were recorded using a digital source meter (Keithley, 2400) under an 3A grade AM 1.5 simulated sunlight (100 mW cm⁻², Oriel Sol 3A Solar Simulator, USA) with a scan rate of 100 mV s⁻¹ and a voltage step of 10 mV. The incident light intensity was calibrated with a Si solar cell (Oriel Instruments, Model 91150V). The monochromatic incident photon-to-electron conversion efficiency (IPCE) was measured on an electrochemical workstation (Zennium Pro., Zahner) fitted with a CIMPS-IPCE system and Thales software under the direct current (DC) mode using a tunable LED lamp (365–1020 nm, TLS03) as the monochromatic light source. Electrochemical impedance spectroscopy (EIS)

was recorded on an electrochemical workstation (Zennium Pro., Zahner) under dark condition. The measured data were fitted by using a Z-view software.

RESULTS AND DISCUSSION

The top-view SEM images of c-TiO₂ and m-TiO₂ films are shown in Fig. 1a, b. A compact surface morphology is observed for the c-TiO₂ sample while the m-TiO₂ sample displays a typical porous feature. It is known that the mesoporous structure of m-TiO₂ would favor the penetration of perovskite precursors. The contact angles of DMF/DMSO mixed solution (with the molar ratio of 9:1), i.e., the solvent of perovskite precursor solution on the TiO₂ surface were illustrated in the insets of Fig. 1a, b. Both of c-TiO₂ and m-TiO₂ film samples show quite low contact angles around 3°. The superb wettability of both ETL films towards the perovskite precursors is beneficial to the formation of high quality perovskite films. Atomic force microscopy (AFM) measurements of the morphology of TiO₂ ETLs (Fig. 1c, d) reveal that, the c-TiO₂ film yields a more compact morphology (root-mean-squared (RMS) = 5.19 nm) with clear individual grains when compared with the more porous texture-like sponge of m-TiO₂ that shows almost doubled roughness value (RMS = 11.9 nm).

The XRD patterns of planar and mesoporous MAPbI₃ perovskite films (Fig. 2a) show well-resolved diffraction peaks, revealing the formation of well-crystallized perovskites for both films. The diffraction patterns exhibit a preferential orientation indexed to the (110) and (220) lattice planes, as characterized by diffraction peaks at the angles of 14.2° and 28.5° [40]. The diamond symbol highlights the characteristic peaks belonging to conducting FTO substrates. Fig. 2b illustrates a unit cell of

Figure 1 Top-view SEM and AFM images of (a, c) c-TiO₂ and (b, d) m-TiO₂ films. The insets illustrate the contact angle of corresponding films.

Figure 2 (a) XRD patterns of the planar and mesoporous perovskite films, (b) diagram of a unit cell of MAPbI₃ perovskite, (c) UV-vis absorption spectra, and (d) $(Ah\nu)^2$ vs. $h\nu$ plots for determining the absorption onsets of planar and mesoporous perovskite films.

MAPbI₃ lattice, depicting a dominating diffraction plane. It is revealed that the insertion of underlying m-TiO₂ framework exerts no evident effects on the crystal structure of perovskite films. The incomplete conversion of PbI₂ into MAPbI₃ often occurs for perovskite films, and this phenomenon is more pronounced for planar perovskite film than that of mesoporous one [41,42]. In this study, no diffraction peaks arising from commonly reported impurity phases such as MAI and PbI₂ were detected, demonstrating the conversion was completed. And the successful preparation of perovskite crystals free of impurities, which can be attributed to our well-controlled processing technology, would benefit a better comparative study of PSCs with different architectures.

