

Control of TiO₂ electron transport layer properties to enhance perovskite photovoltaics performance and stability

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ABSTRACT

This study demonstrates the effect of electron collection and transportation for TiO₂ electron transport layer (ETL) of the mesoscopic perovskite solar cells (PSCs). The influence of compact TiO₂ layer (c-TiO₂) with various spray cycles, the particle size effect of mesoporous TiO₂ (meso-TiO₂) film and post-treatment of TiO₂ electrode for perovskite solar cells have been studied systematically. We further optimize the meso-TiO₂ thickness to enhance the electron collection and transport efficiency and to reduce the anomalous J-V hysteresis phenomenon of PSCs. After adjusting the fabrication process of TiO₂ ETL, the highest performance of small cell PSC shows the power conversion efficiency (PCE) of 19.39% in the reverse scan and 19.12% in the forward scan, respectively. A sub-module PSC within an active area of 11.7 cm² exhibits impressive PCE of 16.03% under the illumination of 100 mW/cm² (AM1.5G). Moreover, it also shows an outstanding PCE of 25.49% under the illumination of 6000 lx of T5 indoor light source.

1. Introduction

Organic-inorganic based perovskite solar cells (PSCs) are considered to be the most competitive photovoltaic technology. Since Miyasaka group first reported CH₃NH₃PbX₃ perovskite sensitized solar cells which exhibited a power conversion efficiency (PCE) of 3.8%, the PCE of PSCs have been raised to over 24.2% in a decade [1–3]. Many researchers focus on the various chemistries of perovskite active layers, including doping, [4,5], substitution, [6–8], and interfacial engineering [9–11]. Our group adopted Ba²⁺ in CH₃NH₃Pb_{1-x}Ba_xI_{3-y}Cl_y to partially replace lead cations, and it can be stably processed in the environment containing moisture and exhibits the PCE of 14.9% [4]. Kanatzidis group fabricated a perovskite material with 50% of Sn doping concentration (CH₃NH₃Sn_{0.5}Pb_{0.5}I₃), which can efficiently regulate the bandgap of the perovskite material from 1.55 to 1.17 eV. Besides, CH₃NH₃Sn_{0.5}Pb_{0.5}I₃ shows superior film coverage and morphology, which ensures connectivity between grains and overcomes short-circuiting and charge leaking issues. This shows the broadest light absorption and highest short-circuit photocurrent density of ~20 mA/cm² [8]. For interfacial engineering, N. G. Park group reported a grain boundary healing process and achieved a PCE of 20.4% [12]. S. I. Seok

group showed a two-step process based on an intramolecular exchange between organic cations and DMSO molecules to fabricate FAPbI₃ based PSCs with exceeding 20% of PCE [13]. They further managed the content of iodide in perovskite film by addition of iodide ion in the fabrication process and thus decrease the deep-level defects and improve the PCE to 22.1% [14]. For the physical characteristics of perovskite active layers, many researchers also focus on studying the generation of electron and hole, carrier separation, recombination, and transportation. Therefore, a high-performance PSC consists of not only the composition and quality of perovskite layer, but also the properties of electron and hole transport layers [15–22] and interface engineering [23–26].

As a potential electron-transporting material, it should exhibit wide bandgap allowed more light to pass through to perovskite active layer, good electron mobility to facilitate electron collection, and proper band alignment with perovskite active layer to promote electron migrate to electron transport layer (ETL) and block the hole to pass through [27–29]. TiO₂-based electron transport materials attract a lot of interest due to the proper electronic band levels and the ease of fabrication. TiO₂-based ETL is preferred to facilitate interfacial charge transfer and to diminish charge carrier trapping and thus enhancing the PCE. Our

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group used zinc-doped mesoscopic TiO_2 ETL to reach the optimal band alignment with perovskite and get an improved PCE of 18.3% [29]. The high-performance PSCs have been achieved with n-i-p mesoscopic device architecture, in which a compact TiO_2 (c- TiO_2) layer and a mesoscopic TiO_2 (meso- TiO_2) film play essential roles in charge collection, charge transport, and the scaffold for loading the high-quality perovskite active layer and also be seen as an excellent electron-hole separator [26,29–32]. This part needs to be systematically and clearly articulated.

Many methods have been used to prepare c- TiO_2 layer, including atomic layer deposition, [33,34], spin coating, [35], and spray pyrolysis [36,37]. For the spray pyrolysis method, it combines the processes, including nebulization, precipitation, pyrolysis, and sintering. Through these sequential and continuous processes, we can construct particles with homogeneous compositions and can precisely control the chemical composition during the solid-state reaction. Therefore, the spray pyrolysis method is commonly used to fabricate dense TiO_2 thin layer which exists fewer defects and shows efficient charge carrier transport property. The meso- TiO_2 film helps with electron injection and transport in PSCs. Meso- TiO_2 film helps the generated charge carriers in the perovskite active layer to be well separated and reduces the charge accumulation and electron-hole flux balance [38–40]. As well known, anatase TiO_2 were widely used in PSCs as electron transport materials. However, other phases of TiO_2 were also studied in PSCs and showed attractive results [41–43]. Furthermore, the charge injection from the perovskite layer to the TiO_2 layer can be enhanced by increasing the perovskite/meso- TiO_2 interfacial area, that is, the improvement of surface area of the meso- TiO_2 . Decreasing TiO_2 NP size is expected to be beneficial to the PSC photovoltaic performance. However, enlarging the surface area of TiO_2 NP does not always give an improvement in PCE, because electron transport and penetration of perovskite precursor solution into meso- TiO_2 film should be simultaneously considered [38–40]. Although the study on the size effect of TiO_2 NPs for ETL has previously published, it only focuses on fully printable mesoscopic PSC [44]. To obtain high performance PSCs, the size effect of TiO_2 for n-i-p type mesoscopic PSC should be studied thoroughly.

