Introduction

To meet the challenge of energy crisis, mesoscopic solar cells (MSCs), such as dye-sensitized solar cells (DSSCs) and mesoscopic perovskite solar cells (MPSCs), have attracted significant attention from many researchers.1–5 For an efficient mesostructure-based solar cell, electron transport material (ETM) is an essential component where TiO₂ is the dominantly used material.6–8 The TiO₂ film not only acts as a holder for the light harvester (dyes or perovskites), but also supplies pathways for electron transport and extraction. The major difference between TiO₂ in DSSCs and that in MPSCs is the thickness, which is generally several micrometers in DSSC but only several hundred nanometers in MPSCs. Various efforts have been devoted towards designing TiO₂ photoanodes,9–13 whereas TiO₂ single crystals with a mesoporous structure have been investigated and applied into MSCs due to their reduced carrier traps and large surface area as compared to polycrystals.16–20 Most of the TiO₂ mesoporous single crystals have been prepared by a hard template method with a complex synthesis process.20–25 However, we have reported a simple evaporation-driven oriented assembly method (EDOA) to synthesize mesoporous TiO₂ anatase single crystals.16,17 They show an ultrahigh surface area over 110 m² g⁻¹ and photoconversion efficiency (PCE) over 11% in N719-based DSSCs.

Except in DSSCs, mesoporous TiO₂ single crystals were also adopted into MPSCs. Snaith’s group prepared mesoporous single-crystal anatase TiO₂ with a surface area of ~70 m² g⁻¹ and a particle size of ~2 μm from seeded nucleation and hard template method.18 When these materials were applied in the MPSC, the resulting MPSC showed a PCE of 7.3%. However, subsequently, few studies were reported on the adoption of mesoporous anatase single crystals into MPSCs. This may be primarily attributed to the following two reasons: first, mesoporous single-crystal anatase normally has a relatively large size and is prepared by the hard template-assisted method;18,21,25,26 this makes them difficult to form high qualified films and be adopted in many techniques (such as printing technique) as compared to those with smaller particle sizes (<150 nm). Second, the thickness of ETMs in the conventional MPSC is only several hundred nanometers; this makes it almost impossible to use the ETM with a micrometer particle size. Therefore, fabrication of mesoporous single-crystal anatase with a smaller particle size (<150 nm) shows great potential in large-scale fabrication of ETMs and is meaningful for the development of efficient MPSCs.

To date, the PCE of perovskite solar cells has been improved from 3.8% to a certified 22.7%.27 However, the use of expensive...
hole-transporting materials (HTMs) (usually spiro-OMeTAD or PTAA) and thermal evaporated noble metal (Au or Ag) back contact, which are utilized in conventional MPSCs with the structure of FTO/compact-TiO₂/mesoporous TiO₂ or Al₂O₃/ perovskite/HTM/Au, increases the device cost and affects the stability. Due to the excellent electron and hole transport properties of the perovskite light absorber, an HTM-free fully printable MPSC based on triple EDOA method. This material was applied as an ETM (mp-TiO₂/mp-ZrO₂/mp-carbon)/perovskite was developed by our group to reduce the material cost and enhance the stability. Moreover, the recombination between the perovskite and the carbon counter electrode is larger than that in a similar device with an HTM, which makes the efficiency of HTM-free devices lag behind. Various strategies, such as material modification, architecture design, and solvent engineering, have been adopted to improve the efficiency.

Herein, we fabricated the mesoporous single-crystal anatase (named M-TiO₂) nanoparticles with a large surface area (169 m² g⁻¹) and a small size (about 120 nm in length and 60 nm in width) by a simple EDOA method. This material was applied as an ETM to a fully printable hole-conductor-free MPSC based on triple mesoporous layers. As expected, M-TiO₂ with a relatively small particle size formed a high-quality film. Moreover, the MPSC based on M-TiO₂ shows an average PCE of 12.96% and a maximum PCE of 13.47%, which is a 25% increase of PCE than that of the P25-based device, mainly due to the improved electron extraction from perovskite to ETM and further increase in the short-circuit current (JSC). This suggests that the application of mesoporous single crystal M-TiO₂ as an ETM is an effective way to achieve efficient fully printable hole-conductor-free MPSCs.