The UV-vis absorption spectra of perovskite films are presented in Fig. 2c. Compared with the planar film, the mesoporous film exhibits similar light absorption of perovskite layers over the visible region of the solar spectrum, implying the similar thickness of both perovskite films as confirmed by cross-sectional SEM images as shown later. The stronger absorption of mesoporous film in the UV part arises from the stronger light absorption of m-TiO₂ layer. The effective band gap of MAPbI₃ were further evaluated by extrapolating the linear portion of the $(Ah\nu)^2$ versus $h\nu$ plots at $A=0$ according

to Equation (1) [43,44]:

$$(Ah\nu)^2 = c(h\nu - E_g), \quad (1)$$

where A is the absorption coefficient, ν is the frequency, E_g denotes the band gap, h is the Planck constant and c is a constant. The equation describes the relationship between the band gap for direct inter-band transition and the absorption coefficient near the absorption edge. As performed in Fig. 2d, an effective band gap of 1.58 eV is estimated for MAPbI₃, in a good agreement with the values reported in literatures [8]. The similar optical band gaps for both planar and mesoporous MAPbI₃ films corroborate with the identical crystal structure and chemical composition (no impurity phases) as revealed by XRD patterns.

Fig. 3 presents the top-view SEM images of the planar and mesoporous perovskite films. Both architectures deliver compact, uniform and pinhole-free features of perovskite films. A fair amount of perovskite grains are larger than 200 nm, indicating the formation of high-quality films through the one-step method. Moreover, in contrast to the planar architecture, the mesoporous architecture provides relatively larger crystal sizes, as confirmed by the size statistics of perovskite crystals (insets of Fig. 3a, b). The presence of m-TiO₂ leads to the increase

Figure 3 Top-view SEM images of (a, c) the planar and (b, d) mesoporous perovskite films. Insets present the size distributions of perovskite crystals.

of average grain sizes from around 150 to 250 nm, with some of grains exceeding 600 nm. This fact implies that an improved crystallization quality of perovskite films can be obtained with the presence of m-TiO₂ framework.

The cross-sectional view SEM images (Fig. 4a, b) show typical device architectures of FTO/c-TiO₂/perovskite/Spiro-OMeTAD/Ag and FTO/c-TiO₂/m-TiO₂/perovskite/Spiro-OMeTAD/Ag for planar and mesoporous PSCs, respectively. Both perovskite layers share a similar thickness around 500 nm. The incorporation of m-TiO₂ does not significantly influence the thickness of the perovskite layer, considering that the precursors can infiltrate into the m-TiO₂ layer (about 200 nm in thickness) to grow perovskite crystals, which is in contrast to thicker perovskite film on rougher TiO₂ layer [45]. The cross-sectional SEM images further confirm more pronounced difference toward the grain sizes along the vertical direction of perovskite growth. That is, the mesoporous architecture yields larger perovskite grain sizes than the planar architecture. The schematic drawings of device structures (Fig. 4c, d) highlight the size comparison of the perovskite grains. As illustrated, the presence of m-TiO₂ leads to the growth of larger perovskite grains. The formation of larger perovskite crystals for the mesoporous architecture might involve two kinetic processes, i.e., a fast heterogeneous nucleation and an anomalous grain growth, which have been proposed for the dynamic growth process of perovskite materials [30,46,47]. Since the nucleation energy barrier at the heterogeneous interface of TiO₂/PbI₂ is lower than that at the homogeneous interface [24,30], the m-TiO₂ nanoparticles afford numerous heterogeneous nucleation sites

Figure 4 Cross-sectional view SEM images and schematic illustration of the device structures for (a, c) planar and (b, d) mesoporous PSCs.

that facilitate the nucleation of perovskite grains at the initial nucleation stage. Meanwhile, a great number of TiO₂ nanoparticles with large interfacial contact area would lead to the formation of many reentrant edges at the TiO₂/perovskite interface, which has been demonstrated to promote the growth of perovskite grains during the subsequent annealing of perovskite films [47]. The annealing process drives the migration of the grain boundaries, and results in the growth of numerous small grains and the infiltration of them into each other [48]. Such an anomalous grain growth process induced by the presence of m-TiO₂ layer produces increased perovskite grain sizes for the mesoporous films. By comparison, the planar films without m-TiO₂ nanoparticles involve a normal grain growth scenario, in which the perovskite grains undergo a slower increase of grain size with the annealing treatment. This anomalous grain growth mechanism offers a possible explanation for the increased grain sizes of perovskite films fabricated on the m-TiO₂ layer; however, the in-depth understanding of the grain growth dynamic process of perovskite materials remains to be further studied. The larger grain size would cause the decrease of the number of grain boundaries, contributing to the facilitated charge transport and suppressed charge recombination [33].