In this study, we systematically study the spray cycles of c- TiO_2 , TiO_2 NPs size, meso- TiO_2 film thickness and post-treatment of TiO_2 electrode to realize the charge injection and electron transport properties of the TiO_2 ETL. The correlations between the properties of ETL and PSC performance are studied and achieved excellent PCEs of 19.39% and 16.03% for small cell and sub-module PSCs, respectively. Moreover, improvement of J-V hysteresis behavior, PSC performance under dim light conditions, and short-term stability of device under thermal conditions are investigated in detail.

2. Experimental section

2.1. Preparation of TiO_2 nanoparticles of various sizes and TiO_2 paste

TiO_2 nanoparticles and TiO_2 paste preparation and the fabrication of electrode were carried out based on the studies reported previously with the exception of autoclave temperature variation [45,46]. Typical synthesis of TiO_2 nanoparticles (TiO_2 NPs) can be described as follows. At room temperature, 125 mL of titanium isopropoxide (97%) was added to 750 mL of 0.1 M nitric acid solution under vigorous stirring, and a white precipitate forms instantaneously. After the hydrolysis, the slurry was immediately heated to 80 °C then vigorously stirred for 12 h, and the peptization was achieved. To remove nonpeptized agglomerates, the solution was filtered on a glass frit. To adjust the final solids concentration to ~7.0 wt%, water was added to the filtrate. The reaction temperature and reaction time depend on the desired particle size. The growth of particles up to 15–36 nm was achieved under hydrothermal conditions in a titanium autoclave with various synthesis parameters. The reaction temperatures ranged from 160 °C to 240 °C, and the reaction time ranged from 12 to 24 h. During the autoclaving,

sedimentation occurred. In order to disperse the particles, a titanium ultrasonic horn was utilized. After the sonication process, the colloidal suspension was introduced by a rotary evaporator and consequently evaporated to a TiO_2 with a concentration of 15.0 wt%. The screen-printable TiO_2 pastes were homogeneously mixed with 4.23 g TiO_2 NP, 55 mL of ethyl cellulose, and 45 mL of terpineol. The thickness of TiO_2 film was measured by a profilometer (Sloan Dektak 3030). Pore diameter, pore volume and surface area of TiO_2 were measured by Brunauer–Emmett–Teller method (BET, Micrometrics Instruments ASAP 2020), utilizing accelerated porosimetry and surface area.

2.2. Preparation of perovskite solar cells

The perovskite solar cells preparation procedure flow chart is shown in Figure S1. By spraying titanium diisopropoxide bis(acetylacetonate) (75.0 wt% of $\text{Ti}(\text{AcAc})_2\text{O}i\text{Pr}_2$ in isopropanol) solution at 450 °C, the TiO_2 compact layer was deposited onto the surface of FTO glass substrate. A mesoporous TiO_2 film with various particle sizes was screen printed onto the c- TiO_2 /FTO glass using TiO_2 pastes synthesized above and heated to 500 °C for 30 min and then put in $\text{TiCl}_4(\text{aq})$ solution (0.3 M) at 70 °C for post treatment if need. Li-treated mesoporous TiO_2 film was accomplished by spin coating a 0.1 M solution of Li-TFSI in acetonitrile. The solution was prepared freshly before the application in nitrogen atmosphere. 200 μL were poured on meso- TiO_2 /c- TiO_2 /FTO glass. After 10 s of loading time, the spinning programme started with an acceleration of 1,000 rpm/s to a final speed of 3,000 rpm, the substrate was left spinning for 30 s. Both Li-treated and untreated TiO_2 electrodes were completed with a second calcination step at 450 °C for 30 min. After cooling down to room temperature, TiO_2 electrodes were transferred to a nitrogen-filled glove box (< 5.0 RH%). $\text{CH}_3\text{NH}_3\text{I}$ (MAI) was synthesized by stirring 27.86 mL CH_3NH_2 (40% in methanol, Aldrich) and 30 mL HI (57 wt% in water, Aldrich) in a 250 mL round-bottom flask at 0 °C for 4 h. The precipitate was recovered by evaporating at 55 °C for 1 h. The synthesized MAI was dissolved in ethanol, recrystallized in diethyl ether, and finally dried at 60 °C in a vacuum oven for 24 h. A mixed solution of PbI_2 (1.25 M) and MAI (1.25 M) dissolved in γ -butyrolactone (GBL) and DMSO (5/5, v/v) was coated onto the TiO_2 electrodes by a two-step spin-coating process at 1000 rpm for 10 s and then at 5000 rpm for 20 s. The perovskite films were treated with 50 μL toluene drop-casting in the second spin-coating step. The films were thermally treated on a hot plate at 100 °C for 10 min. For the corresponding hole-transporting material (HTM) solution from previous step, Spiro-OMeTAD was dissolved in chlorobenzene (50 mg/mL), 17.5 μL solution of lithium bis(trifluoromethane)sulfonimide (Li-TFSI, 520 mg) in 1.0 mL acetonitrile, and 28.5 μL 4-*tert*-butylpyridine (TBP) were added directly. The solution of as-prepared HTM was spin-coated onto the substrate glass of $\text{CH}_3\text{NH}_3\text{PbI}_3$ /meso- TiO_2 /c- TiO_2 /FTO at 2000 rpm for 30 s. Lastly, 100 nm of Ag cathode layer was thermally evaporated onto the substrate glass. The active area of small cell and sub-module (five cells in series on 5 cm \times 5 cm substrate) were fixed at 0.16 cm² and 11.7 cm², respectively. The schematic of sub-module PSC showed in Figure S1.

