Contents lists available at ScienceDirect

Electrochimica Acta

ELSEVIER



journal homepage: www.elsevier.com/locate/electacta

Enhanced Efficiency and stability of Perovskite Solar Cells using Porous Hierarchical TiO₂ Nanostructures of Scattered Distribution as Scaffold



Xian Hou^a, Likun Pan^b, Sumei Huang^a, Wei Ou-Yang^a, Xiaohong Chen^{a,*}

^a Engineering Research Center for Nanophotonics & Advanced Instrument, Ministry of Education, School of Physics and Materials Science, East China Normal University, Shanghai 200062, China

^b Shanghai Key Laboratory of Magnetic Resonance, School of Physics and Materials Science, East China Normal University, Shanghai 200062, China

ARTICLE INFO

Article history: Received 11 January 2017 Received in revised form 24 March 2017 Accepted 26 March 2017 Available online 27 March 2017

Keywords: perovskite solar cells mesoscopic porosity TiO₂ stability metal-organic frameworks

ABSTRACT

A type of quasi-mesoscopic perovskite solar cells (QM-PSCs) with porous hierarchical TiO₂ (hier-TiO₂) nanostructures of scattered distribution as scaffold was investigated. The porous hier-TiO₂ nanostructures were synthesized by sintering MIL-125(Ti) of metal-organic frameworks (MOFs) at 500 °C in air and which were partly inherited from the ordered porosity of MIL-125(Ti). The ordered hier-TiO₂ nanostructures were scattered on compact TiO₂ layer to form a quasi-mesoscopic scaffold of scattered distribution, which can offer enough growth space for perovskite grains and promote the ordered growth of perovskite grains. The QM-PSCs shows a power conversion efficiency (PCE) of 16.56%, much higher than PCE (11.38%) of PSCs with conventional small TiO₂ nanoparticles (npt-TiO₂ as scaffold and PCE (6.07%) of planar PSCs with compact TiO₂ layer. The PCEs of PSCs with hier-TiO₂ and npt-TiO₂ remain 47% and 22% of the initial PCE values aging for 30 days in air, indicating that PSCs with hier-TiO₂ scaffold shown better stability and moisture resistance. The enhanced performance of QM-PSCs is primarily attributed to the superior wettability quasi-mesoscopic scaffold with ordered porous hier-TiO₂ nanostructures, which help to form the high quality perovskite film with better crystillinity and less pin-holes, and improve the contact properties between perovksite and electron transport layer.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The organic-inorganic perovskite solar cells (PSCs) have recently attracted enormous attention due to their unique advantages, such as low-temperature solution processed procedure, low-cost and excellent photovoltaic performances [1–3]. To date, the power conversion efficiencies (PCEs) of mesoscopic PSCs and planar PSCs, as two types of typical architectures of PSCs have reached more than 20% [4–8]. Although some kinds of hole/ electron transport layers free PSCs have been well developed and obtained high PCE [9–12], perovskite photoactive layer sandwiched in electron transport layer (ETL) and hole transport layer (HTL) is still a better structure to get efficient and stable PSCs because the competent electron and hole transport layers can promote carrier transport and collection, and even improve the stability of PSCs. The typical mesoscopic PSCs usually use n-type metal oxides such as TiO₂ as a compact electron transport layer,

* Corresponding author. E-mail address: xhchen@phy.ecnu.edu.cn (X. Chen).

http://dx.doi.org/10.1016/j.electacta.2017.03.192 0013-4686/© 2017 Elsevier Ltd. All rights reserved. and employ nano- or submicro-nanoparticles such as TiO_2 [13–15], Al_2O_3 [16] and SiO_2 [17] as the mesoscopic scaffold.

However, the bare CH₃NH₃PbI₃ (MAPbI₃) perovskite has shorter diffusion length of electrons than holes, which results in the transport imbalance of electrons and holes. The carrier mobility of the perovskite layer is related to the composition, morphology and crystalline size, which can greatly affect the performance of PSCs. Cl- or Br-doping have been successfully used to extend the carrier diffusion length of MAPbI₃ perovskite [18,19]. Limited to relatively low electron mobility of TiO₂, doped TiO₂ materials, such as Yttrium doped TiO₂ (Y-TiO₂) [20] and Lithium doped TiO₂ (Li-TiO₂) [21,22] have been developed and succeeded in applying to the compact layer (electron transport layer) and/or mesoscopic scaffold layer, which obviously compensate electron transport flaws of perovskite layer and improve the performance of PSCs. Recent reports further showed that using different sizes of TiO₂ nanoparticles (npt-TiO₂) as scaffold can greatly affect PCE of mesoscopic PSCs [13,23-26]. The early used mesoscopic scaffold fabricated with small size npt-TiO₂ usually forms a labyrinthine structure with narrow space, which increased voids of perovskite and limit the crystalline sizes of perovskite grains inside TiO₂ scaffold, resulting in the decrease of carrier transport ability, and the increase of carrier combination and the leakage current. Yang et al. used 100 nm spherical TiO_2 aggregates as a scaffold layer of PSCs, obtained over 18% PCE, which is obviously higher than PCE of PSCs with small size npt-TiO₂ scaffold [14]. The enhanced performance of PSCs is attributed to the larger growth space of perovskite grains inside scaffold, which help to form high quality of perovskite layer with larger grain size and less pin-holes.

Besides enough growth space inside in scaffold, the crystallization process of the perovskite layer is also controlled by the wettability and the surface morphologies of planar and scaffold layers. The superior wettability can reduce the nucleation barrier, and improve the coverage of perovksite layer and the uniformity of perovskite grains [27]. Chang et al. further demonstrated that the perovskite layer may form better ordered crystallites by introducing a metal-organic frameworks (MOF) material into the perovskite layer because MOF materials belong to an ordered porous crystalline material [28]. Therefore, we expected that using ordered porous TiO_2 nanostructures as scaffold can solve the limitation of grain growth, and also improve the ordered structures of perovskite grains by adjusting the crystallization process of the perovskite layer.

