Sprayed P25 scaffolds for high-efficiency mesoscopic perovskite solar cells†

Haibo Huang, Jiangjian Shi, Songtao Lv, Dongmei Li, Yanhong Luo and Qingbo Meng*

In this work, a spray method has been employed to deposit mesoscopic scaffold films based on commercial titanium dioxide nanoparticles P25 for the perovskite solar cell for the first time. Uniform mesoporous TiO₂ films with thicknesses ranging from 100 to 600 nm are obtained. Meanwhile, a large size film of 10 × 10 cm² has also been deposited with high uniformity. Transient photocurrent investigation reveals that the charge transport ability of the sprayed P25 film is superior to that of the spin-coated Dyesol 18NRT film, and the charge extraction velocity at the sprayed TiO₂/perovskite interface can be significantly promoted by using titanium diisopropoxide bis(acetylacetonate) (TiAcAc) as the additive. Finally, an efficiency of about 16% for the perovskite solar cell has been achieved using the spray-deposited mesoscopic film, comparable to that with the spin coating method.

To achieve high-uniform and thickness-controllable mesoscopic scaffold films for the solar cell, a digital-controlled spray system was set up in our lab (Fig. S1, ESI†), and the experimental conditions of the spray process have been systematically optimized. More experimental details are given in the ESL†. Here, the P25 nanoparticles dispersed in ethanol (0.0014 M) is used as the spray source, and the film thickness is controlled by different spray circles. Fig. 1(a) and (b) show the top-view scanning electron microscopy (SEM) images of the as-prepared mesoscopic TiO₂ films. In the low magnification image, it can be seen that the FTO glass substrate is completely covered with the P25 nanoparticles. With a higher magnification, the pore structure of the TiO₂ film can be clearly seen in Fig. 1(b), where the P25 nanoparticles interconnect to each other, forming some aggregations more or less. Without any addition of ethyl cellulose, the size of the mesoporous pores is ranging from tens to hundreds of nanometers, which may give an adequate space for the deposition and infiltration of the perovskite absorber. Moreover, the interconnected P25 nanoparticles can give effective pathways for the charge transport.

For comparison, uniform mesoscopic TiO₂ films are also obtained by spin-coating the above mentioned P25 dispersion and the standard Dyesol 18NRT paste onto the FTO substrates, as shown in Fig. 1(c) and (d). When the P25 dispersion is spin coated, the mesoporous pore sizes are smaller than those obtained by the

Uniform, thickness-controllable and large-size mesoscopic TiO₂ films based on commercial P25 nanoparticles are prepared by a spray method, which have been applied in the perovskite solar cells, achieving a high efficiency of 16%. This spray method shows promising application in the large-scale production of mesoscopic solar cells.

Perovskite solar cells (PSCs), in which the perovskite organic metal halides act as the absorber, have been rapidly developed in the past five years,1–7 achieving a certified efficiency exceeding 20%. Although high efficiency can be obtained in the planar cell8–11 by carefully controlling the crystal process of the perovskite absorber, the cell based on the mesoscopic structure still has some advantages in mechanical connectivity and charge extraction.12 With the mesoscopic film, the perovskite absorber can be easily deposited by using solution-processed methods. Moreover, the charge separation and extraction in the cell can also be accelerated with the mesoscopic TiO₂/perovskite structure.13 Thus, the existence of the mesoscopic film is still considered to play an important role in the improvement of the cell performance and mechanical strength.

To achieve efficient PSCs, large-scale manufacturing technologies are highly desired due to its next-stage commercial application. For this purpose, the technologies such as spray and printing have been developed for the deposition of the perovskite absorber, mainly in planar cells.14 When it comes to the mesoscopic cell, the mesoscopic film is first needed in a decimeter or larger scale. Besides, the thickness, uniformity and pore structure of the film have to be accurately controllable for high efficiency.15,16 At present, the spin coating is the most widely used method to deposit the mesoscopic scaffold with a thickness of submicrometer and high uniformity. However, the spin coating method cannot be used in the large-scale production. Therefore, a simple technology for the deposition of large-scale mesoscopic films with controllable thickness and uniformity is expected.

