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Ma, Shaoyang; Ye, Tao; Wu, Tingting; Wang, Zhe; Wang, Zhixun; Ramakrishna, Seeram; Vijila, Chellappan; Wei, Lei

2018

Ma, S., Ye, T., Wu, T., Wang, Z., Wang, Z., Ramakrishna, S., ... Wei, L. (2019). Hollow rice grain-shaped TiO₂ nanostructures for high-efficiency and large-area perovskite solar cells. *Solar Energy Materials and Solar Cells*, 191, 389-398. doi:10.1016/j.solmat.2018.11.028

<https://hdl.handle.net/10356/143481>

<https://doi.org/10.1016/j.solmat.2018.11.028>

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Hollow Rice Grain-Shaped TiO₂ Nanostructures for High-Efficiency and Large-Area Perovskite Solar Cells

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Abstract

Hollow rice grain-shaped titanium dioxide (TiO₂) nanostructures (NSs) with the radius of 200-300 nm are fabricated by electrospinning titanium isopropoxide solution and further calcination. The resulting hollow rice grain-shaped TiO₂ NSs are highly porous, which are beneficial to the infiltration of perovskites and provide a large contact area, as the building blocks to construct the mesoporous TiO₂ layer for the large-area (the active area is 1 cm²) CH₃NH₃PbI₃ based perovskite solar cells (PSCs). By varying the spin coating speed (2000 rpm, 4000 rpm, and 8000 rpm, respectively), the performance of PSCs changes with different TiO₂ NSs distribution densities. The optimized PSC employing the 4000 rpm spin coating speed exhibits a photovoltaic conversion efficiency (PCE) of 14.2% with the short circuit current density (J_{SC}) of 21.6 mA cm⁻², open circuit voltage (V_{OC}) of 1.07 V and fill factor (FF) of 0.61, which is superior to the plain structure based control group with the PCE of 9.6%. Furthermore, the PSC possesses a reproducible PCE value with weak hysteresis in its current density-voltage (J - V) curves. Moreover, photoluminescence (PL) measurements and finite-difference time-domain (FDTD) optical simulations reveal the enhanced fast charge carrier extraction/transport and light absorption in the proposed system, which makes electrospun hollow rice grain-shaped TiO₂ NSs a promising electron transportation material for high-efficiency and large-area photovoltaic devices.

Keywords: Electrospinning, rice grain shape, TiO₂, perovskite solar cell, finite-difference time-domain (FDTD) simulation

1. Introduction

Metal halide perovskites, as the emerging light absorbing materials due to their excellent optoelectronic properties, have been applied to various of photovoltaic devices in recent years [1-10]. The photovoltaic conversion efficiency (PCE) of perovskite solar cell (PSC) has kept growing and the highest certificated efficiency of single-junction PSC has reached 22.7% [11]. But the active area of the PSC with the highest PCE is typically less than 0.1 cm², which may cause some potential problems such as measurement contacts, film uniformity and peripheral effects [12-15]. Especially, when the active area increases substantially based on the same fabrication technique, the PCE usually drops significantly [16,17]. So, it is critical to explore new techniques and materials that are suitable for achieving large-area PSCs with high PCE [18].

Among the functional layers of a PSC, the mesoporous titanium dioxide (meso-TiO₂) layer plays an important role as an active scaffold for electron transportation from perovskite light-absorber to the outer circuit through its conduction band (CB) [1-3,19]. As an electron transporting path, the mesoporous TiO₂ layer has to meet some requirements, such as providing nanoporous for better infiltration of perovskite, enlarging the contact area of TiO₂/perovskite, and enabling defects-free to reduce the loss of charge carriers. To meet these requirements, the meso-TiO₂ layer is commonly fabricated using TiO₂ nanoparticles (NPs) with the sizes of around 30 nm for small-area PSCs and the total thickness of an optimized meso-TiO₂ layer is around 200 nm [4,20-26].

However, the traditional meso-TiO₂ layer constructed by small radius nanoparticles may not be suitable for fabricating large-area PSC, since the surface states generated from the large amount of grain boundaries can trap the photogenerated free electrons, resulting in the degraded device performance[15-18,27-29]. Thus, the isolating distributed nanostructures with relatively big TiO₂

nanoparticles can be a potential solution to address this issue to efficiently transport most of the photogenerated free electrons with reduced charge carrier recombination centre. Meanwhile, such structure can benefit for adjusting optical power distribution within the system [24]. Furthermore, electrospinning/electrospray technology has been applied to fabricate meso-TiO₂ layer, as the resulting isolating distributed TiO₂ nanostructures (NSs) offer much reduced grain boundaries, larger contact area between TiO₂ NSs and the light absorber, and specific electron transport direction [30-34].