Herein, the ordered porous hierarchical TiO₂ (hier-TiO₂) nanostructures were synthesized by sintering the MIL-125(Ti) MOFs at 500 °C in air, because hier-TiO₂ nanostructures can partly inherit the ordered porosity of MIL-125(Ti) after burning off organic ligands. The porous hier-TiO₂ nanostructures were spin-coated on compact TiO₂ layer and formed a scaffold of scattered distribution, and sequentially fabricated a quasi-mesoscopic PSCs. This scattered distribution scaffold shows superior wettability and which is



Fig. 1. (a) XRD patterns of MIL-125(Ti) and hier-TiO₂. (b) HRTEM, (c) SEM and (d) TEM images of hier-TiO₂ nanostructures. (e) N₂ adsorption-desorption isotherms of npt-TiO₂ and hier-TiO₂. (f) Pore size distributions from the adsorption branch through the BJH method.

benefit to grow large and uniform perovsite grains. As a results, the photovoltaic performance and stability of the quasi-mesoscopic PSCs with hier-TiO₂ nanostructures scaffold compared to mesoscopic npt-TiO₂ scaffold and planar compact TiO₂ layer have been obviously improved.

2. Experimental

2.1. Preparation of hierarchical TiO₂ slurry

MIL-125(Ti) was synthesized by modifying the procedure reported elsewhere [29]. Typically, a mixture of 3.0 g terephthalic acid, 6 ml anhydrous methanol, 1.56 ml Ti(OC₄H₉)₄ and 54 ml dimethylformamide (DMF) were loaded into a 100 ml autoclave with a Teflon cup and heated at 120 °C for 20 h. Upon cooling down, the white suspension of MIL-125(Ti) was centrifuged at 4000 rpm for 10 min and washed with anhydrous methanol for several times. The synthesized MIL-125(Ti) were sintered at 380 °C for 5 h and 500 °C for 30 min to produce porous hier-TiO₂ nanostructures.

The 0.1 g porous hier-TiO₂ was dispersed in 1 ml ethanol, then added 0.5 ml α -terpinol and 0.05 g ethyl cellulose into solution to increase the viscosity, and continuously stirred overnight to form the hier-TiO₂ slurry.

2.2. Preparation of quasi-mesoscopic hier-TiO₂ scaffold

The patterned FTO substrates were ultrasonically cleaned using deionized water, acetone and isopropanol, then treated under UV- 353

ozone for 15 min. A compact TiO₂ layer with 40 nm thickness was spin-coated on FTO substrate and sintered at 500 °C for 30 min. The hier-TiO₂ slurry was spin-coated onto compact TiO₂ layer and then heated at 500 °C for 30 min. Finally, the samples were immersed in 40 mM TiCl₄ aqueous solutions for 30 min at 70 °C and washed with deionized water and ethanol, followed by annealing at 500 °C for 30 min in air. The hier-TiO₂ scaffold was scattered on the compacted TiO₂ layer. For reference of TiO₂ nanoparticles (npt- TiO_2) scaffold, the TiO_2 nanoparticles (18-NRT) were diluted with ethanol at 1:3.5 mass ratio, and its corresponding fabrication procedure is similar to that of hier-TiO₂ scaffold.

2.3. Fabrication of PSCs

The MAPbI₃ layer was prepared using a typical two-step spincoating procedure. 20 µl PbI₂ solution (1 M, PbI₂ in a mixture of DMF/DMSO = 7:3, vol:vol) was spin-coated on hier-TiO₂ scaffold layer and dried at 40 °C for 3 min. 200 µl CH₃NH₃I (MAI) solution in 2-propanol (8 mg ml^{-1}) was dropped on the PbI₂-coated substrate to stay for 2 min, then spun at 4000 rpm for 30 s and heated at 100 °C for 30 min to form MAPbI₃ layer. Subsequently, 72.3 mg Spiro-OMeTAD (>99.5%, Polymer Light Technology Corp., Xi'an, China.), 28.8 µl TBP and 17.5 µl Li-TFSI acetonitrile mixture solution (520 mg ml^{-1}) were dissolved in 1 ml chlorobenzene and then spin-coated onto the perovskite layer to form a 60 nm thickness hole transport layer. Finally, a 80 nm thick AgAl alloy electrode was thermally evaporated onto hole transport layer and the active area of device is $0.10 \,\mathrm{cm}^2$.



Fig. 2. Top-view SEM images of (a) compact TiO₂, (b) mesoscopic npt-TiO₂ and (c) quasi-mesoscopic hier-TiO₂. Insets are the contact angles of the corresponding TiO₂ layer measured with a mixture solvent of DMF and DMSO (7:3, vol:vol). Cross-section and top-view SEM images of MAPbl₃ prepared by two-step spin-coating procedure on top of (d and g) compact TiO₂, (e and h) mesoscopic npt-TiO₂, and (f and i) quasi-mesoscopic hier-TiO₂ layers, respectively.