The *J-V* curves of the best-performing planar and mesoporous PSCs, measured under reverse scanning (RS) and forward scanning (FS) modes, are shown in Fig. 5a, b, respectively. The corresponding photovoltaic parameters are summarized in Table 1. Under the RS mode, the planar device acquires an open-circuit voltage (*V*_{oc}) of 1.05 V, short-circuit current density (*J*_{sc}) of 22.54 mA cm⁻², and fill factor (FF) of 68.42%, yielding an

Figure 5 (a, b) The typical J - V curves for the best performing planar and mesoporous PSCs, obtained from RS and FS under the illumination of one sun (AM1.5, 100 mW cm⁻²). (c) IPCE of the best device, and the intergrated photocurrent from the IPCE is 21.89 mA cm⁻². (d) PCE statistics of the planar and mesoporous PSCs, with each type based on 20 devices.

Table 1 The photovoltaic parameters derived from J - V curves of the best-performing planar and mesoporous PSCs, measured under the illumination of one sun (AM1.5, 100 mW cm⁻²)

Devices	Sweep	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	η (%)	HI
Planar	RS	1.05	22.54	68.42	16.19	0.055
	FS	1.02	20.94	67.38	14.39	
Mesoporous	RS	1.10	22.95	72.02	18.18	0.029
	FS	1.09	22.73	70.61	17.49	

optimized PCE of 16.19%. In contrast, the mesoporous device exhibits a much higher PCE of 18.18% coupled with V_{oc} of 1.10 V, J_{sc} of 22.95 mA cm⁻², and FF of 72.02%. That is, the mesoporous architecture produces considerable increase in all of the main parameters compared with the planar architecture. The J - V curves measured under different scanning models reflect that the I - V hysteresis is also associated with the presence or absence of m-TiO₂. Compared with the planar structure, much lower degree of hysteresis is obtained for the mesoporous structure. With the aim of quantitatively evaluating the degree of I - V hysteresis, we define a hysteresis index (HI) based on Equation (2) [33,49]:

$$HI = \frac{J_{RS}(0.8V_{oc}) - J_{FS}(0.8V_{oc})}{J_{RS}(0.8V_{oc})} \quad (2)$$

The HI values of planar and mesoporous devices are estimated to be 0.055 and 0.029, respectively. The presence of m-TiO₂ is beneficial to the suppression of I - V hysteresis. Since the low frequency capacitance is regarded to be the origin of I - V hysteresis in lead halide PSCs, severe I - V hysteresis observed in the planar architecture might be explained by the fact that the capacitive charges to be stored are much larger in contrast to the mesoporous architecture [33]. Owing to the high quantity of capacitive charges, the photogenerated carriers can be hardly extracted and collected at a short setting time without the assistance of m-TiO₂ layer. The significantly reduced hysteresis with the presence of m-TiO₂ layer implies that the capacitive charges are rapidly dissipated by efficient charge separation. Moreover, the capacitive

charge tends to be stored in smaller crystals and would be reduced by increasing the crystal size [33]. The increase of perovskite crystal sizes for mesoporous devices coincides with the fact of the alleviated I - V hysteresis.