Here, we demonstrate hollow rice grain-shaped TiO₂ NSs with large surface area and abundant nanopores by simple and versatile electrospinning followed with calcination. Then, they are applied to construct the meso-TiO₂ layer of PSCs. The optimized distribution condition of rice grain-shaped TiO₂ NSs is explored and analysed by various methods including absorption and photoluminescence. To study the optical power distribution and transmittance in different TiO₂/perovskite models, we carried out the finite-difference time-domain (FDTD) optical simulations. And we have observed enhanced light absorption of perovskite film in the rice grain-shaped TiO₂ NSs based sample. The champion PCE of 14.2% is obtained for large area PSC with an active area of 1 cm², increased by about 47.9% compared to 9.6% of its plain counterpart. This improvement is attributed to a combination of multiple reasons, including the reduced grain boundaries (surface states), large contact area between TiO₂/perovskite and direct transportation introduced by rice grain-shaped TiO₂ NSs. And the minimized nonradiative recombination and trapping of photogenerated carriers and optical adjustment also contribute to the promotion of the performance.

2. Materials and methods

2.1 Materials

Unless otherwise specified, all materials were purchased from Sigma-Aldrich. Spiro-OMeTAD was purchased from Merck KGaA. Methylammonium iodide (MAI) was purchased from Dyesol. PbI₂ was purchased from Tokyo Chemical Industry Co., Ltd. (TCI).

2.2 Synthesis of rice grain-shaped TiO₂ NSs

To prepare the electrospinning solution, 1.5 g polyvinyl acetate (PVAc, M_w = 500000) was dissolved in 10 mL N,N-dimethyl acetamide (DMAc). After magnetic stirred at 60 °C for 6 h, 1 mL titanium isopropoxide (TTIP) and 1.5 mL acetic acid were added into the solution and further stirred for 1 h to acquire a homogeneous solution. Electrospinning process was then carried out with a commercial electrospinning setup (ET-2535, Ucalery). The applied electric field was 20 kV, distance between needle and collector was 10 cm and the feed rate was 1 mL/h. The as-spun freestanding fiber membrane was carefully peeled off the aluminium substrate, first solidified at 280 °C in the air for 1 h and finally sintered at 500 °C in the air atmosphere for 2 h. Heating rate for both process was 2 °C/min. The resulting hollow rice grain-shaped TiO₂ NSs were manually grinded for better dispensability in ethanol, and polyvinylpyrrolidone (PVP) was used to adjust the viscosity of the TiO₂ paste.

2.3 Perovskite solar cell fabrication

FTO glass [Nippon Sheet Glass Co., Ltd.(NSG)] was cleaned with detergent (2% Hellmanex III solution), DI water, acetone, isopropanol (IPA), and dried with clean pure N₂. The substrate underwent an UV ozone treatment for 10 min at 100 °C prior to deposition of compact TiO₂ layer. A thin (~40 nm) TiO₂ layer was deposited on top of the FTO by spin-coating TiO₂ precursor solution at 5000 rpm

for 30 s. Then, it was heated at 450 °C for 30 min in air. The TiO₂ precursor solution was prepared by diluting TTIP (1 mL) and 12 M HCl solution (10 µL) in ethanol (10 mL). Then meso-TiO₂ layer was deposited by spin coating method using the TiO₂ paste prepared above under the speed of 8000, 4000 and 2000 rpm, respectively. The substrate was then annealed at 500 °C for 20 min. Next, perovskite film was deposited on the substrate by a spin-coating process in a glovebox. A mixture of 461 mg of PbI₂, 159 mg of CH₃NH₃I, 78 mg of DMSO (molar ratio 1:1:1) and 600 mg of DMF was prepared at room temperature and stirred for 1 h. The completely dissolved precursor solution was spin-coated on the prepared FTO substrate at 2500 rpm for 35 s, when 0.5 mL of diethyl ether was slowly dripped on the rotating substrate in 8 s. The obtained transparent film was then heated at 50 °C for 3 min and 100 °C for 12 min to form a dense CH₃NH₃PbI₃ film. A ≈150 nm Spiro-OMeTAD (Merck KGaA) layer as hole transporting material (HTM) was deposited by spin coating at 3000 rpm, 30 s. The spiro-OMeTAD solution was prepared by dissolving 74 mg spiro-OMeTAD, 28.5 µL 4-tert-butylpyridine, 17.5 µL of a stock solution of 520 mg mL⁻¹ lithium bis (trifluoromethylsulfonyl) imide in acetonitrile, and 29 µL of a stock solution of 100 mg mL⁻¹ tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tri s(bis(trifluoromethylsulfonyl) imide) in acetonitrile in 1 mL chlorobenzene. Finally, 80 nm of gold was deposited as an electrode by thermal evaporation with an average deposition rate of 0.3 Å s⁻¹.