2.4. Characterization

The morphology, structure and composition of the samples were respectively investigated by scanning electron microscopy (SEM, Hitachi S-4800), transmission electron microscopy (TEM, [EM-2100), X-ray diffraction (XRD, Holland Panalytical PRO PW3040/60) with Cu K α radiation (V = 30 kV, I = 25 mA). The light absorption and scattering spectra were measured using a UV-vis spectrophotometer (Hitachi U-3900). The N₂ adsoprtion-desorption isotherms were recorded at 77 K with a Micromeritcs Tristar 3000 analyzer (Tristar, USA). The TiO₂ samples were degassed in vacuum at 200 °C for 8h prior to measurement. The Brunauer-Emmett-Teller (BET) method was adopted to calculate the surface area and the Barrett-Joyner-Halenda (BJH) method was used to determine the average pore size. The photocurrent density-voltage (J-V) curves were measured using a Keithley model 2440 Source Meter under the illumination of AM 1.5G and 100 mW/cm² simulated solar light from a Newport solar simulator system. During the photovoltaic measurements, all devices were masked with a mask to define the active area of 0.10 cm². The photovoltagetime and photocurrent-time profiles during on-off cycles of illumination were measured using Autolab PGSTAT 302N electrochemical workstation. The incident photon to current conversion efficiency (IPCE) was measured using a Newport Optical Power Meter 2936-R controlled by TracQ Basic software.

3. Results and discussion

The organic ligands in MIL-125(Ti) were burned off and the ordered hierarchical titanium oxide with porosity was formed due to partly inheriting ordered porosity of MIL-125(Ti). Fig. 1a shows the XRD patterns of prepared MIL-125(Ti) and hier-TiO₂. The crystal structure of MIL-125(Ti) is composed of µ-OH cornersharing TiO₆ octahedra chains through Ti⁴⁺ ions, which are interconnected by terephthalic acid molecules to develop threedimensional architecture [29–31]. For the hier-TiO₂, the XRD peaks at 25.3°, 37.9°, 47.8° and 54.7° correspond to (101), (004), (200) and (105) crystal planes of anatase TiO₂, and the peaks at 27.4° , 35.9° and 41.2° belong to (110), (101) and (111) crystal planes of rutile TiO₂, respectively. This indicated that the hier-TiO₂ nanostructures belong to a mixed crystal structure of anatase and rutile. Fig. 1b shows the HRTEM image of hier-TiO₂. The lattice fringes with interplanar distances of 0.351 nm and 0.238 nm correspond to the (101) and (004) planes of anatase TiO₂ (JCPDS 65-5714) and the one with 0.324 nm is assigned to the (110) plane of rutile TiO₂ (JCPDS 21-1275), which is consistent with the observed XRD results. The hier-TiO₂ nanostructures show a similar circular plate morphology and its sizes are about 200–300 nm, as shown in Fig. 1c. The abundant pores in hier-TiO₂ nanostructures can be observed from TEM image in Fig. 1d, indicating that the hier-TiO₂ nanostructures partly inherited the porosity of MIL-125(Ti). Nitrogen adsorption-desorption isotherms of hier-TiO₂ and npt-TiO₂ are shown in Fig. 1e. The specific surface areas of hier-TiO₂ and npt-TiO₂ are $87.36 \text{ m}^2 \text{ g}^{-1}$ and $42.35 \text{ m}^2 \text{ g}^{-1}$, respectively. The mean pore size value of hier-TiO₂ is about 10 nm, as shown in Fig. 1f, which is significantly larger than the pore size of about 6 nm for npt-TiO₂. The larger surface area and pore size for hier-TiO₂ indicate the formation of porous structure by sintering MIL-125(Ti) at 500 °C, which is consistent with the observation of TEM image in Fig. 1d.

The SEM images of planar compact TiO₂ layer, mesoscopic npt- TiO_2 layer and hier-TiO_2 layer are shown in Fig. 2a-c. The npt-TiO_2 layer stacked onto the smooth and compact TiO₂ layer shows lots of tiny gaps inside npt-TiO₂ scaffold. While the hier-TiO₂ was scattered on the compact TiO₂ layer, which is apparently different from npt-TiO₂ scaffold with a continuous stack. Therefore, this scattered distribution scaffold of hier-TiO₂ nanostructures was defined as a quasi-mesoscopic scaffold to distinguish the conventional mesoscopic scaffold. The mixture solvent with DMF and DMSO was used to preciously observe the wettability behavior between perovskite and TiO₂ layers. The contact angles of hier-TiO₂ scaffold and npt-TiO₂ scaffold layer are respectively 2° and 7°, indicating that the hier-TiO₂ scaffold layer has superior wettability compared to mesoscopic npt-TiO₂ scaffold and planar compact TiO₂ layer. The abundant porosity of hier-TiO₂ increases the surface roughness of nanostructures and capillary effect, which contributes to the superior wettability. Therefore, the porous hier-TiO₂ scaffold would reduce the nucleation barrier, which can improve the uniformity of grains and crystalline quality of perovskite layer. The scattered distribution of porous hier-TiO₂ scaffold can further overcome the crystalline size limitation and improve the filling rate of perovskite layer. However, the small pore sizes and the zigzag structures of conventional mesoscopic scaffold layer fabricated with such as 20 nm small size TiO₂ nanoparticles usually deteriorate the effect of perovskite filling into npt-TiO₂ scaffold layer, especially in poor wettability condition, which can form more voids and limit the crystalline size, as shown in Fig. 2e.

The MAPbI₃ layer was fabricated using a typical two-step spincoating procedure and the detail schematic diagram of process is shown in Fig. 3. Fig. 2d–i show the cross-section and top-view SEM images of MAPbI₃ layer onto the planer compact TiO₂ layer, mesoscopic npt-TiO₂ scaffold layer and quasi-mesoscopic hier-TiO₂ scaffold layer, respectively. From the cross-section SEM images, the thickness of MAPbI₃ onto the compact TiO₂ layer is about 390 nm. The MAPbI₃/npt-TiO₂ film is about 700 nm and a MAPbI₃ layer with



Fig. 3. Schematic diagram of fabricated P-PSCs, M-PSCs and QM-PSCs.

about 400 nm thickness was accumulated on top of mesoscopic npt-TiO₂ scaffold layer. Some voids inside mesoscopic npt-TiO₂ layer can obviously be observed due to the inferior infiltration of MAPbI₃ material. However, the hier-TiO₂ scaffold was fully infiltrated and almost surrounded by MAPbI₃ grains and only slight hier-TiO₂ nanostructures scaffold can be observed. The total thickness of MAPbI₃/hier-TiO₂ films is only about 420 nm. The average grain sizes of perovskite grown on the hier-TiO₂ and compact TiO₂ are respectively about 320 nm and 290 nm, which is larger than that (~270 nm) of perovskite grains on npt-TiO₂ layer. This is because the scattered distribution of hier-TiO₂ scaffold can offer enough space of crystalline growth and the ordered porous hier-TiO₂ nanostructures is helpful to crystal growth of perovskite layer [32].