The IPCE spectrum of the best-performing mesoporous PSC is shown in Fig. 5c. The spectrum exhibits a maximum value of external quantum efficiencies exceeding 90%, indicating the efficient conversion of UV-visible photons to electron-hole pairs. The integrated photocurrent density is around 21.89 mA cm^{-2} , in good agreement with the J_{sc} value obtained from the J - V curves. To test the reliability of the PSCs, 20 devices were fabricated for each type of cells with the corresponding PCE statistics shown in Fig. 5d. The planar and mesoporous devices obtain average efficiencies of 15.41% and 17.40%, with small deviations of 0.51% and 0.57%, respectively.

To check the device performance of PSCs under the work condition, the photocurrent densities of the planar and mesoporous devices under their maximum power point (MPP) were tested. Both devices display steady J_{sc} during 110 s measurement (Fig. 6a), demonstrating the high power output ability of both types of PSCs. The change of the V_{oc} of planar and mesoporous PSCs was also measured with the illumination of different light intensities under the RS mode (Fig. 6b). It is found that

both devices show monotonic increase in V_{oc} with the light intensities, according to the relationship expression of V_{oc} and light intensity as the following Equation (3) [34,50]:

$$V_{\text{oc}} = \frac{nk_{\text{B}}T}{q} \ln\left(\frac{I_{\text{L}}}{I_0} + 1\right), \quad (3)$$

where n represents the ideal factor of solar cells, k_{B} is the Boltzmann constant, T expresses the absolute temperature, q represents the elementary charge, I_{L} is the photogenerated current, and I_0 denotes the inverse saturation current of PN junction in photovoltaic devices. It is well known that the deviation of the slope from unity $k_{\text{B}}T/q$ indicates a trap-assisted recombination in solar cells [50–52]. The ideal factor n values of the planar and mesoporous devices were fitted to be 1.30 and 1.27, respectively. The slight decrease of n in the mesoporous device implies a reduced charge recombination and efficient charge extraction [50]. The suppressed charge recombination should contribute to the enhancement of V_{oc} and FF for the mesoporous device, as confirmed in Fig. 5.

The J - V curves of the planar and mesoporous PSCs measured in the dark are shown in Fig. 6c. It is revealed that both devices perform well as diodes, being able to afford a good current rectification. The rectification ratios

Figure 6 (a) Evolution of photocurrent density for the planar and mesoporous devices without encapsulation under MPP tracking and continuous one sun irradiation (AM 1.5G, 100 mW cm^{-2}) at 25°C . (b) Open-circuit voltage (V_{oc}) versus irradiation intensity of the planar and mesoporous PSCs with solid lines denoting for linear fittings. (c) Log-log plots of dark J - V curves of the planar and mesoporous PSCs. (d) Nyquist plots of the planar and mesoporous PSCs, measured in the dark with an applied voltage of 1.0 V. The inset shows the simplified equivalent circuit model for curve fitting.

(herein defined as $J_{V=0.5}/J_{V=-0.5}$) are estimated to be 1.12 and 1.26 for the planar and mesoporous devices, respectively. High rectification ratio implies lower current leakage, which contributes to the decrease of the shunt resistance of devices [53]. Therefore, the dark current measurement reveals that the presence of m-TiO₂ layer prevents the current leakage, which is beneficial to the enhancement of J_{sc} and FF [30,54]. Moreover, the lowest currents do not happen at the bias voltage of zero, which might be associated with the charge-discharge processes occurring in the perovskite or TiO₂ films [55]. Such zero shift is slightly weaker for the mesoporous device, revealing that the presence of the m-TiO₂ layer facilitates the charge separation, resulting in the rapid dissipation of capacitive charges. This result echoes the analysis of I - V hysteresis.