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† Electronic supplementary information (ESI) available: Experimental details and additional figures. See DOI: 10.1039/c5cc01939g
spray process. This difference could come from the obvious difference in film deposition conditions, where the P25 dispersion experiences an atomization and a rapid evaporation in the spray process. Due to the rapid evaporation of the ethanol solvent and the surface tension, the P25 nanoparticles prefer to connect to each other, leading to the aggregation of nanoparticles and the relatively large pores. For the standard TiO2 film with spin coated Dyesol 18NRT, the sizes of the nanoparticles and the pores are both smaller than the P25 films. Since it has been reported that the cell based on larger TiO2 nanoparticles exhibits better performance, it is supposed that the sprayed P25 films with large nanoparticles or aggregations can also produce the high-efficiency mesoscopic perovskite solar cell in spite of the difference in the pore structures.

Besides uniformity, the film thickness can also be well controlled in this spray method. With changing the spray circles, the TiO2 films with thicknesses of about 100, 150, 200 and 600 nm have been obtained, the cross-sectional SEM images of which are shown in Fig. 2(a)–(d), respectively. Some large-sized aggregated TiO2 can also be seen from these images. The profile measurement has also been made, the results of which are shown in Fig. 2(e). As can be seen, for thin films of about 100 and 150 nm, a relatively smooth surface profile is obtained. When increasing the film thickness gradually, the roughness of the film becomes more significant, which may be due to the aggregation of the nanoparticles. Compared to the widely used spin coating method, the spray method has an advantage in depositing large-scale films. With our spray system, a TiO2 film of 10 × 10 cm2 has also been prepared, the photograph of which is shown in Fig. 3(a). To confirm the uniformity of the film, the average thicknesses of eleven positions as marked on this film have been measured, the statistic results of which are given in Fig. 3(b). As can be seen, the average thickness of this film is about 400 nm, and the difference in thickness is within 20 nm. Obviously, the spray method has clear advantages to prepare large-size mesoscopic films with high uniformity, which establishes the first-step and foundation for the large-scale production of mesoscopic solar cells.

When the sprayed TiO2 mesoporous film (1.5 × 1.5 cm2) is used in perovskite solar cells, the influence of the film thickness on the performance of the perovskite solar cells is first optimized. The current-voltage (I–V) results of the cells with different TiO2 film thicknesses are shown in Fig. 4(a). When a thin TiO2 film of about 100 nm is used, a power conversion efficiency (PCE) of 14.2% is achieved with a short-circuit current density (JSC) of 19.1 mA cm−2, an open-circuit voltage (VOC) of 990.8 mV and a fill factor (FF) of 0.75. When increasing the TiO2 film thickness to 150 nm, the JSC is promoted to 20.7 mA cm−2, and thus the PCE is enhanced to 14.9%. Although the JSC can be further improved, the VOC, FF and thus the PCE are obviously decayed with increasing the TiO2 film thickness to 200 nm due to the increased recombination and charge transport resistance, as shown in Fig. 4(a) and Table 1. Thus, 150 nm is chosen as the optimal film thickness.

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**Fig. 1** Top-view SEM images of the mesoscopic TiO2 films deposited with (a) and (b) sprayed and (c) spin-coated P25 and (d) spin-coated Dyesol 18 NRT.

**Fig. 2** Cross-sectional SEM images of the sprayed P25 films with different thicknesses of (a) 100 nm, (b) 150 nm, (c) 200 nm and (d) 600 nm, and (e) the corresponding profile results of each film.

**Fig. 3** (a) Photograph of the large-scale (10 cm × 10 cm) TiO2 film deposited with sprayed P25 and (b) the statistic result of the film thickness at different positions marked with black circles.