Fig. 4a shows the XRD patterns of MAPbI₃ films onto the compact TiO₂, npt-TiO₂ and hier-TiO₂ layer. The diffraction peaks at 14.0° and 28.3° are correctly indexed as (110) and (220) planes of the perovskite crystal structure [33]. The peak intensities of MAPbI₃ film on hier-TiO₂ compared to the compact TiO₂ and npt-TiO₂ were obviously stronger, indicating that the larger crystalline sizes were formed, which is consistent with the observed grains from SEM images. Furthermore, compared to perovskite on compact TiO₂ ($R_{(220)/(110)} = 0.96$) and npt-TiO₂ ($R_{(220)/(110)} = 0.92$), the intensity ratios of (220) and (110) peaks of perovskite on hier-



Fig. 4. (a) XRD patterns of MAPbI₃/compact TiO₂, MAPbI₃/npt-TiO₂ and MAPbI₃/ hier-TiO₂. (b) UV-vis diffuse reflectivity spectra of compact TiO₂ layer (i), npt-TiO₂ scaffold layer (ii) and hier-TiO₂ scaffold layer (iii). UV-vis absorption spectra of MAPbI₃/compact TiO₂ (I), MAPbI₃/npt-TiO₂ (II) and MAPbI₃/hier-TiO₂ (III). Inset is the digital photographs of compact TiO₂ layer (i), npt-TiO₂ layer (ii) and hier-TiO₂ layer (iii) on FTO substrate.

TiO₂ scaffold, compact TiO₂ layer and npt-TiO₂ scaffold are 1.01, 0.96 and 0.92, respectively. The increased ratio of $R_{(220)/(110)}$ indicates that the perovskite film onto the hier-TiO₂ scaffold can form better ordered growth of perovskite crystalline grains because the ordered porous crystalline material can induce the perovskite precursor to form more ordered perovskite crystallites [28].

The light scattering intensity of hier-TiO₂ scaffold layer compared to mesoscopic npt-TiO₂ scaffold and planar compact TiO₂ layer was obviously enhanced in the wavelength range from 350 nm to 700 nm, as shown in Fig. 4b. The haze effect of hier-TiO₂ scaffold layer can be clearly observed from the photographs in the inset of Fig. 4b, which intuitively supported this diffuse scattering light effect of the hier-TiO₂ scaffold. Although the conventional mesoscopic scaffold layer with labyrinthine structure can improve the light scattering, the sizes of TiO₂ nanoparticles play an important role to increase the light scattering of scaffold. The greatly enhanced diffuse reflectance of hier-TiO₂ scaffold layer is attributed to the large size circular plate of hier-TiO₂ nanostructures with 200-300 nm diameter, which is roughly consistent with the scattering wavelength range from 350 nm to 700 nm. Fig. 4b shows the UV-vis absorption spectra of MAPbI₃/compact TiO₂, MAPbI₃/npt-TiO₂ and MAPbI₃/hier-TiO₂ layers. The obviously enhanced absorbance intensity of MAPbI₃/hier-TiO₂ is attributed to better crystallinity of the perovskite layer and the haze effect of hier-TiO₂ scaffold. Noticeably, the uplifted absorption tail of MAPbI₃/hier-TiO₂ was possibly ascribed to the increases of the light scattering from enlarged grain sizes of perovskite [34,35].

Three types of PSCs based on planar compact TiO₂ laver. mesoscopic TiO₂ nanoparticles scaffold and guasi-mesoscopic hier-TiO₂ scaffold layers were named as P-PSCs, M-PSCs and QM-PSCs, respectively. A typical cross-section SEM image of QM-PSCs is shown in Fig. 5a. The perovskite grains can be clearly observed and the thickness of perovskite and Spiro-OMeTAD layers are about 430 nm and 80 nm, respectively. The PCE of QM-PSCs is related to the scattered distribution situation of scaffold, which can be controlled by adjusting spin-coating speed of hier-TiO₂ slurry. The spin-coating speed was varied from 1000 rpm to 3000 rpm and the relative J-V curves and parameters of QM-PSCs with different spincoating speed is shown in Fig. 5b and Table S1. The best PCE (16.56%) of QM-PSCs can be obtained at 2000 rpm. The SEM images of hier-TiO₂ scaffold in Fig. S1 indicated that too dilute distribution and severe aggregations of scaffold would both deteriorate the performance of QM-PSCs. Fig. 5c compared the J-V characteristic curves of P-PSCs, M-PSCs and QM-PSCs and the parameters of cells are listed in Table 1. The PCE of the optimized QM-PSCs is 16.56%, which is obviously higher than PCE (6.07%) of P-PSCs, and PCE (11.38%) of M-PSCs. The parameters of fill factor (FF) (71.84%), V_{OC} (1.01 V) and J_{SC} (22.81 mA/cm²) of QM-PSCs are all superior to that of P-PSCs and M-PSCs. The higher FF value of QM-PSCs compared to P-PSCs and M-PSCs is possibly attributed to better crystallinity and larger grain sizes of perovskite with less pinholes, which help to reduce the carrier recombination and improve carrier transport and collection abilities [36,37]. The enhanced Voc and FF of QM-PSCs are further supported by the dark I-V characteristics, as shown in Fig. 5d. The obviously lower reversed saturation current and higher rectification ratio of QM-PSCs compared to M-PSCs and P-PSCs indicated that the perovskite based on hier-TiO₂ scaffold can reduce the leakage current and carrier recombination current, improve carrier transporting and collecting abilities. The reduced leakage current and carrier recombination current usually helps to improve the FF and Voc of PSCs [38]. Furthermore, QM-PSCs present a weaker J-V curve hysteresis compared to P-PSCs and M-PSCs with the scan speed of 100 mV/s, as shown in Fig. 5c. Recent studies have indicated that the ion migration is an important factor to result in hysteresis [39], and the perovskite film with better crystalline