All samples were measured by a Hitachi UV–vis spectrophotometer (U-4100) to determine the UV–vis absorption spectra. With a Bruker powder diffractometer (D8 Discover) equipped with a 2D detector using $\text{CuK}\alpha 1$ radiation, GIXRD data were obtained in the 2-theta range of 10–50°. The scanning electron micrographs (SEM) were measured using a Hitachi S-800 microscope at 10.0 kV. An IPCE spectrometer (EQE-R-3011, ENLI Technology Co. Ltd., Taiwan) measured the incident monochromatic photon-to-current conversion efficiency (IPCE), and it was calibrated with a single-crystal silicon reference cell. The IPCE is calculated by equation:

$$\text{IPCE}(\%) = \text{LHE}(\lambda) \times \phi_{inj} \times \eta_c = 1240 \times \frac{I_{sc} \left(\frac{\text{A}}{\text{cm}^2} \right)}{\lambda(\text{nm}) \times P_{inc} \left(\frac{\text{W}}{\text{cm}^2} \right)} \times 100$$

The LHE(λ) where indicates the light harvesting efficiency, ϕ_{inj} indicates the electron injection efficiency, and η_c indicates the charge collection efficiency.

A solar simulator (Yamashita Denso Corporation, YSS-50A) was utilized as the irradiation light source for the typical current density-voltage (J-V) measurements. The simulated AM 1.5G sunlight intensity was calibrated to 100 mW/cm². By applying the potential external bias to the cell and measuring the photocurrent output with a Keithley model 2400 digital source meter (Keithley, USA), the cell J-V characteristics under illumination of AM 1.5G simulated sunlight were obtained. The J-V hysteresis index is calculated by the following equation [47]:

$$\text{Hysteresis index} = \frac{J_{RS}(0.8V_{OC}) - J_{FS}(0.8V_{OC})}{J_{RS}(0.8V_{OC})}$$

where $J_{RS}(0.8V_{OC})$ and $J_{FS}(0.8V_{OC})$ represent the photocurrent density at 80% of V_{OC} for the reverse scan (RS) and forward scan (FS), respectively.

For the dim light measurement, the cell J-V characteristics were measured by a Keithley model 2400 digital source meter, a Philips T5 fluorescent lamp illumination under 6500 K color temperature, and by changing the distance between light source and cells to control the light intensities. The scan direction was scanned from negative to positive bias. The irradiance and luminance were obtained by a NIST-traceable OPHIR radiometer (PD300-BB-50 mW) and a photometer (PD300-CIE), respectively.

3. Results and discussion

The compact TiO₂ layer (c-TiO₂) of the electrode plays an essential role in the PSCs, which prevents the carrier from directly contacting the conductive glass substrate and the electron-hole recombination at the interface between the conductive glass and perovskite layer. PSC with perfect c-TiO₂ layer improves the open circuit voltage (V_{OC}), fill factor (FF), and cell conversion efficiency. Therefore, we used spray pyrolysis method to prepare the c-TiO₂ layer on FTO glass by controlling the spray cycle number to increase the thickness of c-TiO₂ layer. Fig. 1 shows the SEM images of surface morphology of FTO and FTO/c-TiO₂ layers (cycle number: 1, 2, 5 and 10). The thin film grew with FTO surface crystal structure. Fig. 1 (f) shows a cross section view of compact and smooth c-TiO₂ layer on FTO with optimization of spray-2L condition. As the film got too thick (5L and 10L), the surface began to accumulate and produce some particles and resulted in the rough surface.

Fig. 2 (a) shows the cyclic voltammetry (CV) analysis, and the relationship between the spray layers and the cathodic peak current (i_{pc}) value. The electrolyte medium for CV measurement of various c-TiO₂ films is in 0.5 mM K₄Fe(CN)₆ and K₃Fe(CN)₆ with 0.5 M KCl aqueous solution. The values were recorded at a scan rate of 50 mV/s. PSC efficiency is also illustrated in Fig. 2 (b). The i_{pc} value and the ratio of $i_{pc}(\text{c-TiO}_2)/i_{pc}(\text{FTO only})$ are listed in Table S1. The i_{pc} obviously decreased when the FTO coated the c-TiO₂ layer and the spray-2L had a lowest i_{pc} value, which indicated the best-blocking effect on surface redox reaction. However, the i_{pc} increased again when spray cycle number increased up to 5L and 10L. This was due to the increase of surface area and could be explained by Randles-Sevcik equation, where the i_{pc} and surface area (A) be proportional to each other.