**Experimental**

**Material preparation and device fabrication**

A (5-AVA)₃PbI₃ perovskite precursor solution was prepared according to a reported procedure. M-TiO₂ were synthesized by the EDOA approach in an acidic tetrahydrofuran (THF)/Pluronic F127/H₂O/HCl/acetic acid (HOAc)/titanium tetrabutoxide (TBOT) mixed solution. For a typical synthesis, 1.5 g of Pluronic F127 (PEO₁₀₆PPO₇₀PEO₁₀₆, Mw = 12,600 g mol⁻¹), 0.1 g of H₂O, 2.0 g of HOAc, and 1.8 g of concentrated HCl (36 wt%) were dissolved in 30 ml of THF. The mixture was vigorously stirred for 30 min to form a transparent solution. Sequentially, 3.0 g of TBOT was added dropwise under vigorous stirring for 30 min to form a clear golden yellow solution. After this, the obtained solution was transferred into a volumetric flask and left it in a drying oven to evaporate THF at 60 °C for 24 h to completely remove all the solvents. The milky white precipitate obtained was finally calcined in a tubular furnace under N₂ at 350 °C for 2 h and under air at 400 °C for 2 h to obtain a uniform olive-shaped mesoporous M-TiO₂. The obtained M-TiO₂ nanoparticles were prepared as a slurry according to the reported literature. The P25 slurry was fabricated by the same method except that M-TiO₂ nanoparticles were replaced by the commercial P25 powder (Degussa P25).

Then, the titania slurry was diluted with terpineol to obtain a suitable thickness.

Fully printable triple-layer MPSCs were prepared according to literature, except that TiO₂ layers were prepared from M-TiO₂ or P25 slurry. Briefly, FTO-coated glasses were first etched with a laser to obtain the required electrode pattern. The sheets were then sequentially cleaned ultrasonically for 20 min in dilute detergent, deionized water, and ethanol, followed by drying with hot air. A thin TiO₂ compact layer was first deposited on the FTO-coated glass by spray pyrolysis deposition at 450 °C with a di-isopropanoxytitanium (acetyl acetonate) solution. After the substrate was allowed to cool, a TiO₂ monocristalline layer (M-TiO₂ or P25) was deposited on top of the TiO₂ compact layer by screen printing and then sintered at 500 °C for 40 min. Subsequently, a 2 μm ZrO₂ spacer layer and a 10 μm mesoporous carbon layer were screen-printed on top of the TiO₂ mesoporous layer and then sintered at 400 °C for 40 min. After cooling down to room temperature, the 35 wt% (5-AVA)₃PbI₃ (5-ammoniumvaleric acid (5-AVA)) perovskite precursor solution (0.5475 g MAI, 1.6158 g PbI₂ and 0.02994 g 5-AVA) were dissolved in 3.6 ml γ-butyrolactone and then stirred at 60 °C overnight) was infiltrated by drop casting via the top of the carbon counter electrode. After drying at 50 °C for more than 1 h, the mesoscopic solar cells containing perovskite were obtained. The P25 and M-TiO₂ film-based MPSCs were made on one substrate half-and-half for better comparison. All the ETM films used for characterizations and devices are with the same thickness.