2.4 Characterization

J-*V* characteristics were measured in the glovebox with a solar simulator (SAN-EI Electric XES-301S 300W Xe Lamp JIS Class AAA) and a Keithley 2400 sourcemeter. The solar cells were masked with metal apertures to define the active areas which were typically 1 cm². IPCE was recorded with a Keithley 2400 sourcemeter combined with an Oriel 300-W Xe lamp, an Oriel Cornerstone 130 monochromator, and an SRS 810 lock-in amplifier (Stanford Research Systems). A calibrated Si diode was used as the reference. The surface and cross-section morphologies of the samples were investigated by a scanning electron microscope (JEOL FESEM 6340F) at 5 kV. The morphologies of the samples were studied by using a transmission electron microscope (TEM, JEOL 2010). X-ray diffraction (XRD) experiments were conducted by Shimadzu XRD-6000 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54 \text{ \AA}$). The optical absorption spectra were measured on a PerkinElmer Lambda 950UV/VIS/NIR spectrometer and the samples for this study were prepared with the same procedures of device fabrication. PL spectra were recorded by using FluoroMax-4 (HORIBAs industry) and the emission for the number of the absorbed photons at the excitation wavelength has been corrected. The perovskite samples for PL measurements were fabricated with the same method as solar cell fabrication.

2.5 FDTD simulations

The simulations of optical power distribution and transmittance within the compact-TiO₂/perovskite functional layers with and without rice grain-shaped TiO₂ NSs were conducted by means of FDTD methods (Lumerical FDTD Solutions). The FDTD model was set as follows (the FTO glass substrate, spiro-OMeTAD layer and gold electrode were not involved in the model for the purpose of reducing complexity of the system): thickness of compact- TiO₂ was set to 40 nm, thickness of perovskite layer was 600 nm, and the thickness of the grain-shaped TiO₂ layer was 200 nm. The morphology of the grain-shaped TiO₂ layer was derived from SEM image. The monitor was placed 200 nm above of the compact TiO₂ layer.

3. Results and discussion

Figure 1 schematically illustrates the fabrication process of PSC using rice grain-shaped TiO_2 NSs as the meso- TiO_2 layer via electrospinning. Firstly, the polyvinyl acetate (PVAc)/ titanium isopropoxide (TTIP) solution was prepared and adjusted to a proper viscosity for electrospinning, and acetic acid is added to prevent the TTIP from fast hydrolization (more details can be found in the Experimental Session, Synthesis of rice grain-shaped TiO_2 NSs). The SEM image of the as-spun fibers in Figure 1 shows the continuity and uniformity of the resulting fibers with the diameter ranging from 150 nm to 350 nm. The as-spun fibers were solidified at 280 °C and then calcined at 500 °C for an hour to remove all the polymer components. The hollow rice grain-shaped TiO_2 NSs were manually grinded and dispersed into polymer solution to form a uniform suspension solution which was applied to construct the meso- TiO_2 layer by spin-coating onto the TiO_2 compact layer. Next, the perovskite light absorber ($\text{CH}_3\text{NH}_3\text{PbI}_3$) and HTM layers were deposited successively, and gold electrode was finally attached by thermal evaporation.

Figure 1. Fabrication of PSC using rice grain-shaped TiO_2 NSs as the meso- TiO_2 layer via electrospinning.