For the device performance, we found that the PSC coated with 2L c-TiO₂ had the best performance and the smallest hysteresis index (HI), but the HI values increased when spraying cycle number increased to 5L and 10L. The reason is that the increased spray cycle numbers cause the increase of c-TiO₂ layer thickness. It increased the series resistance of the device, and the flower-like interface (spray-5L and 10L) may increase the probability of electron-hole recombination and charge accumulation at the interface, and resulting in the reduce of FF and V_{OC} and higher HI value (A device without hysteresis presents a HI of zero, while a higher value of HI indicates a more pronounced hysteresis.). Therefore, PSC with spray-2L c-TiO₂ layer showed the high power conversion efficiency at 16.93%.

Furthermore, the meso-TiO₂ film can provide a mesoporous framework to facilitate percolation of the perovskite solution, which can significantly increase the contact area between the perovskite material and the electron transport layer (ETL), and can effectively collect and inject the electron into ETL [40]. Therefore, four kinds of meso-TiO₂ films with thickness of 100, 150, 300 and 500 nm (as shown in Figure S2) and four kinds of TiO₂ NPs size of 22, 25, 30 and 36 nm were prepared, respectively, to investigate the effects of the interfaces on photovoltaic performance of PSCs.

Figure S3 shows the steady-state PL spectra of the perovskite film deposited on the lone c-TiO₂ film and c-TiO₂/meso-TiO₂ film with various thicknesses. It appeared that the meso-TiO₂/perovskite samples exhibited more evident PL quenching compared to the lone c-TiO₂ film/perovskite sample, which demonstrated more effective electron extraction at meso-TiO₂/perovskite interface. The samples with 100 nm, 150 nm and 300 nm meso-TiO₂ films showed the similar PL intensities. Further, we found that the PSC with 150 nm meso-TiO₂ film had the best conversion efficiency of 17.81% for the reversed scan and 16.49% for the forward scan with an HI value of 0.054 (as shown in Figure S4

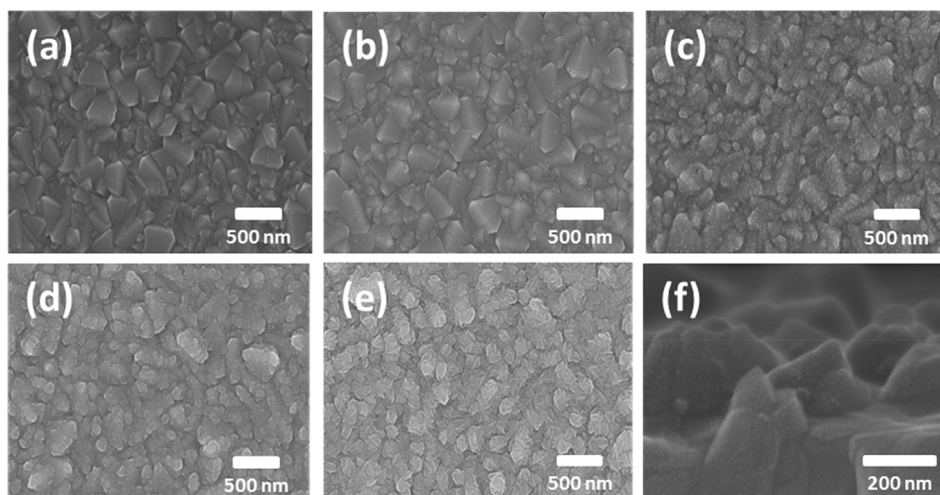


Fig. 1. The SEM top view images of c-TiO₂ by spray pyrolysis with various spray cycles: (a) FTO only; (b) 1 layer; (c) 2 layers; (d) 5 layers and (e) 10 layers. (f) The cross section view of spray-2L.

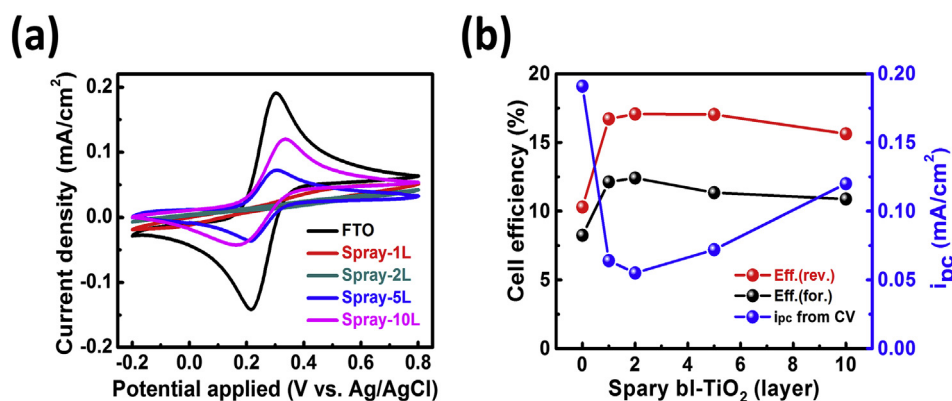


Fig. 2. (a) The CV measurement of c-TiO₂ films with various spray cycles. (b) The relationship between spray c-TiO₂ layer and cell performance.

