Supporting Information For

Hole-Conductor-Free Mesoscopic TiO₂/CH₃NH₃PbI₃ Heterojunction Solar Cells based on Anatase Nanosheets and Carbon Counter Electrodes

Yaoguang Rong, Zhiliang Ku, Anyi Mei, Tongfa Liu, Mi Xu, Songguk Ko, Xiong Li and Hongwei Han*

Michael Grätzel Center for Mesoscopic Solar Cells, Wuhan National Laboratory for Optoelectronics, School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan, Hubei 430074, P. R.China.

E-mail: hongwei.han@mail.hust.edu.cn;
Fax: +86 027 877 930 27; Tel: +86 027 877 930 27

1. Experimental Section

Synthesis of TiO₂ nanosheets. The synthesis of the nanosheets was followed a typical experimental procedure¹. 10 ml Ti(OBu)₄ (98%) and 1.2 ml hydrofluoric acid (HF) solution (47%) were mixed in a 150 ml dried Teflon autoclave which was kept at 180 °C for 24 h to yield the nanosheets. After the reaction was cooled to room temperature, the white powder was separated by high-speed centrifugation and washed with ethanol followed by distilled water for sever times.

Device Fabrication and Measurement. FTO glass plates with high transparency in the visible range purchased from CSG Holding Co. LTD. After the pre-treatment of the glass substrate including the laser structuring of FTO layer and washing of the glass, a dense TiO₂ layer was deposited on the glass substrate by spray pyrolysis deposition with di-isoproxytitaniumbis (acetyl acetonate) solution. Then a 0.6 µm nanoporous TiO₂ nanosheet layer, a 1 µm ZrO₂ spacer layer, and a 10 µm carbon CE were screen printed on the substrate layer by layer (the slurries were prepared as we reported previously²,³). The TiO₂
layer and ZrO$_2$ layer were sintered at 500 °C for 30 min, and the carbon CE was sintered at 400 °C for 30 min. The deposition of perovskite CH$_3$NH$_3$PbI$_3$ into the three porous films was achieved by a two-step sequential method. Firstly, the porous films were infiltrated with PbI$_2$ by spin-coating a PbI$_2$ solution in DMF (462 mg ml$^{-1}$, ~1 M) that was kept at 70 °C. After drying, the films coated with PbI$_2$ were dipped in a solution of CH$_3$NH$_3$I in 2-propanol (10 mg mL$^{-1}$) for 10 min. The color of the films would change from yellow to dark brown when CH$_3$NH$_3$PbI$_3$ formed. Photocurrent density–voltage characteristics were measured with a Keithley 2400 source meter under simulated AM1.5 one sun illumination (100 mW cm$^{-2}$). The active area of the device was fixed to 0.13 cm$^2$ with a mask. The scan rate was 250 mV/s and the scan direction was from open-circuit to short-circuit. The distributions of photovoltaic parameters of 40 devices (20 devices based on NP and 20 devices based on NS) were presented in Figure S3. The $IPCE$ measurements were performed with a 150 W xenon lamp (Oriel) fitted with a mono-chromator (Cornerstone 74004) as a monochromatic light source. The impedance measurements were performed using a potentiostat (EG&G, M2273) in the dark. The X-ray diffraction (XRD) experiments were carried out on D8 advance X-ray diffractometer with Ca Kα radiation ($\lambda=1.5418$). The SEM images were taken using Nova NanoSEM 450. The TEM images were taken using Tecnai G2 20. The thickness of the layers was measured by a profilometer (Vecco, Dektak 150).

2. The Shape simulation of TiO$_2$ crystal synthesized in the presence of HF

TiO$_2$ nanosheets (NS) were synthesized via a simple hydrothermal rout using tetrabutyl titanate as the precursor and HF solution as the solvent. As the volume of HF increased, the TiO$_2$ crystals may have larger size along a-axis and expose more (001) facets, resulting in a
shape transformation from octahedral bipyramid to truncated octahedral bipyramid, finally to nansheets.\textsuperscript{5,6}

\textbf{Figure S1.} Shape simulation of TiO\textsubscript{2} crystal synthesized in the presence of HF.

3. Comparison of drop-coating method and two-step sequential deposition method

The absorption spectra of NS and NP films coated with perovskite (using drop-coating method and sequential deposition method respectively) have been characterized in the range of from 400 nm to 850 nm. For the NP and NS films coated with perovskite, their absorption spectra almost overlapped each other in the range of from 400 nm to 850 nm, indicating similar light harvesting efficiencies.

To characterize the nano-structure of NP and NS, we have carried out BET tests. The surface areas of NP and NS were 61.5 m\textsuperscript{2}/g and 58.4 m\textsuperscript{2}/g, respectively. The BJH desorption cumulative volumes of pores were 0.552 cm\textsuperscript{3}/g and 0.544 cm\textsuperscript{3}/g, respectively. These results indicated that the amount of perovskite deposited in the pores of TiO\textsubscript{2} films were almost the same. Thus, the light harvesting efficiency of the perovskite coated NP and NS layers would be similar, which was in accordance with the results of absorbance spectra.
For the comparison of drop-coating method and sequential deposition method, the absorbance of sample using sequential deposition method was much higher than that of sample using drop-coating method in the range of from 500 nm to 800 nm. This result indicated that the sequential deposition method was a more efficient method for loading perovskite in the mesoscopic films. And the enhancement of light harvesting efficiency would result in a larger Jsc for the devices fabricated with sequential deposition method correspondingly.

**Figure S2.** The absorption spectra of TiO$_2$ films coated with perovskite: NP-1 for TiO$_2$ NP film deposited perovskite using drop-coating method, NS-1 for TiO$_2$ NS film deposited perovskite using drop-coating method, NP-2 for TiO$_2$ NP film deposited perovskite using two-step sequential method, NS-2 for TiO$_2$ NS film deposited perovskite using two-step sequential method; Inset: Digital images of hole-conductor-free mesoscopic TiO$_2$/CH$_3$NH$_3$PbI$_3$ heterojunction solar cells based on carbon counter electrodes.
4. **Histograms for photovoltaic parameters of the devices**

![Histograms](image)

**Figure S3.** The histograms for photovoltaic parameters of (a) $J_{sc}$, (b) $V_{oc}$, (c) $FF$ and (d) $PCE$ of devices using NP (20 devices) and NS (20 devices) as the electron collectors.

5. **Impedance spectroscopy measurements**

Figure S4 shows the impedance spectroscopy results of the nanosheets based devices. The diameter of the second semicircle in the low frequency region increased along with the decrease of the forward bias value, while the first semicircle in the high frequency region unchanged. Compared with the results reported previously, the first and second semicircle should represent the impedance at the interface of Perovskite/CE and TiO$_2$/Perovskite, respectively.$^{8-10}$
Figure S4. a) Nyquist plots of hole-conductor-free mesoscopic TiO$_2$/CH$_3$NH$_3$PbI$_3$ heterojunction solar cells measured in dark condition with a forward bias of 0.2, 0.4 and 0.6 V in the dark. b) the expanded range of the ordinate and abscissa from a).

6. References