Figure 2 is the morphology characterization of the hollow rice grain-shaped TiO_2 NSs. Figure 2a and 2b are SEM images of the resulting fibers solidified at 280 °C and sintered at 500 °C, respectively. When the as-spun fibers were solidified at 280 °C for 1 h, the rice grain-shaped structures started to form, but the polymer components remained. After further sintered at 500 °C for 1 h, the polymers were totally removed and only the rice grain-shaped TiO_2 NSs were kept. As shown in Figure 2b, the resulting hollow NSs can benefit the infiltration of perovskite solution. Figure 2c and 2d are the corresponding TEM images of TiO_2 NSs obtained under two temperatures, which show that the size of rice grain-shaped TiO_2 NSs is around 500 nm in length and 200~300 nm in diameter. Also, the hollow structure is revealed with a shell thickness around 50 nm. As shown in Figure 2d, the resulting

rice grain-shaped TiO_2 NS consists of abundant small TiO_2 NSs crystal grain which makes the structure porous and provides large contact surface with the perovskite material [32-34], indicating that this NS is very befitting to fabricate the meso- TiO_2 layer of PSCs. To find out the crystal nature of the NS, Figure 2e and 2f are the high resolution TEM images of the TiO_2 NSs treated at 280 °C and 500 °C, respectively. In Figure 2e, there are no obvious crystal structures, which means the TiO_2 NSs are in the transformation from amorphous state to crystalline phase [35] (XRD patterns is shown in Figure S1), while the lattice structure in Figure 2f indicates that the TiO_2 NSs after calcined at 500 °C are in the crystalline anatase state.

The selected area electron diffraction (SAED) pattern in the inset also supports this result.

Figure 2. SEM images of the hollow rice grain-shaped TiO_2 NSs (a) solidified at 280 °C and (b) sintered at 500 °C, low resolution TEM of TiO_2 NSs (c) solidified at 280 °C and (d) sintered at 500 °C, and high resolution TEM of TiO_2 NSs (e) solidified at 280 °C and (f) sintered at 500 °C. Insets are selected area electron diffraction (SAED) patterns.

Secondly, meso-TiO₂ layer were formed by spin coating hollow rice grain-shaped TiO₂ NSs suspension solution. As illustrated in Figure 3, the expected isolating distributed TiO₂ NSs are obtained. To explore the best condition to form this meso-TiO₂ layer, different spin coating speed (8000, 4000, and 2000 rpm, respectively) was adopted to vary the TiO₂ NSs density, as shown in Figure 3a-3c. When using higher spin coating speed, the distribution of rice grain-shaped TiO₂ NSs became more dispersed, while lower spin coating speed resulted in denser distribution of the TiO₂ NSs. Figure 3d is the XRD patterns of TiO₂ NS powder and the meso-TiO₂ layer fabricated by different spin coating speeds. The well-resolved diffraction peaks are indexed to (101), (004), (200), (105) and (211), indicating the anatase nature of the TiO₂ NSs[30, 36, 37], and there is no obvious peak shift when these TiO₂ NSs coated into meso-TiO₂ layer.

Figure 3. SEM images of the distribution of the hollow rice grain-shaped TiO₂ NSs at the spin-coating speed of (a) 8000 rpm, (b) 4000 rpm, and (c) 2000 rpm, respectively. (d) XRD pattern of the spin-coated meso-TiO₂ layer.

Then, the perovskite layer was deposited on the meso-TiO₂ layer (more details can be found in the Experimental Session, Perovskite solar cell fabrication). Figure 4 shows how the density of rice grain-shaped TiO₂ NSs affects the morphology of perovskite layer surface. For the perovskite layer based on lower distribution density of rice grain-shaped TiO₂ NSs, the size of perovskite crystal is more uniform, and the surface is smoother. But with the increasing of the distribution density, some surface areas start to show smaller perovskite crystal sizes, and even protuberances (indicated with the dotted circles) appear on the perovskite surface. We believe these are caused by the fluctuant underlying surface due to the piled up TiO₂ NSs. In Figure 4d, the XRD patterns of perovskite layers with and without meso-TiO₂ layer are identical [6], except one peak is derived from TiO₂.

Figure 4. SEM images of the perovskite layer on top of the meso-TiO₂ layer fabricated at the spin-coating speed of (a) 8000 rpm, (b) 4000 rpm, and (c) 2000 rpm, respectively. (d) XRD pattern of the perovskite layer.