and Table S3). The main reason was that when the meso-TiO₂ film got too thick (such as 500 nm), it lead to an increase in the series resistance (the increased area of TiO₂/TiO₂ interface), which lead to a longer charge transport length. The thicker meso-TiO₂ film also made the perovskite precursor ineffective to penetrate and to deposit into the mesoporous film (generate vacancies in the meso-TiO₂ film). Those mainly influenced the PSC performance. After optimizing the above conditions, the charge injection from the perovskite to the TiO₂ layer could be further improved by increasing the perovskite/meso-TiO₂ interfacial area. The surface area of the TiO₂ NPs is expected to be beneficial to the PSC performance. To investigate the effect of the particle size of meso-TiO₂ on the photovoltaic properties, we fabricated four c-TiO₂/150 nm meso-TiO₂ PSCs containing the above mentioned sized TiO₂ NPs to investigate the effects on the interfaces such as perovskite/TiO₂ or TiO₂/TiO₂ on photovoltaic performance.

As for the TiO₂ particle size effect, Fig. 3 shows the SEM images of those 4 kinds of TiO₂ NPs. The mean diameters measured from the SEM images were 22.6, 25.0, 30.2 and 37.6 nm. The XRD patterns (Figure S5) confirms the meso-TiO₂ film containing anatase-phase TiO₂ NPs (JCPDS card no. 21-1272) from the main peak of the XRD pattern ($2\theta = 25.281^\circ$) which corresponds to the (101) plane. Moreover, the

Table 1

BET surface area, pore volume and pore diameter of meso-TiO₂ films with various TiO₂ NPs.

TiO ₂ particle size (nm)	S_{BET} (m ² /g)	Pore volume (cm ³ /g)		Pore diameter (nm)	
		BJH Adsorption	BJH Desorption	BJH Adsorption	BJH Desorption
22	86.23	0.353	0.351	13.53	12.19
25	85.11	0.383	0.386	14.93	13.59
30	67.86	0.479	0.478	23.99	22.06
36	55.35	0.504	0.503	30.75	27.97

structural characteristics of TiO₂ film such as BET surface area, total pore volume, and mean pore size of each film with various sizes of TiO₂ NPs are summarized in Table 1. The pore diameter of 13.5–30.8 nm, the pore volume of 0.35–0.50 cm³/g, and the surface area of 86.2 to 55.4 m²/g can be successfully tuned by controlling the size of TiO₂ NPs. The UV-vis of TiO₂ film and TiO₂/perovskite films are shown in Figure S6. The absorbance of c-TiO₂/meso-TiO₂ PSCs with various TiO₂ NPs shows little difference, which means that the perovskite films are not affected by the TiO₂ particles and pore size in the meso-TiO₂ film.

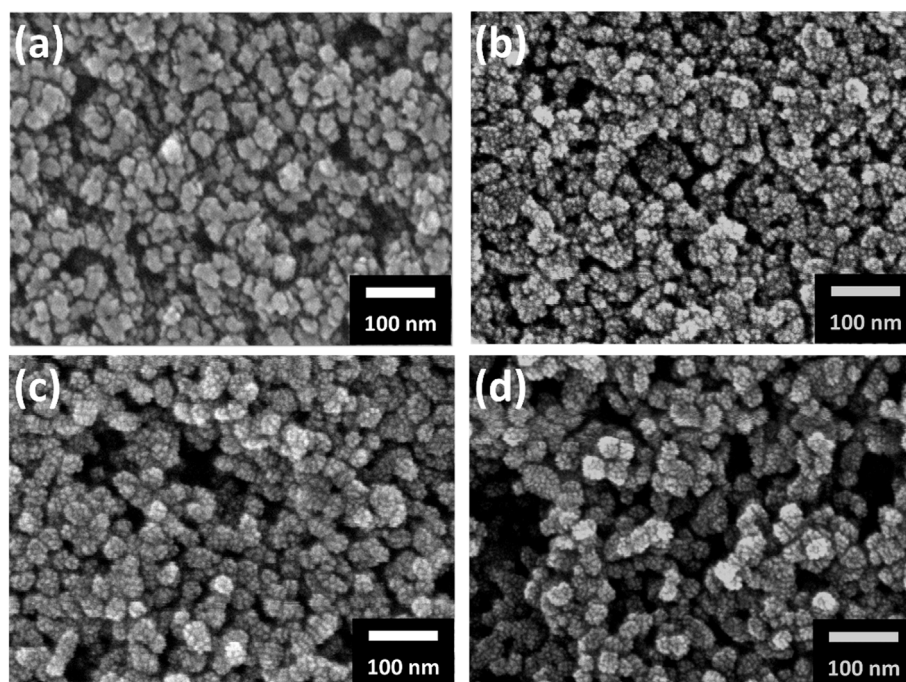


Fig. 3. Surface microstructure of meso-TiO₂ films with various TiO₂ NPs of (a) 22 nm; (b) 25 nm; (c) 30 nm and (d) 36 nm.