**Characterizations**

Transmission electron microscopy (TEM) and High-resolution TEM (HRTEM) were conducted using a JEOL JEM-2100F (UHR) microscope (Japan) operating at 200 kV. For TEM measurements, the samples were dispersed in ethanol and then dried on a holey carbon film Cu grid. Field-emission scanning electron microscopy (FESEM) images were obtained using the Hitachi Model S-4800 field-emission scanning electron microscope. Nitrogen sorption isotherms were measured at 77 K using a Micromeritics Tristar 3020 analyzer (USA). Before measurements, the samples were degassed in vacuum at 180 °C for at least 6 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas. Using the Barrett–Joyner–Halenda (BJH) model, the pore volumes and pore size distributions were derived from the adsorption branches of isotherms. The X-ray diffraction (XRD) patterns were obtained by a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). Time resolved photoluminescence (PL) measurements were conducted at 760 nm using excitation with a 482 nm light pulse at a frequency of 4 MHz via the Horiba Jobin Yvon Fluoromax-4 fluorometer. The lifetime was obtained by fitting the PL data with an exponential decay function. The steady state PL was measured using LabRAM HR800 (Horiba JobinYvon) with the excitation wavelength of 532 nm.

**Photovoltaic measurements**

Photocurrent density–voltage (J–V) characteristics were measured using a Keithley 2400 source/meter and a Newport solar...
Results and discussion

FESEM images (Fig. 1A and B) show that the obtained typical M-TiO$_2$ nanoparticles have a uniform 3D oliver-like shape with an average length and width of about 120 and 60 nm, respectively. The TEM image (Fig. 1C) further demonstrates that the mesopore channels of M-TiO$_2$ nanoparticles are distributed throughout from the center to the surface, and all the mesopores are highly opened. HRTEM images obtained for a single mesoporous particle (Fig. 1D) clearly show the perfect continuous 2D single-crystalline atomic lattices with a spacing of 0.47 nm, corresponding to the (002) planes of a single-crystal anatase. All the mesopore walls are constructed by oriented anatase nanocrystallites with a size of around 9 nm. The selected area electron diffraction (SAED) pattern obtained along the [010] zone further confirms the single-crystalline characteristics of M-TiO$_2$ nanoparticles (Fig. 1E).

As shown in Fig. S1 (ESI†) and Fig. 2, the P25 film (Fig. S1A, ESI†) is composed of nanoparticles with a mean size around 30 nm, whereas M-TiO$_2$ (Fig. 2A) is made of nanoparticles with a size around 100 nm, which is in accordance with the results shown in Fig. 1. Both P25 (Fig. S1B, ESI†) and M-TiO$_2$ (Fig. 2B) show a uniform morphology without an obvious cracking and aggregation. The XRD pattern of M-TiO$_2$ (Fig. 2C) reveals a highly crystalline anatase phase (space group I4$_1$/amd, JCPDS card No. 21-1272). The average crystallite size is calculated to be around 9.5 nm according to the Scherrer equation,$^{12}$ which is in agreement with the domain size of the M-TiO$_2$ nanocrystal walls obtained from the TEM results. Nitrogen adsorption–desorption isotherms (Fig. 2D) show type IV curves, which are characteristic for mesoporous materials. The distinct capillary condensation at $P/P_0 = 0.40–0.7$ suggests the uniform primary mesopore channels of M-TiO$_2$. The average pore size calculated by the BJH model (inset of Fig. 2D) is about 8 nm. The BET surface area and pore volume are calculated to be as high as $\sim 169$ m$^2$ g$^{-1}$ and 0.51 cm$^3$ g$^{-1}$, respectively. On the other hand, the commercial P25 shows that the BET surface area and pore volume are only $\sim 46$ m$^2$ g$^{-1}$ and 0.39 cm$^3$ g$^{-1}$, respectively, as shown in Fig. S2 in the ESI†. The large surface area enables more perovskites being incorporated into the mesoporous titania films; this can be confirmed by the absorption spectra of M-TiO$_2$/perovskite and P25/perovskite films shown in Fig. S3 in the ESI†.