**Fig. 4** Current–voltage results of the perovskite solar cells, in which the mesoscopic TiO2 film is deposited with (a) sprayed P25 and (b) spin-coating (SC) methods.
Table 1  Cell performance, PL lifetime (τd) and charge transport time (τr) of the cells, where the mesoscopic TiO2 films are deposited with spray and spin-coating methods, respectively.

<table>
<thead>
<tr>
<th>TiO2 film</th>
<th>Jsc (mA cm(^{-2}))</th>
<th>Voc (mV)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>τd (ns)</th>
<th>τr (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray 100 nm</td>
<td>19.1</td>
<td>990.8</td>
<td>0.75</td>
<td>14.2</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>150 nm</td>
<td>20.7</td>
<td>996.5</td>
<td>0.72</td>
<td>14.9</td>
<td>27.1</td>
<td>2.7</td>
</tr>
<tr>
<td>200 nm</td>
<td>22.1</td>
<td>945.2</td>
<td>0.61</td>
<td>12.7</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>150 nm/TiAcAc</td>
<td>21.65</td>
<td>1010.2</td>
<td>0.73</td>
<td>16.0</td>
<td>9.8</td>
<td>2.4</td>
</tr>
<tr>
<td>Spin-coating P25-150 nm</td>
<td>20.3</td>
<td>974.1</td>
<td>0.71</td>
<td>14.1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>18NRT-150 nm</td>
<td>20.5</td>
<td>1031.1</td>
<td>0.73</td>
<td>15.3</td>
<td>6.7</td>
<td>5.8</td>
</tr>
</tbody>
</table>

For comparison, the perovskite solar cells based on spin coated 150 nm-thick mesoscopic TiO2 films with P25 dispersion and Dyesol 18NRT, respectively, have also been prepared, the performance of which are shown in Fig. 4(b) and Table 1. The film based on the Dyesol paste leads to the PCE of about 15.5%, mainly due to its high Voc of about 1031 mV. When P25 dispersion is spin coated to give the mesoporous TiO2 film, a PCE of about 14.1% is achieved, a little lower than the spray ones. Although a comparable performance can be obtained by the spray method, the cell based on the sprayed P25 still exhibits a lower PCE than the standard cell. As has been discussed, the pore structures, connectivity between the nanoparticles and charge transport properties of the mesoscopic TiO2 films are supposed to be different, which could be one of the origins for the difference in cell performance.

To further investigate the charge extraction and charge transport properties of the mesoscopic TiO2 films derived from different deposition methods, the transient photoluminescence (PL) of the TiO2/CH\(_3\)NH\(_2\)PbI\(_3\) films and the transient photocurrent of the cell have been measured. To probe the difference in charge transport ability, a pulse red-light laser at 660 nm is applied for the photocurrent measurements. As can be seen in Fig. 5(a) and Table 1, the charge extraction ability of the spin coated Dyesol film is obviously superior to that of the sprayed P25 film. The spin coated Dyesol film with a smaller size of the nanoparticles has a higher surface area, and this higher surface area contributes to a larger connecting area of the TiO2/CH\(_3\)NH\(_2\)PbI\(_3\) interface for charge extraction. In this case, the photo-induced free electrons in the perovskite can be extracted faster, which avoids the charge accumulation at the TiO2/CH\(_3\)NH\(_2\)PbI\(_3\) interface, thus lowering the recombination occurring in the depletion region. On the other hand, the charge extraction velocity is much slower for the sprayed P25 based TiO2 film, mainly due to its larger size of nanoparticles and lower interface area. This slower extraction will lead to charge accumulation and more serious recombination at the TiO2/CH\(_3\)NH\(_2\)PbI\(_3\) interface, lowering the Voc of the cell. Thus, the charge extraction ability of the sprayed P25 film need to be further enhanced for better cell performance. Despite poorer charge extraction ability, the sprayed P25 film exhibits superior charge transport properties to the Dyesol film. As in Fig. 5(b), the charge transport time (τr) for the Dyesol film based cell is about 5.8 µs, two times of that based on the sprayed P25 film. This result is consistent with the diffusion constant of the TiO2 films with different sizes of nanoparticles. The smaller TiO2 nanoparticles may have more surface trap states, and the charge has to transport across more TiO2 boundaries to be collected, both of which can slow the charge transport ability of the mesoscopic film. Thus, the spray film with larger P25 nanoparticles has better charge transport ability.