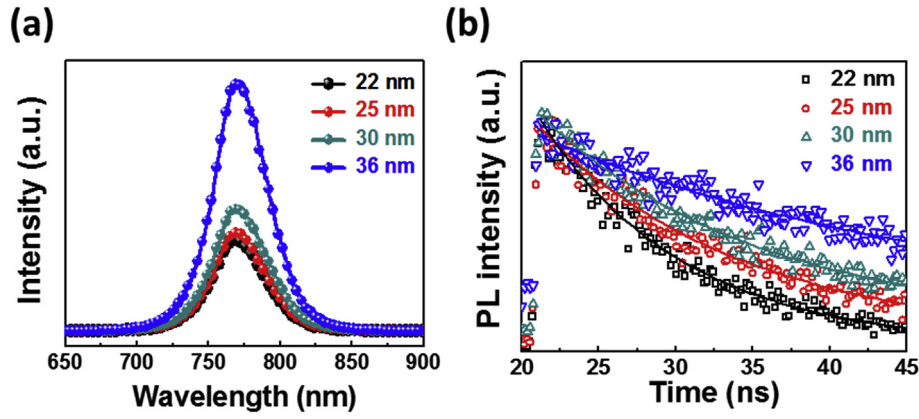


Fig. 4. (a) PL spectra and (b) TRPL spectra of perovskite/meso-TiO₂ films with various TiO₂ NPs sizes.

Therefore, the changes in photoelectric properties are also not influenced by the perovskite film thickness.

Furthermore, to investigate the electron transport behavior and the carrier lifetime, the PL measurements of the perovskite films were investigated. Fig. 4 shows the charge injection and recombination properties of the prepared meso-TiO₂/perovskite film substrates with various NPs sizes were evaluated using steady-state PL and TRPL. It appeared (Fig. 4 (a)) that the meso-TiO₂ film with smaller NPs exhibited more evident PL quenching compared to the ones with larger NP size. This meant more effective electron extraction with larger contact area at TiO₂/perovskite interface. This can be mainly attributed to the fully penetration of perovskite precursor solution in meso-TiO₂ film and increased interface area. The TRPL spectra of all samples collected at 768 nm after excitation with a 532 nm laser and presented in Fig. 4 (b). The TRPL decay plots can be fitted by a bi-exponential decay function shown as below:

$$F(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$

where A_1 and A_2 represent time independent coefficient of amplitude fraction, τ_1 is fast decay time and τ_2 is slow decay time [48]. The average decay time (τ_{ave}) was calculated using the following equation:

$$\tau_{avg} = \frac{\sum_i A_i \tau_i}{\sum_i A_i}$$

When the perovskite film was deposited directly on the lone c-TiO₂ (c-TiO₂/perovskite film), its average PL decay time (τ_{ave}) was 64.65 ns. For the c-TiO₂/meso-TiO₂/perovskite samples, the τ_{ave} dropped to 9.96 ns for 22 nm NPs, 13.32 ns for 25 nm NPs, 15.02 ns for 30 nm NPs, and 31.00 ns for 36 nm NPs. For comparison purpose, the τ_{ave} for the meso-TiO₂ with the commercial TiO₂ P25 (particle size ~30 nm) is 39.39 ns, due to P25 TiO₂ containing ~20% Rutile phase and has a lower electron transport behavior [49]. This confirms that the electron extraction is faster from the perovskite into the TiO₂ ETL when the meso-TiO₂ pair with a high ratio anatase and smaller TiO₂ particle. This is beneficial to the effective charge separation at the perovskite/ETL interface and more balance between electron and hole transport in device, resulting in a higher FF and V_{OC} and a lower HI value. The effect of Li-doping on the meso-TiO₂ films in the PSCs was also investigated.

Fig. 5 shows the size effects of meso-TiO₂ film (including Li-treated or not) on photovoltaic parameters of PSC. It was found that the FF and V_{OC} values of PSC increased with decreasing TiO₂ particle size, and the PSCs with Li-treated TiO₂ showed the higher cell performance and lower hysteresis behavior. The reason is that the Li-treated can improve the conductivity of meso-TiO₂ film, and it has been confirmed by the previous report [50]. The PSCs with smaller TiO₂ NP sizes (22 nm and 25 nm) showed apparent improvement in FF and PCE, especially when using Li-treated meso-TiO₂ film. Moreover, we have also investigated

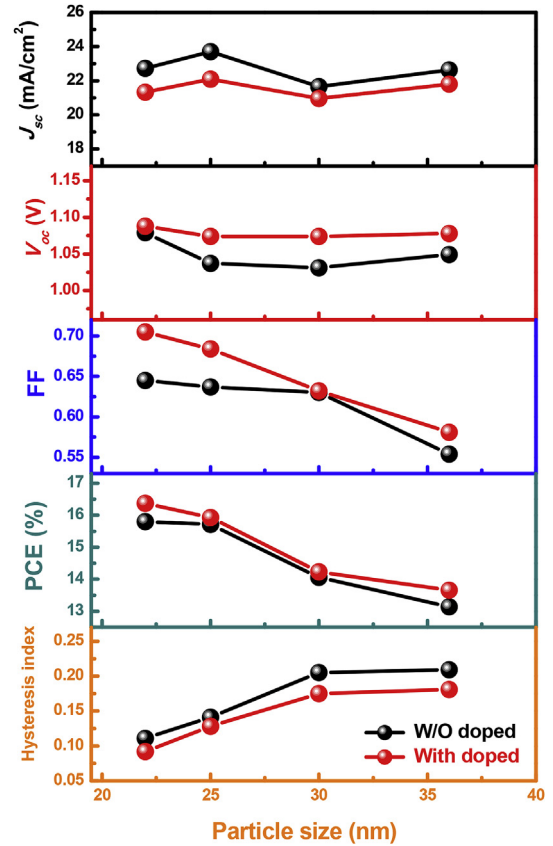


Fig. 5. The relationship between photovoltaic parameters of perovskite solar cell and TiO₂ nanoparticle size (with and without Li-treated meso-TiO₂ film).

the size effect in the meso-TiO₂ film for the perovskite film prepared by the blade coating process for reference (Table S4). We found that perovskite films prepared by spin cast and blade cast processes have similar tendency results, which the PSC with smaller TiO₂ NP in meso-TiO₂ film shows a better cell performance.