Next, HTM and gold electrode were attached successively by spin coating and thermal evaporation, respectively. Figure 5 shows the cross-section SEM images of the completed PSC devices based on different distribution densities of the hollow rice grain-shaped TiO₂ NSs. As shown in Figure 5a and 5b, for low TiO₂ NSs density, the functional layers of a PSC contact seamlessly with each other, which are beneficial for the smooth transportation of photogenerated carriers from the perovskite light absorber to the outer circuit. Furthermore, each layer of the PSC is well controlled in thickness. But the superfluous accumulated TiO₂ NSs shown in Figure 5c brought by the low spin coating speed can cause local destruction of the device perfection (compared to the plain device in Figure 5d), which is corresponding to the protuberances in Figure 4c. These micrometre scale local protuberances produce barriers preventing the uniform disperse of perovskite layer and further the attachment of HTM and gold electrode, which will cause negative impact on the PSC performance.

Figure 5. Cross-section SEM images of the PSC device structure based on TiO₂ NSs at the spin-coating speed of (a) 8000 rpm, (b) 4000 rpm, (c) 2000 rpm and (d) plain structure.

Figure 6 describes the photovoltaic performance of all 4 groups of PSCs based on different distribution densities of the hollow rice grain-shaped TiO₂ NSs. Different spin coating speeds are used to differ the experimental groups, for example, PSC-2000 rpm represents the PSC based on the meso-TiO₂ layer fabricated using the 2000 rpm spin coating speed, and PSC-Control is the plain PSC without the meso-TiO₂ layer. Figure 6a presents the typical current density-voltage (J - V) curves of these devices. Despite the short circuit current density (J_{SC}) of the plain PSC is higher than most PSCs with meso-TiO₂ layer, the highest J_{SC} value is yielded by the PSC-4000 rpm group. While the open circuit voltage (V_{OC}) mainly increases with the distribution density of the hollow rice grain-shaped TiO₂ NSs, only drops when there are too many accumulated TiO₂ NSs. Both the J_{SC} and V_{OC} of the PSC-4000 rpm are superior to other groups. The average PCE shown in Figure 6b also shows the same trend that the PCE keeps increasing with the distribution density of the hollow rice grain-shaped TiO₂ NSs and then drops at the speed of 2000 rpm. The highest average PCE of 12.7% is obtained by the PSC-4000 rpm group. Figure S2 shows the PCE distribution of the best performed group PSC-4000 rpm. In addition, Table 1 summarizes the photovoltaic parameters of the champion devices from each group. The PSC-4000 rpm yields the highest PCE of 14.2% with the J_{SC} of 21.6 mA, V_{OC} of 1.07 V and fill factor (FF) is 0.61, which is comparable to some previous reported results [15, 18]. Figure S3 provides the J - V curve of the PSC based on meso-TiO₂ layer using conventional TiO₂ NPs with average size of 30 nm, and the corresponding photovoltaic parameters are shown in Table S1 (XRD spectra are shown in Figure S4). The performance of TiO₂ NPs based PSC is inferior to the TiO₂ NSs based device for all parameters including J_{SC} , V_{OC} , FF and PCE, but superior to the plain structure device only except for J_{SC} . This result supports our assumption that compared to uniform meso-TiO₂ layer, isolating distributed TiO₂ NSs with reduced grain boundaries are more suitable for large area PSCs [38, 39]. Furthermore, the J - V curves measured under dark condition (shown in Figure S5) indicates that the defect densities within the PSC-4000 rpm device are lower than that of the control device [40], which means the rice grain-shaped TiO₂ NSs can help to reduce the recombination center of the PSC and prevent the recombination of photogenerated carriers. Impedance spectroscopy was measured and studied by equivalent circuit fitting [41], the results are shown in Figure S6. The results indicate that PSC-4000 rpm device shows a lower recombination resistance than the PSC-Control device, which matches the previous study [42]. The IPCE curves shown in Figure 6c are in good agreement with this trend and the integrated photocurrent that is expected to be generated under AM1.5G irradiation is shown in Figure S7. To be specific, the conversion of photons into electricity of PSCs with the meso-TiO₂ layer is more effective at the shorter wavelength region, and the PSC-4000 rpm behaves the best. Also, the hysteresis effect is found insignificant within the PSC-4000 rpm, as shown in Figure S8. A preliminary stability investigation of these PSCs have been operated for 60 days, which shows that the device stored in the glovebox at room temperature behaves relatively stable, with just a 1.0% PCE drop in the entire testing period (as Table S2 shows).

Figure 6. (a) J - V curves, (b) average PCE, (c) IPCE, (d) absorption spectra, (e) PL spectra and (f) partial enlarged PL spectra of the control and hollow rice grain-shaped TiO_2 NSs based samples.

Table 1. Photovoltaic parameters of champion device of all PSC groups.