The schematic of the structure of fully printable MPSC is shown in Fig. 3A. Mesoporous TiO$_2$, ZrO$_2$, and carbon films are screen-printed on a glass/FTO/C-TiO$_2$ substrate layer by layer. Then, the perovskite precursor solution was dropped on the surface of carbon layer and infiltrated into the triple layers through the mesochannels in porous films. Fig. 3B shows the energy level diagram of the MPSC. Due to the alignment of energy levels of the device components, the electron transfers from perovskite ($\sim 3.9$ eV) to TiO$_2$ ($\sim 4.0$ eV), and the holes transfer from perovskite ($\sim 5.4$ eV) to carbon layer ($\sim 5.0$ eV). The energy level of the conduction band edge of ZrO$_2$ is at $\sim 3.4$ eV, which prevents the electrons injected into TiO$_2$ from reaching the back contact.

The cross-sectional image of the triple-layer MPSC based on M-TiO$_2$ and P25 is presented in Fig. 3C. For both samples, the

![Fig. 1](image1.png)  
![Fig. 2](image2.png)  
![Fig. 3](image3.png)
TiO$_2$ (M-TiO$_2$ or P25) and ZrO$_2$ mesoporous layers are deposited on an FTO glass substrate with C-TiO$_2$ and have a thickness of $\sim 1\,\mu m$ and $\sim 2\,\mu m$, respectively. Only parts of the C films are shown herein due to the magnification times. However, the thicknesses of the C layer also should be the same as the ZrO$_2$ and C layers are printed at one time from the same slurry, whereas the thickness of ZrO$_2$ is suggested to be similar based on the SEM images. C-TiO$_2$ is too thin to be distinguished in the cross-sectional image. It should be noticed that the boundary between M-TiO$_2$/perovskite and ZrO$_2$/perovskite is indistinct due to the excellent infiltration of perovskite and highly qualified M-TiO$_2$ film with a large surface area. The enlarged SEM image (Fig. S4, ESI†) of M-TiO$_2$/perovskite further proves that perovskite is well-penetrated into the pores of the whole TiO$_2$ layer.

Fig. 4A shows the $J$–$V$ curves of the champion M-TiO$_2$ and P25-based MPSC. Both devices show little hysteresis. The PCE of the control cell is 10.80%, similar to that in the report of our group, where 10.20% with the same materials and structure is obtained.$^{43}$ The $J_{SC}$ increases from 20.28 mA cm$^{-2}$ for the P25 solar cell to 23.21 mA cm$^{-2}$ for the M-TiO$_2$ solar cell. Thus, the increased $J_{SC}$ contributes to the greatly improved PCE of the M-TiO$_2$ based device, from 10.80% for the P25 solar cell to 13.47% for the M-TiO$_2$ solar cell, which is a 25% increase. Although higher PCE has been obtained by our team via doping of perovskite, modification of counter electrode, post-treatment of device etc.,$^{34–37}$ use of mesoporous single-crystal anatase as electron transport materials has not been reported to date. In future work, more efficient HTM-free C-PSCs can be constructed by combination of other strategies and this novel ETM.

Fig. 4B shows the maximal steady-state photocurrent output and corresponding power outputs of M-TiO$_2$ and P25-based MPSC for the first 200 seconds. Both devices show that steady state conditions are achieved after approximately 40 s. The M-TiO$_2$ device has a current density of 20.61 mA cm$^{-2}$ at 650 mV, corresponding to a PCE of 13.40%, whereas the P25 device has 17.20 mA cm$^{-2}$ at 620 mV, corresponding to a PCE of 10.66%, which are in accordance with the $J$–$V$ results. Fig. S5 (ESI†) shows the IPCE curves for the M-TiO$_2$ and P25 cells over the spectral range from 300 to 800 nm. It shows that the...
perovskite solar cell with M-TiO2 has a much higher IPCE value than that obtained with P25, which is in accordance with the obviously improved JSC.