Fig. 5. (a) Cross-section SEM image of QM-PSCs. (b) J-V curves of PSCs with hier-TiO₂ scaffold spin-coated at 1500 rpm (QM-1500), 2000 rpm (QM-2000), 2500 rpm (QM-2500) and 3000 rpm (QM-3000), respectively. (c) J-V curves, (d) dark J-V characteristics of P-PSCs, M-PSCs and QM-PSCs fabricated with two-step spin-coating procedure. (e) Normalized PCE values of PSCs with aging time. (f) XRD patterns of MAPbI₃/compact TiO₂ layer, MAPbI₃/npt-TiO₂ and MAPbI₃/hier-TiO₂ aging for 30 days.

Table 1Parameters of P-PSCs, M-PSCs and QM-PSCs prepared by two-step procedure.

devices	Scan direction	$V_{OC}(V)$	J _{SC} (mA/cm ²)	FF (%)	PCE (%)
P-PSCs	Forward	0.90	15.13	37.42	5.10
	Reverse	0.93	15.29	42.73	6.07
M-PSCs	Forward	0.97	21.58	46.73	9.89
	Reverse	0.97	20.88	56.20	11.38
QM-PSCs	Forward	1.01	22.53	69.32	15.75
	Reverse	1.01	22.81	71.84	16.56

quality and superior contact properties with carrier transport layers can always alleviate the hysteresis of J-V [40]. Herein, the quasi-mesoscopic hier-TiO₂ scaffold promote the crystallization of MAPbI₃ as well as facilitate the contact between MAPbI₃ and TiO₂ layers, which possibly alleviated the hysteresis of QM-PSCs.

Fig. 5e shows the normalized PCE values as a function of aging time for three types of cells. The devices without encapsulation were stored in dry cabinet with a relative humidity (RH) of 30% at room temperature. The P-PSCs were almost failed after 10 days, while the PCEs of QM-PSCs and M-PSCs remain 47% and 22% of the initial PCE values aging for 30 days, indicating that PSCs with hier-TiO₂ scaffold have better stability and moisture resistance. Fig. 5f gives the XRD patterns of MAPbI₃/compact TiO₂, MAPbI₃/npt-TiO₂ and MAPbI₃/hier-TiO₂ after stored for 30 days in RH 30% at room temperature. The stronger peak intensity at 12.7° for MAPbI₃/ compact TiO₂ and MAPbI₃/npt-TiO₂ compared to MAPbI₃/hier-TiO₂ can be observed, indicating that MAPbI₃ on compact TiO₂ and npt-TiO₂ are more easily decomposed into PbI₂. While the weak peak of PbI₂ at 12.7° for MAPbI₃/hier-TiO₂ film suggested that MAPbI₃ on hier-TiO₂ scaffold shows better moisture resistance, which further supports the better stability of QM-PSCs. The enhanced stability of MAPbI₃/hier-TiO₂ film is partly attributed to better crystalline and larger grain sizes of perovskite grown on hier-TiO₂ scaffold layer [41]. The porous nanostructures of hier-TiO₂ scaffold may also help to tightly anchor perovskite grains and improve grains stability.

The statistic PCE histogram of 32 devices from each type of PSCs is shown in Fig. S2. The relative narrow distribution of PCEs reveals good reproducibility of PSCs and the average PCEs of P-PSCs, M-PSCs and QM-PSCs are about 6.67%, 11.72% and 15.98%, respectively, indicating that using quasi-mesoscopic hier-TiO₂ scaffold has obvious advantages for improving the efficiency of PSCs.

Fig. 6a presents the IPCE spectra of P-PSCs, M-PSCs and QM-PSCs. The whole IPCE values of QM-PSCs are significantly higher than that of P-PSCs and M-PSCs. The enhanced light absorption, improved carrier transport and collection ability, and reducing carrier recombination are all helpful to enhancing IPCE values [38]. To evaluate the universality of quasi-mesoscopic hier-TiO₂ scaffold, the perovskite layer using one-step spin-coating procedure was also fabricated. The J-V curves of PSCs with one-step procedure are shown in Fig. S3, and Table S2 lists the related parameters of cells. The PCE of QM-PSCs fabricated with one-step procedure is 16.66%, which is comparable to PSCs with two-step procedure, indicating whether using one-step or two-step procedures fabricating perovskite layers is almost irrelative to PCEs of PSCs.