TiAcAc is usually applied as a stabilizer and a chelation ligand for depositing uniform and crack-free TiO2 films. To further enhance the connectivity between the sprayed nanoparticles and adjust the TiO2/CH\(_3\)NH\(_2\)PbI\(_3\) interface, a certain amount of TiAcAc has also been introduced as an additive in the P25 dispersion. It is found that the charge extraction velocity at the TiO2/CH\(_3\)NH\(_2\)PbI\(_3\) interface is significantly accelerated, comparable to that of the Dyesol film, as seen with the transient PL results in Fig. 5(a) and Table 1. Besides, the charge transport ability of the spray TiO2 film has also been enhanced, as shown in Fig. 5(b). When TiAcAc is introduced, a continuous TiO2 layer coating on the P25 nanoparticles is supposed to appear after annealing, which helps to improve the interface connectivity between TiO2 and CH\(_3\)NH\(_2\)PbI\(_3\), and passivate the surface trap states of the TiO2 film, thus promoting the charge extraction and transport. With these improvements, the performance of the cell based on the spray method has been further enhanced. I–V result of the best-performed cell is shown in Fig. 6(a). A PCE of 16.03% has been achieved with a Jsc of 21.65 mA cm\(^{-2}\), a Voc of 1010.2 mV and an FF of 0.73. The integration of the external quantum efficiency (EQE) spectrum yields a Jsc of about 20.3 mA cm\(^{-2}\), as in Fig. 6(b), basically agreeing with the I–V result. When considering the I–V hysteresis, a PCE of about 15.0% can also be achieved by averaging the forward and backward I–V curves, as shown in Fig. S2 (ESI†).
Uniform, thickness-controllable and large-scale mesoscopic TiO$_2$ films have been prepared by a spray method with commercial and cost-effective P25 as the source, and a high-efficiency perovskite solar cell has been achieved using the sprayed mesoscopic film. Moreover, it is found that the charge transport ability of the sprayed P25 film is superior to that of the spin-coated Dyesol 18NRT film, and that the charge extraction velocity at the sprayed TiO$_2$/perovskite interface can be significantly promoted using the TiAcAc additive. The spray method in this work can provide the possibility of preparing large-size and large-scale mesoscopic films, which is the first-step and foundation for the large-scale production of perovskite solar cells.

This work was supported by National Key Basic Research Program (No. 2012CB932903), and Natural Science Foundation of China (No. 51372270, 51372272, 21173260, 11474333, 91233202, 91433205 and 51421002).

Notes and references

Supporting information for

Sprayed P25 scaffolds for High-Efficiency Mesoscopic Perovskite Solar Cells

Experimental details

Spray TiO\textsubscript{2} mesoscopic film

A spray system as shown in Figure S1 was set up for the deposition of mesoscopic TiO\textsubscript{2} films. The commercial P25 nanoparticles were dispersed in the ethanol with rigorous stirring and ultrasonic. The concentration of the TiO\textsubscript{2}(P25) dispersion has been optimized, and 0.0014 M was determined as the best condition.