	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
PSC-Control	21.2	0.97	0.47	9.6
PSC-8000 rpm	21.4	0.99	0.55	11.8
PSC-4000 rpm	21.6	1.07	0.61	14.2
PSC-2000 rpm	19.5	1.04	0.61	12.4

To explore the reasons behind this phenomenon, the absorption spectra were measured, as shown in Figure 6d, indicating that the PSC based on meso- TiO_2 layer can absorb light more efficiently, which means that more photons are converted into electron hole pairs and contribute to the generated electricity. Furthermore, the PL was tested to analyse the carriers behaviour within the TiO_2 /perovskite system [26]. As shown in Figure 6e, the PL intensity of the plain structure based control group is far larger than the meso- TiO_2 layer based samples. This means that the extraction/transport of the photogenerated electron in the TiO_2 compact/perovskite sample is relatively slow, but after the introduction of the grain-shaped meso- TiO_2 layer, the photogenerated electrons can be extracted/transported more easily and lead to higher PCE. Among all the PSCs based on meso- TiO_2 layer, the PSC-4000 rpm shows the lowest PL intensity as the partial enlarged PL spectra, as shown in

Figure 6f, which means that the PSC-4000 rpm group exhibits the fastest extraction/transport of electrons. Figure S9 can better explain the electron transportation mechanism within the meso-TiO₂ layer based PSCs with different distribution densities of the rice grain-shaped TiO₂ NSs. To be more specific, the distribution density is related to the spin coating speed. When higher speed is adopted, the distribution of the rice grain-shaped TiO₂ NSs is more dispersed, while lower speed will cause denser distribution of the rice grain-shaped TiO₂ NSs. The meso-TiO₂ layer plays a role as an active scaffold to enable the electron transportation from the perovskite light absorber to the FTO layer through its conduction band (CB), as shown in Figure S9a. Photoinduced electrons generated in perovskite tend to inject into the CB of the nearest TiO₂ NS and the electrons transport/inject more efficiently into the TiO₂ CB with more TiO₂ NSs, which will reduce the recombination probability, thus enhance the V_{OC} of the device. So, when the population of the hollow rice grain-shaped TiO₂ NSs is small in relative terms of the substrate area, the performance of the meso-TiO₂ layer based PSCs is enhanced with the increasing quantity of the rice grain-shaped TiO₂ NSs. Thus, the enhanced J_{SC} and FF can be obtained in the PSC-4000rpm. However, when using a lower spin coating speed to fabricate the meso-TiO₂ layer, the hollow rice grain-shaped TiO₂ NSs tend to be denser and start to pile up, resulting in no direct contact with the substrate, as shown in Figure S9b. In this case, some photogenerated electrons must pass through the interface between the upper and lower TiO₂ NSs before they can finally reach the substrate. Therefore, the distance, in which electrons need to transport to the substrate, is extended and more free electrons might be annihilated during this period, which lead to a reduction in the number of electrons that finally reach the outer circuit. Besides, the protuberances in Figure 4c compromise the integrity of the device structure, which also limit the device performance. Therefore, the performance of the PSC-2000 rpm is worse than that of the PSC-4000 rpm. And these reasons also apply to the trend of IPCE curves and PL spectra.

FDTD is a commonly used method to explore optical related effect within PSCs [23]. To further verify the optical power distribution modulation effect of isolated TiO₂ NSs [30], FDTD simulations were carried out on the compact-TiO₂/perovskite models with and without rice grain-shaped TiO₂ mesoporous layer. The meso-TiO₂ (grain-shaped) model is built based on the area selected from Figure 3b, as shown in Figure S10. Figure 7 shows the simulated optical power distribution at the meso-TiO₂/perovskite interface of rice grain-shaped TiO₂ NSs based model and the identical position in the control model. As can be seen, the introduction of rice grain-shaped TiO₂ NSs caused a remarkable local optical field enhancement (Figure 7b, 7d and 7f) compared to the plain control model (Figure 7a, 7c and 7e), especially at shorter incident wavelength region, which is in well agreement with the IPCE results in Figure 6c. This local optical enhancement can benefit the optical absorption of the perovskite layer, as discussed in previous results [23,24,30]. And the FDTD simulation result also indicates that the optical transmittance of rice grain-shaped TiO₂ NSs based model at meso-TiO₂/perovskite interface is also better than that of the plain control model as shown in Figure S11.