To understand the mechanism of enhanced performance of OM-PSCs, the carrier transport and collection properties were further investigated. Fig. 6b shows the photocurrent density (J_{ph}) of three types of cells. J_{ph} is defined as $J_{ph} = J_{light} - J_{dark}$, where J_{light} and J_{dark} are the current density under one sun illumination and in the dark, respectively. The effective voltage (Veff) was defined as $V_{eff} = V_0 - V_a$, where V_0 is the voltage at which $J_{ph} = 0$ and V_a is the applied bias voltage [42,43]. Noticeably, the J_{ph} of three cells was linearly increased with V_{eff} at low V_{eff} rang (< 0.4 V), and gradually approached a saturated photocurrent (J_{sat}) at the high V_{eff} range. In general, the J_{sat} correlates to the maximum exciton generation rate (G_{max}), exciton dissociation probability, and carrier transporting and collection probability at a high V_{eff} region. G_{max} is mainly governed by the light absorption of the perovskite layer [44]. The relative larger J_{sat} of QM-PSCs compared to P-PSCs and M-PSCs indicated that the perovskite layer of QM-PSCs has better light absorption. Assuming all photogeneration excitons for one cell are dissociated into free carriers at a high Veff, Jsat is only limited by the carrier transport and collection abilities. Therefore, carrier



Fig. 6. (a) IPCE spectra, and (b) J_{ph}-V_{eff} plots with double logarithmic axis for P-PSCs, M-PSCs and QM-PSCs. (c) Photovoltage-time and (d) photocurrent-time profiles of PSCs during on-off cycles of illumination.

transporting and collecting probability at any V_{eff} can be directly obtained from the ratio of $J_{\rm ph}/J_{\rm sat}$. The carrier transporting and collection probabilities of P-PSCs, M-PSCs and QM-PSCs are 57.68%, 83.69% and 92.33%, indicating that QM-PSCs have better carrier transport and collection abilities.

Fig. 6c and d show the photovoltage-time and photocurrenttime profiles during on-off cycles of illumination. When the illumination was switched on, three kinds of PSCs can quickly respond for the photovoltage and photocurrent. However, when the illumination was switched off, QM-PSCs compared to P-PSCs and M-PSCs showed a much longer decay time of V_{oC}, indicating that the reduced carrier recombination in QM-PSCs can efficiently improve charge separation and extraction according to the excition lifetime equation ($\tau_r = -k_B T/e(dV/dt)^{-1}$). Similarly, when the illumination was switched off, the faster response of photocurrent in QM-PSCs suggested that carriers can be quickly transported and extracted from the perovskite layer to electrodes [45]. These results further explained the mechanism of the enhanced performance of QM-PSCs.

4. Conclusions

The ordered porous hier-TiO₂ nanostructures were synthesized by sintering MIL-125(Ti) MOFs in air, because of partly inherited from the ordered porosity of MIL-125(Ti). The porous hier-TiO₂ nanostructures were scattered on top of planar compact TiO₂ layer to form a quasi-mesoscopic scaffold of scattered distribution, which can offer enough space for growth of perovskite grains and promote the ordered growth of perovskite grains. The PCE of quasimesoscopic PSCs with hier-TiO₂ scaffold reached 16.56%, which is obviously higher than PCE (11.38%) of PSCs with npt-TiO2 scaffold and PCE (6.07%) of planar PSCs with compact TiO₂ layer. Furthermore, the PCE of PSCs with hier-TiO₂ scaffold without encapsulation remains 47% of the initial PCE value aging for 30 days, indicating that PSCs with hier-TiO₂ scaffold have better stability and moisture resistance. The enhanced performance of quasi-mesoscopic PSCs is attributed to the ordered porous hier-TiO₂ nanostructures, scaffold with scattered distribution and superior wettability of scaffold, which help to form high quality perovskite layer with better crystalline and less pin-holes. Therefore, it is a good strategy to develop efficient and stability PSCs using the ordered porous hier-TiO₂ nanostructures to construct a scaffold with scattered distribution.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (61275038 and 11274119).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. electacta.2017.03.192.

References

- B. Saparov, D.B. Mitzi, Organic-Inorganic Perovskites: Structural Versatility for Functional Materials Design, Chem. Rev. 116 (2016) 4558–4596.
 P. Wang, J. Zhang, R.J. Chen, Z.B. Zeng, X.K. Huang, L.M. Wang, J. Xu, Z.Y. Hu, Y.J.
- [2] P. Wang, J. Zhang, R.J. Chen, Z.B. Zeng, X.K. Huang, L.M. Wang, J. Xu, Z.Y. Hu, Y.J. Zhu, Planar Heterojunction Perovskite Solar Cells with TiO₂ Scaffold in Perovskite Film, Electrochim. Acta 227 (2017) 180–184.