EIS were conducted to obtain the insight into the recombination processes inside the solar cells. Fig. 6d shows typical Nyquist plots of impedance spectra for PSC devices measured in the dark with an applied voltage of 1.0 V, approaching the value of V_{oc} . The inset gives the simplified equivalent circuit model for fitting the Nyquist plots, on the basis of a transmission line model in literatures [56,57]. Herein the equivalent circuit consists of two resistors (R_s and R_{rec}) and a constant phase element (CPE). Specifically, R_s corresponds to the series internal resistance of devices, mainly referring to the resistance of conductive electrode; while R_{rec} accounts for the charge recombination resistance occurring at the interfaces [50]. The nonideal capacitor of CPE is generally defined by CPE-T and CPE-P that are correlated to the interface capacitor and an ideal capacitor, respectively [58,59]. The data can be well-fitted with such a simple circuit. The charge transfer resistance (R_{ct}), which is the signature of the charge transport resistance, cannot be clearly identified in our case owing to its comparatively much smaller value than R_{rec} . The fitted parameters of R_s , R_{rec} , CPE-T, and CPE-P are listed in Table 2. As shown, both planar and mesoporous devices share similar values for R_s due to the use of identical electrode in this study. Moreover, based on the fitting results of the semicircles for Nyquist plots, the R_{rec} of the mesoporous device (1348 Ω) is much larger than that of the planar device (845.5 Ω). The larger R_{rec} implies the effective suppression of electron-hole recombination, which might mainly be attributed to the larger perovskite crystals with decreased interface defects and the faster electron extraction at the large-area TiO₂/perovskite interface.

It is well known that, for any of device architectures, following the exciton dissociation, the charge extraction

Table 2 The parameters employed for the fitting of the impedance spectra of the planar and mesoporous PSCs

Devices	R_s (Ω)	R_{rec} (Ω)	CPE-T (F)	CPE-P (F)
Planar	11.1	845.5	1.1×10^{-8}	0.92
Mesoporous	15.8	1348	6.1×10^{-9}	0.96

yield increases when the charge injection is faster than the PL decay of perovskites or the electron-hole recombination inside the perovskite layer [60]. Hence, besides strong light harvesting, efficient dissociation of the photogenerated carriers is also of great importance for constructing highly efficient PSCs. To explore the insights into charge extraction kinetics inside different device architectures, the steady-state PL and time-resolved PL (TRPL) were conducted (Fig. 7). As shown, the steady-state PL spectra reveal an opposite intensity changing trend for perovskite films depending on the laser incident sides. When the laser is incident from the perovskite side (Fig. 7a), the mesoporous perovskite film has a stronger PL intensity than the planar perovskite and the control FTO/perovskite sample; in this case, the bottom ETL exerts a very little effect on the photogenerated carriers, hence the stronger PL intensity demonstrates the higher quality of the perovskite film [50]. The enhanced PL of the mesoporous film might be associated with the larger perovskite crystals with less charge recombination sites that would promote the fast charge transport, as confirmed by the SEM characterization. On the contrary, the mesoporous perovskite film yields more severe quenching in contrast to the planar perovskite film when irradiated from the glass side (Fig. 7b), implying that the introduction of m-TiO₂ layer contributes to the accelerated

Figure 7 (a, b) Steady-state PL spectra and (c, d) TRPL decays of the planar and mesoporous perovskite film samples, with the excitation laser incident from perovskite side and glass side, respectively.

charge extraction from the perovskite to the ETL. Herein it is worth noting that, when the laser is incident from the glass side (Fig. 7b), there is a slight red-shift in PL peak for perovskite films on FTO substrate compared with that on the planar or mesoporous TiO₂ layers. The MAPbI₃ perovskite films fabricated on TiO₂ layers exhibit an emission maximum centered at around 772 nm, which is in a good agreement with the previous literatures [49,61], while the PL peak is red-shifted to around 778 nm for the perovskite film directly deposited on FTO substrate. Such a red-shift phenomenon may be ascribed to slight changes in stoichiometry or crystallization of perovskite materials on different substrates (i.e., TiO₂ and FTO), which has been reported for perovskite films fabricated on different metal oxides and transparent conducting substrates (TCOs) [16,62]. Moreover, the difference in the refractive indice for various substrates might also contribute to this small shift in view of some optical effects [16]. This result demonstrates the importance of the substrate toward the formation of perovskite films.