Before spray, the FTO/compact TiO\textsubscript{2} substrate was preheated to 100 °C for the fast evaporation of the ethanol solvent in the P25 source. The work of this spray system can be controlled with a digital controller, and the movement of the spray gun is also controlled by the stepping motor. When digitally turn on the spray gun, the P25 dispersion will be sprayed out and deposited onto the substrates. After 1 s, the spray gun will be automatically turned off. This is a spray circle. For each circle, 2 nm-thick TiO\textsubscript{2} film can be deposited. After the spray process, the TiO\textsubscript{2} film is annealing at 500 °C for 30 min. For the addition of titanium diisopropoxide bis(acetylacetonate) (TiAcAc), a certain amount of TiAcAc is added into the P25 dispersion with continuous stirring. The optimal molar ratio of TiO\textsubscript{2}(P25)/TiAcAc is about 4.

Cell fabrication

Firstly, a dense TiO\textsubscript{2} underlayer with a thickness of about 20 nm was spin coated onto the pre-cleaned laser patterned FTO glass, which was then sintered at 500 °C for 30 min. The TiO\textsubscript{2} mesoscopic film was then sprayed onto the FTO/compact TiO\textsubscript{2} substrates, and annealed at 500 °C for another 30 min. After that, TiO\textsubscript{2} films were treated with 25 mM TiCl\textsubscript{4} solution at 70 °C for 40 min and sintered at 500 °C for 30 min.
CH₃NH₃PbI₃ absorber layer was deposited by a two-step deposition method in the N₂-glove box. Firstly, 1.3 M PbI₂ dissolved in DMF was spin coated onto the TiO₂ film twice at a speed of 3500 rpm for 30 s and then heat treated at 90 °C for 2 min to remove the DMF solvent. After the PbI₂ film cooling to room temperature, it was dipped into 10 mg/ml CH₃NH₃I solution with isopropanol as the solvent. After immersion in the solution (70 °C) for about 2 min, the CH₃NH₃PbI₃ film was obtained. The obtained CH₃NH₃PbI₃ films were then heat treated at 115 °C for 30 min in air with humidity of about 20% on a hotplate. After heat treatment, the films were kept in dark in air for overnight. A 300 nm hole transport layer was then deposited by spin-coating Spiro-OMeTAD solution in chlorobenzene on the CH₃NH₃PbI₃ layer. Finally, Au was thermal evaporated (Kurt J. Lesker) as electrode (80 nm) for heterojunction solar cells at an atmospheric pressure of 10⁻⁷ Torr.

Characterizations

Current-voltage (I-V) characteristics were measured by an additional voltage from the Keithley 2602 source meter together with a sunlight simulator (Oriel Solar Simulator 91192, AM 1.5 100 mW/cm²) calibrated with a standard silicon reference cell. The solar cells were masked with a black aperture to define the active area of 0.1 cm². Impedance spectra were measured on IM6ex electrochemical workstation in the dark under different DC positive biases, in which scan frequency was in the range of 100 K ~ 100 mHz with the amplitude of the perturbation bias of 10 mV. X-ray diffraction (XRD) was measured with a Bruker X-ray diffractometer with Cu Kα as the radiation source. The scanning electron microscopy images of the films were obtained with FEI-SEM (XL 30 S-FEG). The external quantum efficiency of the cell was obtained with a lab-made IPCE spectrometer. The transient photoluminescence were measured with the PL spectrometer (Edinburgh Instruments, FLS 920) together with a pulsed diode laser (445 nm, 0.8 μJ/cm²). An optical filter at 590 nm was used to filter out the excitation light during measurements. Transient photocurrent were measured with a pulsed red-light laser (1 KHz, pulse width 35 ns) at 660 nm and a sub-nanosecond resolved digital oscilloscope (Tektronix DPO 7104) with a sampling resistance of 50 Ω.
Figures

Figure S1. Schematic diagram of the spray system we set up.

Figure S2. (a) Forward, backward and the average current-voltage curves of one of the best performed perovskite solar cells based on the spray P25 film, and (b) the statistic histogram of the cell efficiency (backward scanning).