- [3] P. Liu, Z.H. Yu, N. Cheng, C.L. Wang, Y.N. Gong, S.H. Bai, X.Z. Zhao, Low-cost and Efficient Hole-Transport-Material-free perovskite solar cells employing controllable electron-transport layer based on P25 nanoparticles, Electrochim. Acta 213 (2016) 83–88.
- [4] Efficiency Records Chart http://www.nrel.gov/ncpv/images/efficiency_chart. ipg.
- [5] N.J. Jeon, J.H. Noh, W.S. Yang, Y.C. Kim, S. Ryu, J. Seo, S.I. Seok, Compositional engineering of perovskite materials for high-performance solar cells, Nature 517 (2015) 476–480.
- [6] D. Bi, W. Tress, M.I. Dar, P. Gao, J. Luo, C. Renevier, K. Schenk, A. Abate, F. Giordano, J.P. Correa-Baena, J.D. Decoppet, S.M. Zakeeruddin, M.K. Nazeeruddin, M. Grätzel, A. Hagfeldt, Efficient luminescent solar cells based on tailored mixed-cation perovskites, Sci. Adv. 2 (2016) e1501170.
- [7] X. Li, D. Bi, C. Yi, J.D. Décoppet, J. Luo, S.M. Zakeeruddin, A. Hagfeldt, M. Grätzel, A vacuum flash-assisted solution process for high-efficiency large-area perovskite solar cells, Science 353 (2016) 58–62.
- [8] M. Saliba, T. Matsui, J.Y. Seo, K. Domanski, J.P. Correa-Baena, M.K. Nazeeruddin, S.M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt, M. Grätzel, Cesiumcontaining triple cation perovskite solar cells: improved stability, reproducibility and high efficiency, Energy Environ. Sci. 9 (2016) 1989–1997.
- [9] W.A. Laban, L. Etgar, Depleted hole conductor-free lead halide iodide heterojunction solar cells, Energy Environ. Sci. 6 (2013) 3249–3253.
- [10] A.Y. Mei, X. Li, L.F. Liu, Z.L. Ku, T.F. Liu, Y.G. Rong, M. Xu, M. Hu, J.Z. Chen, Y. Yang, M. Grätzel, H.W. Han, A hole-conductor-free, fully printable mesoscopic perovskite solar cell with high stability, Science 345 (2014) 295–298.
- [11] W. Ke, G. Fang, J. Wan, H. Tao, Q. Liu, L. Xiong, P. Qin, J. Wang, H. Lei, G. Yang, Efficient hole-blocking layer-free planar halide perovskite thin-film solar cells, Nat. Commun. 6 (2015) 1–7.
- [12] L. Huang, Z. Hu, J. Xu, X. Sun, Y. Du, J. Ni, H. Cai, J. Li, J. Zhang, Efficient planar perovskite solar cells without a high temperature processed titanium dioxide electron transport layer, Sol. Energy Mater. Sol. Cells 149 (2016) 1–8.
- [13] I.S. Yang, J.S. You, S.D. Sung, C.W. Chung, J. Kim, W.I. Lee, Novel spherical TiO₂ aggregates with diameter of 100 nm for efficient mesoscopic perovskite solar cells, Nano Energy 20 (2016) 272–282.
- [14] Y. Huang, J. Zhu, Y. Ding, S.H. Chen, C.N. Zhang, S.Y. Dai, TiO₂ Sub-microsphere Film as Scaffold Layer for Efficient Perovskite Solar Cells, ACS Appl. Mater. Interfaces 8 (2016) 8162–8167.
- [15] X. Hou, T.T. Xuan, H.C. Sun, X.H. Chen, H.L. Li, L.K. Pan, High-performance perovskite solar cells by incorporating a ZnGa₂O₄:Eu³⁺ nanophosphor in the mesoporous TiO2 layer, Sol. Energy Mater. Sol. Cells 149 (2016) 121–127.
- [16] K. Cao, Z.X. Zuo, J. Cui, Y. Shen, T. Moehl, S.M. Zakeeruddin, M. Grätzel, M.K. Wang, Efficient screen printed perovskite solar cells based on mesoscopic TiO₂/Al₂O₃/NiO/carbon architecture, Nano Energy 17 (2015) 171–179.
- [17] S.H. Hwang, J. Roh, J. Lee, J. Ryu, J. Yun, J. Jang, Size-controlled SiO₂ nanoparticles as scaffold layers in thin-film perovskite solar cells, J. Mater. Chem. A 2 (2014) 16429–16433.
- [18] S.D. Stranks, G.E. Eperon, G. Grancini, C. Menelaou, M.J.P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza, H.J. Snaith, Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber, Science 342 (2013) 341–344.
- [19] M.J. Yang, T.Y. Zhang, P. Schulz, Z. Li, G. Li, D.H. Kim, N.J. Guo, J.J. Berry, K. Zhu, Y. X. Zhao, Facile fabrication of large-grain CH₃NH₃Pbl_{3-x}Br_x films for high-efficiency solar cells via CH₃NH₃Br-selective Ostwald ripening, Nat. Comm. 7 (2016) 12305.
- [20] H.P. Zhou, Q. Chen, G. Li, S. Luo, T. Song, H.S. Duan, Z.R. Hong, J.B. You, Y.S. Liu, Y. Yang, Interface engineering of highly efficient perovskite solar cells, Science 345 (2014) 542–546.
- [21] J.H. Heo, M.S. You, M.H. Chang, W.P. Yin, T.K. Ahn, S.J. Lee, S.J. Sung, D.H. Kim, S. H. Im, Hysteresis-less mesoscopic CH₃NH₃PbI₃ perovskite hybrid solar cells by introduction of Li-treated TiO₂ electrode, Nano Energy 15 (2015) 530–539.
- [22] M. Saliba, T. Matsui, K. Domanski, J.Y. Seo, A. Ummadisingu, S.M. Zakeeruddin, J.P. Correa-Baena, W.R. Tress, A. Abate, A. Hagfeldt, M. Grätzel, Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance. Science 354 (2016) 206–209
- [23] S.D. Sung, D.P. Ojha, J.S. You, J. Lee, J. Kim, W.I. Lee, 50 nm sized spherical TiO₂ nanocrystals for highly efficient mesoscopic perovskite solar cells, Nanoscale 7 (2015) 8898–8906.
- [24] Y.H. Yu, J.Y. Li, D.L. Geng, J.L. Wang, L.S. Zhang, T.L. Andrew, M.S. Arnold, X.D. Wang, Development of Lead Iodide Perovskite Solar Cells Using Three-Dimensional Titanium Dioxide Nanowire Architectures, ACS Nano 9 (2015) 564–572.