Owing to the hysteresis behavior being a significant issue in accurately characterizing the device efficiency, the steady-state photocurrent and PCE output at the maximum power point should be measured to gain the precise efficiency of the PSC [51]. Here, the on/off step photocurrent output of the PSCs with various sizes of TiO₂ NP ETLs are measured under one sun light illumination (100 mW/cm²) and gives a constant bias of V_{max} for over 300 s. As shown in Fig. 6, the photocurrent output rose to the maximum current value and the time to steady-state varied with NPs sizes. The on/off step test photocurrent

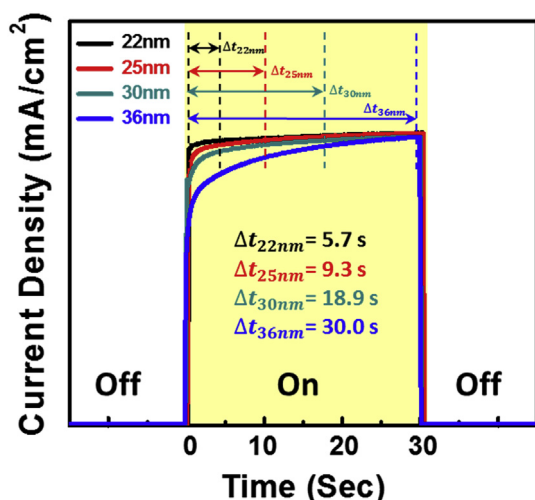


Fig. 6. J-t plot of on/off step light measurement for PSCs with various TiO_2 NP sizes to understand the time required to reach stable.

output of all devices were highly stable. The PSCs with smaller sized TiO_2 NPs, such as 22 and 25 nm, had a higher stable current and needed shorter time to reach the stable current (< 10 s). For PSCs with larger sized TiO_2 NPs, such as 36 nm, had a lower stable current and needed longer time of more than 30 s to reach the stable current. This evidences the smaller particle size has better electron extraction efficiency, thus results in a less J-V hysteresis behavior. It works in correspondence with the above analysis results.

In order to further improve the TiO_2 - TiO_2 connection in meso- TiO_2 film, the meso- TiO_2 ETL was put into TiCl_4 (aq) at 70°C for post-treatment process and the effect on PSC performance is illustrated in Figure S9. Post-treatment for 30 min had a better PSC performance (improve the conversion efficiency from $\sim 16\%$ to $> 18\%$), but the performance decreased when the post-treatment went on for longer time. It was due to too much TiO_x forming in meso- TiO_2 film and reduced the pore size. This created difficulty in penetrating the $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor solution and in formatting some voids in the meso- TiO_2 film. Fig. 7(a) shows that after optimizing the fabrication process of TiO_2 ETL, the champion PSC device had a PCE of 19.39% for the reverse scan and 19.16% for the forward scan under the illumination of $100\text{ mW}/\text{cm}^2$ (AM 1.5G).

The optimal TiO_2 ETL for PSC has been well investigated in the above. Here we demonstrate a sub-module PSC that constructed from a series connection of five cells (substrate area: 25 cm^2 and active area: 11.70 cm^2). The J-V curve and photograph of the sub-module PSC is shown in Fig. 7(b). The CO_2 -laser patterning FTO process was adopted to fabricate an effective and integrated series connection between the

cells in the sub-module. the J_{SC} , V_{OC} , FF and PCE of $4.14\text{ mA}/\text{cm}^2$, 5.21 V , 0.743 and 16.03% , respectively, were achieved under 1 sun illumination. The PCE of the sub-module PSC shows more than 16% which is related to the well control and uniformity of each layers preparation in this perovskite solar sub-module.

Furthermore, we also measured the performance of PSCs under low light intensity of T5 light source. The PCE were higher than 20% under the illumination intensity of 1000 – 6000 lx , and showed the excellent PCE of 25.49% under 6000 lx (as shown in Figure S10). The PSC showed a better cell performance under the T5 fluorescent light source than that under a solar simulator because the T5 fluorescent light illuminates wavelength ranging from 350 to 750 nm (1.65 eV) and the spectral response of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ in this study nicely covers this entire spectra. Moreover, we also put the performance of dye-sensitized solar cell (DSSC) for reference. The performances of PSC are better than that of DSSC under both the T5 light source and the solar simulator, which means that PSC has a better light-harvesting and light-to-electron conversion property under dim light conditions. With the low-cost solution process, such PSCs can be easily regarded as one of the most promising candidates for indoor or dim light energy harvesting.