The impact of m-TiO₂ layer in facilitating the charge extraction is further supported by TRPL measurement *via* time-correlated single photon counting (TCSPC). With the incident from the perovskite side (Fig. 7c), the incident laser cannot pass through the hundreds of nanometer-perovskite layer and reach the underlying ETL, that is, the bottom TiO₂ layer has a negligible effect on the photogenerated carriers and the PL decay is dominated by the carrier recombination dynamics in the MAPbI₃ perovskite. The planar and mesoporous films show typical mono-exponential decays with the fitted lifetimes of 25.1 and 30.3 ns, respectively. The prolonged lifetime for the mesoporous sample confirms relatively low non-radiative recombination in the MAPbI₃ perovskite. With the incident from the glass side (Fig. 7d), under which condition the photogenerated electrons move close to the ETL, the mesoporous sample exhibits much faster PL decay compared with the planar sample, indicative of enhanced interface charge extraction with the presence of m-TiO₂. Specifically, under such condition, the PL decay can be determined by three components, bulk radiative recombination, interface recombination *via* surface

trapping, as well as carrier extraction by ETL, of which the interface recombination is supposed to be negligible considering the remarkable performance of PSCs. With the aim of quantitatively evaluating such dynamic processes, we have fitted the PL decays by a bi-exponential function as described by Equation (4) [41,50]:

$$y = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + y_0, \quad (4)$$

where τ_1 and τ_2 denote the fast decay and slow decay, respectively, A_1 and A_2 are the corresponding decay amplitudes, and y_0 is a constant for the baseline offset. Both of the PL decay curves are well fitted, and the resultant parameters are summarized in Table 3. The fast decay can be ascribed to the quenching of free electrons in the perovskite through the electron extraction to TiO₂, whereas the slow decay could be ascribed to radiative recombination of photo-induced carriers in perovskites [41,50]. The planar sample shows a fast decay of $\tau_1 = 2.57$ ns, with a weight fraction of 39%. By contrast, the mesoporous sample provides a much faster decay of $\tau_1 = 1.98$ ns, coupled with a significantly increased fraction of 92%. This result further indicates that, in the case of planar film, the electrons generated inside the perovskite away from the c-TiO₂ cannot be efficiently extracted, while the presence of m-TiO₂ framework benefits the efficient interface charge extraction of the photogenerated electrons from perovskites to ETLs [30].

Fig. 8a, b schematically illustrate the interface electron extraction and carrier recombination processes in the case of incident from the glass side (i.e., working condition of PSCs) for the planar and mesoporous devices, respectively. Under the illumination, there will be many photo-induced electrons and holes in the perovskite films, a large portion of which are quickly extracted with the help of ETL and HTL, while the other part of which involve the radiative recombination with opposite charges or recombination by traps. By comparison, the presence of m-TiO₂ is conducive to the electron extraction from the perovskite to ETL as a result of large interfacial contact area, thereby lowering the recombination rate in PSCs [41]. The facilitated extraction of photogenerated

Table 3 The parameters employed for the fitting of the TRPL spectra of planar and mesoporous perovskite films

Sample	Incident direction	τ_1 (ns)	A_1	τ_2 (ns)	A_2	$A_1/(A_1+A_2)$
Planar	Perovskite side	/	/	25.1	1.01	/
	Glass side	2.57	0.46	12.5	0.72	39%
Mesoporous	Perovskite side	/	/	30.3	0.95	/
	Glass side	1.98	1.42	12.2	0.12	92%

Figure 8 Schematic illustration of the electron extraction and carrier recombination processes for (a) planar and (b) mesoporous devices, respectively. The laser is incident from the glass side, identical to the working condition of PSCs.

electrons from the perovskite grains to the outside circuit contributes to the suppression of charge recombination in the perovskite film and improves the charge collection efficiency in PSCs.