- [25] S.M. Kang, S. Jang, J.K. Lee, J. Yoon, D.E. Yoo, J.W. Lee, M. Choi, N.G. Park, Moth-Eye TiO₂ Layer for Improving Light Harvesting Efficiency in Perovskite Solar Cells, Small 12 (2016) 2443–2449.
- [26] S. Jang, J. Yoon, K. Ha, M.C. Kim, D.H. Kim, S.M. Kim, S.M. Kang, S.J. Park, H.S. Jung, M. Choi, Facile fabrication of three-dimensional TiO₂ structures for highly efficient perovskite solar cells, Nano Energy 22 (2016) 499–506.
- [27] L. Zheng, D. Zhang, Y. Ma, Z. Lu, Z. Chen, S. Wang, L. Xiao, Q. Gong, Morphology control of the perovskite films for efficient solar cells, Dalton Trans. 44 (2015) 10582–10593.
- [28] T.H. Chang, C.W. Kung, H.W. Chen, T.Y. Huang, S.Y. Kao, H.C. Lu, M.H. Lee, K.M. Boopathi, C.W. Chu, K.C. Ho, Planar Heterojunction Perovskite Solar Cells Incorporating Metal-Organic Framework Nanocrystals, Adv. Mater. 27 (2015) 7229–7235.
- [29] Y. Fu, D. Sun, Y. Chen, R. Huang, Z. Ding, X. Fu, Z. Li, An amine-functionalized titanium metal-organic framework photocatalyst with visible-light-induced activity for CO₂ reduction, Angew. Chem. Int. Ed. 51 (2012) 3420–3423.
- [30] C.H. Hendon, D. Tiana, M. Fontecave, C. Sanchez, L. D'arras, C. Sassoye, L. Rozes, C. Mellot-Draznieks, A. Walsh, Engineering the Optical Response of the Titanium-MIL-125 Metal-Organic Framework through Ligand Functionalization, J. Am. Chem. Soc. 135 (2013) 10942–10945.
- [31] S. Hu, M. Liu, K. Li, Y. Zuo, A. Zhang, C. Song, G. Zhang, X. Guo, Solvothermal synthesis of NH₂-MIL-125(Ti) from circular plate to octahedron, CrystEngComm 16 (2014) 9645–9650.
- [32] G. Grancini, S. Marras, M. Prato, C. Giannini, C. Quarti, F.D. Angelis, M.D. Bastiani, G.E. Eperon, H.J. Snaith, L. Manna, A. Petrozza, The Impact of the Crystallization Processes on the Structural and Optical Properties of Hybrid Perovskite Films for Photovoltaics, J. Phys. Chem. Lett 5 (2014) 3836–3842.
- [33] J. Burschka, N. Pellet, S.J. Moon, R. Humphry-Baker, P. Gao, M.K. Nazeeruddin, M. Grätzel, Sequential deposition as a route to high-performance perovskitesensitized solar cells, Nature 499 (2013) 316–319.
- [34] J.H. Im, I.H. Jang, N. Pellet, M. Grätzel, N.G. Park, Growth of CH₃NH₃PbI₃ cuboids with controlled size for high-efficiency perovskite solar cells, Nat. Nanotechnol. 9 (2014) 927–932.
- [35] L.L. Zheng, Y.Z. Ma, S.S. Chu, S.F. Wang, B. Qu, L.X. Xiao, Z.J. Chen, Q.H. Gong, Z.X. Wu, X. Hou, Improved light absorption and charge transport for perovskite solar cells with rough interfaces by sequential deposition, Nanoscale 6 (2014) 8171–8176.
- [36] C.T. Zuo, L.M. Ding, An 80.11% FF record achieved for perovskite solar cells by using the NH₄Cl additive, Nanoscale 6 (2014) 9935–9938.
- [37] C.H. Chiang, Z.L. Tseng, C.G. Wu, Planar heterojunction perovskite/PC71BM solar cells with enhanced open-circuit voltage via a (2/1)-step spin-coating process, J. Mater. Chem. A 2 (2014) 15897–15903.
- [38] Z.Y. Jiang, X.H. Chen, X.H. Lin, X.K. Jia, J.F. Wang, L.K. Pan, S.M. Huang, F.R. Zhu, Z. Sun, Amazing stable open-circuit voltage in perovskite solar cells using AgAl alloy electrode, Sol. Energy Mater. Sol. Cells 146 (2016) 35–43.
- [39] Z. Xiao, Y. Yuan, Y. Shao, Q. Wang, Q. Dong, C. Bi, P. Sharma, A. Gruverman, J. Huang, Giant switchable photovoltaic effect in organometal trihalide perovskite devices, Nat. Mater. 14 (2014) 193–198.
- [40] R.S. Sanchez, V. Gonzalez Pedro, J.W. Lee, N.G. Park, Y.S. Kang, I. Mora Sero, J. Bisquert, Slow dynamic processes in lead halide perovskite solar cells. Characteristic times and hysteresis, J. Phys. Chem. Lett. 5 (2014) 2357–2363.
- [41] T.T. Xu, L.X. Chen, Z.H. Guo, T.L. Ma, Strategic improvement of the long-term stability of perovskite materials and perovskite solar cells, Phys. Chem. Chem. Phys 18 (2016) 27026–27050.
- [42] F.C. Chen, J.L. Wu, C.L. Lee, Y. Hong, C.H. Kuo, M.H. Huang, Plasmonic-enhanced polymer photovoltaic devices incorporating solution-processable metal nanoparticles, Appl. Phys. Lett. 95 (2009) 013305.
- [43] X.K. Jia, Z.Y. Jiang, X.H. Chen, J.P. Zhou, L.K. Pan, F.R. Zhu, Z. Sun, S.M. Huang, Highly efficient and air stable inverted polymer solar cells using LiF-modified ITO cathode and MoO₃/AgAl alloy anode, ACS Appl. Mater. Interfaces 8 (2016) 3792–3799.
- [44] M.F. Xu, X.Z. Zhu, X.B. Shi, J. Liang, Y. Jin, Z.K. Wang, L.S. Liao, Plasmon resonance enhanced optical absorption in inverted polymer/fullerene solar cells with metal nanoparticle-doped solution-processable TiO₂ layer, ACS Appl. Mater. Interfaces 5 (2013) 2935–2942.
- [45] K.Y. Yan, Z.H. Wei, J.K. Li, H.N. Chen, Y. Yi, X.L. Zheng, X. Long, Z.L. Wang, J.N. Wang, J.B. Xu, S.H. Yang, High-Performance Graphene-Based Hole Conductor-Free Perovskite Solar Cells: Schottky Junction Enhanced Hole Extraction and Electron Blocking, Small 11 (2015) 2269–2274.