Finally, the stability of PSC devices under a dark continual thermal environment of 60 and 80°C was investigated. As observed in Fig. 8, the V_{OC} was slightly improved within the first 100 min for both 60 and 80°C conditions, which was due to the energy band alignment at the interface of $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ or $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{HTM}$. The device efficiency decreased only from $\sim 17\%$ to 15% and 13% at 60 and 80°C , respectively, without having any device encapsulations after an 1100 min test. The major decrease of PSC performance at 80°C was the decline of FF in the first 200 min . This might be the result of not well-matched thermal expansion coefficient of layers or the extrinsic factors (e.g., H_2O and O_2) [52] that resulted in the escaping of $\text{CH}_3\text{NH}_3\text{I}$ in $\text{CH}_3\text{NH}_3\text{PbI}_3$ and additives in HTM of device under higher temperature condition.

4. Conclusions

In this study, a hole blocking compact TiO_2 layer (c- TiO_2) was prepared by spray pyrolysis method, and screen printed meso- TiO_2 layers with various TiO_2 particle sizes were hydrothermally synthesized to prepare an optimal mesoporous TiO_2 layer which was used as an electron transport layer of the n-i-p type perovskite solar cell. The use of spray pyrolysis to prepare a high quality c- TiO_2 layer not only improved the electron collection and transportation in the TiO_2 film, but also prevented directly contact between the hole/carrier and the conductive FTO glass. This effectively increased the V_{OC} and FF of PSC. The 2L c- TiO_2 and 150 nm meso- TiO_2 film with 22 nm NPs showed the best properties of electrons injection into the ETL, which effectively improving the J_{SC} , V_{OC} and FF of the PSC and the J-V hysteresis behavior.

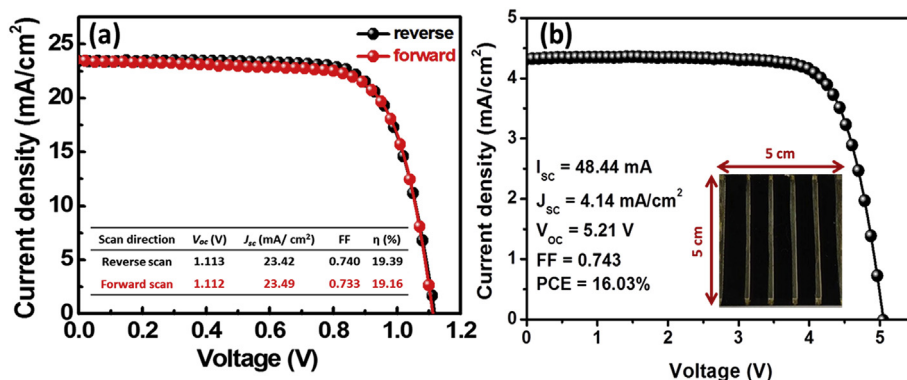


Fig. 7. The J-V curve and efficiency of (a) the champion PSC (active area = 0.16 cm^2) and (b) sub-module PSC (active area = 11.7 cm^2) measured under illumination of $100\text{ mW}/\text{cm}^2$, AM1.5G.

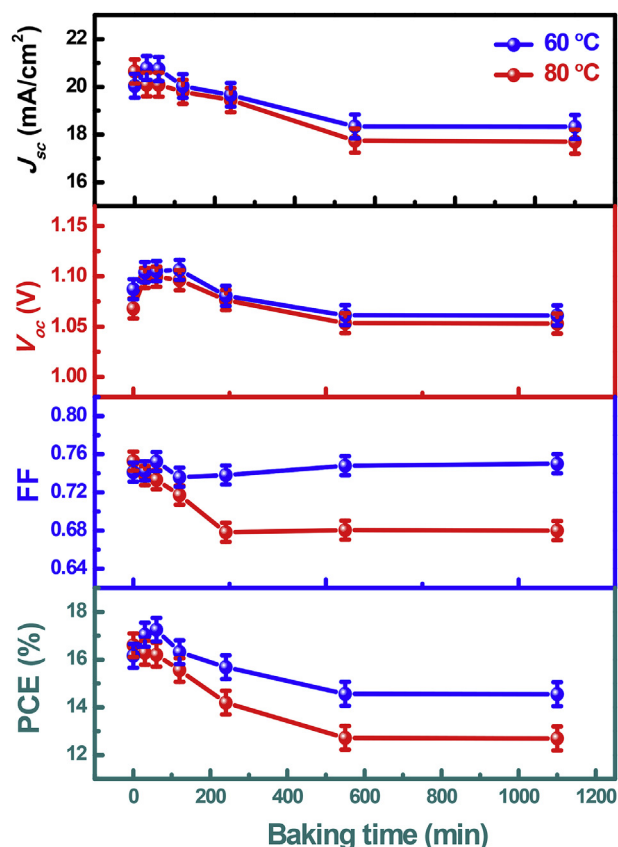


Fig. 8. The thermal stability of PSCs under 60 and 80 °C in dark.

After optimizing the fabrication process of TiO_2 ETL, the PSCs achieved excellent PCEs of 19.39% and 16.03% for small cell and sub-module PSCs, respectively, under the illumination of 100 mW/cm^2 (AM 1.5G) and showed even better PCE of 25.49% under the illumination of 6000 lx of T5 light source.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.orgel.2019.105406>.

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