Figure 7. FDTD simulation results. Simulated optical power distribution within the perovskite layer with incident wavelength at (a, b) 450 nm (c, d) 550 nm and (e, f) 650 nm. (a, c, and e) are PSC-Control device structure and (b, d, and f) are PSC-4000 rpm device structure.

4. Conclusions

In summary, we have exploited an electrospinning method using TTIP solution to fabricate the hollow rice grain-shaped TiO_2 NSs with an average diameter of 200-300 nm. The electrospun hollow rice grain-shaped TiO_2 NSs have been further employed as the isolated distributed mesoporous TiO_2 layer of $\text{CH}_3\text{NH}_3\text{PbI}_3$ based large area PSCs. Detailed electron transportation mechanisms have been discussed based on the difference of TiO_2 NSs distribution condition with various spin-coating speeds. FDTD optical model simulation has been carried out to study the optical power distribution and transmittance in different TiO_2 /perovskite models, and enhanced light absorption of perovskite film has been observed in the rice grain-shaped TiO_2 NSs based sample. The PSC-4000 rpm offers an optimized PCE of 14.2% with the J_{SC} of 21.6 mA, V_{OC} of 1.07 V and FF of 0.61, which is superior to the plain structure based control group with the PCE of 9.6%. PL spectra indicate that carriers' recombination within the TiO_2 /perovskite system with the rice grain-shaped TiO_2 NSs is substantially suppressed, exhibiting notably efficient carrier injection/transportation from the perovskite layer to the carrier transporting layer. This is due to the better infiltration of the perovskite light absorber and the increased contact area between the perovskite and TiO_2 provided by this unique TiO_2 NSs network

and the optimized overall device structure. This work suggests that in the future explorations, various of isolating distributed nanostructures are good choices for electron transport layer in PSCs.

Acknowledgement

This work was supported in part by the Singapore Ministry of Education Academic Research Fund Tier 2 (MOE2015-T2-1-066 and MOE2015-T2-2-010), Singapore Ministry of Education Academic Research Fund Tier 1 (RG85/16), and Nanyang Technological University (Start-up grant M4081515: Lei Wei).

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at

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Supplementary Information

Hollow Rice Grain-Shaped TiO₂ Nanostructures for High-Efficiency and Large-Area Perovskite Solar Cells

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Figure S1. XRD pattern of TiO₂ NSs after solidified at 280 °C and sintered at 500 °C, respectively.

Figure S2. PSC-4000 rpm group PCE distribution.

Figure S3. J - V curves of the champion device based on plain structure, commercial meso-TiO₂ and hollow rice grain-shaped TiO₂ NSs, respectively.

Figure S4. XRD pattern of TiO₂ NSs based electron transport layer and conventional meso-TiO₂ layer, respectively.

Figure S5. Dark J - V characteristic of control group and the hollow rice grain-shaped TiO_2 NSs samples, respectively.

Figure S6. Complex plane impedance spectroscopy characterization and equivalent circuit fitting for PSC-4000 rpm and PSC-Control devices at forward bias of 0.6V. Symbols are experimental results and solid lines correspond to the fitting using the equivalent circuit depicted showed as inset.

Figure S7. IPCE of PSC-4000 rpm and the integrated photocurrent that is expected to be generated under AM1.5G irradiation

Figure S8. Hysteresis effect of PSC-4000 rpm device.

Figure S9. Photogenerated electrons transporting mechanism within PSCs based on different hollow rice grain-shaped TiO_2 NS distribution density.

Figure S10. Meso-TiO₂ layer model building for FDTD simulation.

Figure S11. Simulated optical transmittance at meso-TiO₂/perovskite interface.

Table S1 Photovoltaic parameters of champion device based on plain structure, commercial meso-TiO₂ and hollow rice grain-shaped TiO₂ NSs, respectively.

	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
Hollow rice grain-shaped NS based group	21.6	1.07	0.61	14.2
Conventional meso-TiO ₂ group	20.3	1.00	0.60	12.1
Plain structure control group	21.2	0.97	0.47	9.6

Table S2. Photovoltaic parameters for the stability of PSC measured under simulated 1 sun (the solar cell was encapsulated and stored in a glovebox).

	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
Initially	21.6	1.07	0.61	14.2
10 days	21.6	1.07	0.62	14.5
20 days	21.4	1.06	0.60	13.7
40 days	21.2	1.05	0.60	13.5
60 days	19.1	1.05	0.59	13.2