Assessments of charge extraction and interfacial charge recombination reveal that the mesoporous device architecture is a more preferable one for MAPbI₃ PSCs [60]. MAPbI₃ materials have diffusion coefficient of electrons (D_e) and holes (D_h) of 0.016 ± 0.004 and $0.2 \pm 0.02 \text{ cm}^2 \text{ s}^{-1}$, respectively [60,63]. Considering that D_e is far smaller than D_h , the holes can be extracted more efficiently than electrons in MAPbI₃-based PSCs. Therefore, the mesoporous hole acceptor is not required while the m-TiO₂ framework should be necessary. The m-TiO₂ layer contributes to the effective separation of photo-generated carriers, as well as the transport and collection of electrons [41,63]. Of course, the compatibility between absorbing materials and device architecture is a critical issue that needs to be considered. Actually, different perovskite absorbing materials might deliver different results. For example, it has been demonstrated that MAPbI_{3-x}Cl_x devices comprising m-TiO₂ usually provide relatively lower efficiencies as a result of incompatibility in the device architecture while their planar devices perform better [41]. This scenario might be closely associated with the comparable intrinsic diffusion lengths of the two types of carriers (i.e., electrons and holes) for MAPbI_{3-x}Cl_x materials, which allows the removal of the m-TiO₂ framework [63]. For MAPbI_{3-x}Cl_x based devices, the incorporation of m-TiO₂ might involve a more pronounced negative effect due to the increase of interface area and massive surface states, which would result in the enhanced probability of charge recombination.

CONCLUSIONS

The present study demonstrates the benefits of m-TiO₂

framework in MAPbI₃ PSCs. The presence of m-TiO₂ layer in the mesoporous architectures offers four advantages: (1) enlarged perovskite crystal grains due to the decrease of heterogeneous nucleation energy barrier at the large interfacial area of m-TiO₂/perovskite, (2) enhanced light harvesting caused by the non-negligible light scattering effect of the m-TiO₂ film, (3) efficient interface charge extraction of photogenerated electrons from the perovskites to ETLs as a result of enlarged TiO₂/perovskite interface, and (4) effective suppression of charge recombination attributed to the decreased interface defects in the perovskite films and the promoted electron extraction at the ETL/perovskite interface. Benefitted from improved light harvesting, electron extraction and charge collection efficiencies, the mesoporous device delivers a remarkable PCE of 18.18%, higher than the planar device of 17.49%; meanwhile, the incorporation of m-TiO₂ also contributes to the reduction of hysteresis. This work emphasizes the great importance of m-TiO₂ framework in constructing high-performance PSCs on the basis of perovskite absorbing materials with non-comparable intrinsic diffusion lengths of electrons and holes.

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Conflict of interest The authors declare no conflicts of interest.

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介孔TiO₂结构在CH₃NH₃PbI₃钙钛矿太阳能电池中的作用

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摘要 平面结构和介孔结构是钙钛矿太阳能电池通常采用的两种器件结构。然而, 不同器件结构如何影响器件性能仍有待进一步深入研究。文献中关于哪种结构更加理想的研究报道不尽一致; 特别是, 介孔TiO₂层的具体作用仍待进一步阐明。在本研究中, 我们通过细致对比研究两种器件结构中的钙钛矿薄膜特性与电池光伏性能, 揭示了介孔TiO₂结构在CH₃NH₃PbI₃钙钛矿太阳能电池中的具体作用。晶体结构、微观形貌、光学和电学性能等系统表征表明, 介孔TiO₂结构有助于增大钙钛矿晶体尺寸、增加薄膜光捕获、提高电子提取及抑制电荷复合。与平面结构相比, 介孔结构器件的效率更高(18.18%), 迟滞更小。本研究揭示了钙钛矿太阳能电池中介孔TiO₂结构的作用, 可为高性能太阳能电池的器件结构设计和优化提供理论指导。