The reproducibility of the devices is surveyed and displayed in Fig. 4C. A similar substantial boost of average JSC from 19.07 mA cm⁻² for P25 MPSC to 22.67 mA cm⁻² for M-TiO2 MPSCs is observed, which is the major factor for the increase of PCE from 10.06% of P25 cell to 12.96% of M-TiO2 cell. The detailed photovoltaic parameter results are summarized in Table S1 (ESI†). It should be noticed that only a small deviation is observed for M-TiO2 devices; this indicates the perfect reproducibility of these devices. Moreover, the stability of MPSCs based on M-TiO2 is supposed to be excellent based on our previous study.⁴⁰,⁴⁴ The MPSCs with the same structure and perovskite materials have shown no degradation under the continuous one-Sun illumination test over 10 000 h, the outdoor test in the hot desert (Jeddah, Saudi Arabia) over a week, and the indoor heat stress for 3 months in an oven filled with ambient air at 80–85 °C.

Time-resolved (Fig. 4D) and steady-state (inset) PL were carried out on FTO/C-TiO2/M-TiO2/perovskite and FTO/C-TiO2/P25/perovskite. The PL decay time of FTO/C-TiO2/M-TiO2/perovskite and FTO/C-TiO2/P25/perovskite exhibits a constant of 5.37 and 6.75 ns, respectively, which reveals that electron injection from perovskite to M-TiO2 is significantly faster than that to P25. The steady-state PL spectra further confirm this. From the intensity of the photoluminescence peak at 764 nm, the perovskite film deposited on M-TiO2 shows a more evident PL quenching as compared to P25 films. These prove that M-TiO2 has successfully enhanced the rate of carrier extraction at the ETM/perovskite interface.

As shown in Fig. 4E, the electron transport from IMPS is faster, and the recombination from IMVS is slower in the M-TiO2 device as compared to that in the P25 device. This is in agreement with the increased performance of M-TiO2 devices and PL results.

From a series of characterizations of M-TiO2 material and M-TiO2-based MPSC, we can conclude that the superior physiochemical properties of M-TiO2 lead to an enhanced device performance as compared to those of P25. First, the high surface-to-volume ratio property of M-TiO2 can affect the perovskite loading and contact area of perovskite/TiO2. With a larger surface area, a larger number of photons could be absorbed. Additionally, a higher portion of the electrons generated in perovskite is injected into the TiO2 network, and the portion of electrons transported through the perovskite layer is speculated to be decreased, which can improve the charge separation.⁴⁵ Second, the single crystal anatase structure can reduce the number of defects and traps in nanocrystals to effectively suppress electron recombination.¹⁴ Third, M-TiO2 with a relatively small particle size favours the formation of a high-qualified film, which means a good boundary interface between M-TiO2/perovskite layer and mp-ZrO2/perovskite layer can be supplied in MPSCs, being beneficial to the charge separation and supression of charge recombination at the interface. Moreover, the high-qualified film proved the suitability for the application of M-TiO2 in the printing technique. This demonstrates great potential for large-scale fabrication of high-qualified single crystal ETMs with a small particle size by a simple method. These ETMs are very important for commercialization and development of efficient MPSCs.

Conclusions
In summary, mesoporous anatase titania was imported into fully printable MPSC as an efficient electron transport material. The combination of desired highly accessible surfaces, single-crystal nanostructure, and suitable particle size of M-TiO2 favors its application in hybrid photovoltaics. The MPSC based on M-TiO2 shows an average PCE of 12.96% with excellent reproducibility and a maximum PCE of 13.47%. Compared to the that of the P25-based MPSCs, a 25% increase of PCE mainly results from the striking increase of current density from 19.07 to 22.67 mA cm⁻². Time-resolved and steady-state PL indicates faster electron extraction from perovskite to M-TiO2. Moreover, IMPS and IMVS show that the electron transport is faster and the recombination is slower in the M-TiO2 device as compared to that in the P25 device. This study demonstrates that the mesoporous anatase single crystal with a small particle size is a promising candidate as electron transport materials for large-scale fabrication of efficient MPSCs.

Conflicts of interest
There are no conflicts to declare.

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Notes and references
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