Surpporting Inforamtion for

Hole-Conductor-Free and Carbon Counter Electrodes Perovskite Solar Cells Based on ZnO Nanorod Arrays

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Experimental Details

1. Preparation of ZnO NR and ZnO/TiO_2 NR arrays

ZnO NR arrays were fabricated via hydrothermal method on a fluorinated tin oxide (FTO) glass substrates. The FTO glass substrates were first etched using Zn and HCl (2 M) aqueous solution to form two detached electrode pattern before ultrasonically cleaned with dilute detergent, diluted hydrochloric acid, and acetone successively. After that, a thin ZnO sol layer was coated on the patterned substrate by a dip-coating method. The sol solution was prepared with 0.05 M $Zn(NO_3)_2{\cdot}6H_2O$ and 0.06 M $C_4H_{11}NO_2$ was dissolved in 100 mL ethanol. A ZnO seed film was finally obtained after being annealed at 500 °C for 30 min.

The precursor aqueous solution for the preparation of ZnO NR array films was

prepared with 1.784 g $Zn(NO_3)_2 \cdot 6H_2O$ and 2.22 g NH_4F dissolved in 200 mL of DI water. The pH value of the solution was adjusted to 8.6 by the addition of ammonia. The precursor solution (60 mL) was then transferred to a Teflon-sealed autoclave comprising substrates pre-coated with a ZnO seed layer. The reaction was performed at 120 ^oC for 4 h to obtain ZnO NR array films with 1μm length. Finally, the resulting films were rinsed with distilled water and dried at 500 ^oC for 1 h.

For the ZnO/TiO_2 NR arrays, the substrates with ZnO NR arrays were immersed in 40 mM of $TiCl_4$ aqueous solutions for 1 h at 70 °C, washed with distilled water and ethanol, followed by annealing at 500 °C for 30 min in air.

2. Preparation of TiO_2 NR array

TiO_2 NR array was prepared on the patterned substrate via hydrothermal method. Before hydrothermal treatment, a TiO_2 seed layer was coated on the substrate by a spin-coating method. 68 mL tetrabutyl titanate and 16.5 mL diethanol amine was dissolved in 210 mL ethanol, following by magnetic stirring for 1 h. 100 mL ethanol and 3.6 mL DI water was dripped into the pre-solution under the magnetic stirring to achieve the TiO_2 sol solution. Spin-coating method was used under the rotate speed of 3000 rpm/min. Then, the substrates with TiO_2 sol solution was annealed at 450 °C for 1 h.

The precursor aqueous solution for the synthesis of TiO_2 NR array films was prepared with 24 mL concentrated hydrochloric acid and 0.8 mol tetrabutyl titanate dissolved into 24 mL of DI water, stirring for 5 min. The precursor solution (60 mL) was then transferred to a teflon-sealed autoclave comprising substrates pre-coated with a TiO_2 seed layer. The reaction was performed at 150 °C for 3 h to obtain TiO_2 NR array films with 1 1μm length. Finally, the resulting films were rinsed with distilled water and dried at 450 ^oC for 1 h.

3. Solar cell fabrication

Screen-printing technique was used to print ZrO_2, and carbon films layer by layer onto the conductive glass coated with ZnO-TiO_2 core-shell NR arrays. 0.462 g PbI_2 was

dissolved in 1mL anhydrous N,N-Dimethylformamide (DMF) by heating at 70 °C overnight to obtain PbI_2 solution. And then, we dropwise added the PbI_2 solution with a dropper drop by drop onto the prepared ZnO/ZrO_2/Carbon film, infiltrating the PbI_2 solution into the film. After the films were fully filled by PbI_2, we dried the film at 50 °C for 3 hours. After that, the films were dipped into a solution of CH_3NH_3I (MAI) in 2-propanol for 15 minutes. Then it was annealed at 70 °C for 30 minutes.

4. Characterization

The X-Ray diffraction (XRD, Philips, X'pert pro, Cu Ka, 0.154056 nm) was employed to characterize the structural properties of the samples. The morphology and structure of the samples were characterized by field emission scanning electron microscopy (FE-SEM, JEOL 6700F) and transmission electron microscopy (TEM, FEI Tecnai F30). Photocurrent density voltage (J-V) curves were characterized with a Keithley 2400 source/meter and a Newport solar simulator (model 91192) giving light with AM 1.5G spectral distribution. A black mask with a circular aperture (0.12 cm^2) smaller than the active area of the square solar cell (0.5 cm^2) was applied on top of the cell. The incident photon conversion 3 efficiency (IPCE) was measured using a 150 W xenon lamp (Oriel) fitted with a monochromator (Cornerstone 74004) as a monochromatic light source. Electrochemical impedance spectroscopy (EIS) of the devices was obtained on an Electrochemical Workstation (CS310). EIS measurements were carried out in the frequency range of 0.01 Hz to 100 kHz at open-circuit voltage with a potential pulse of 10 mV in amplitude.

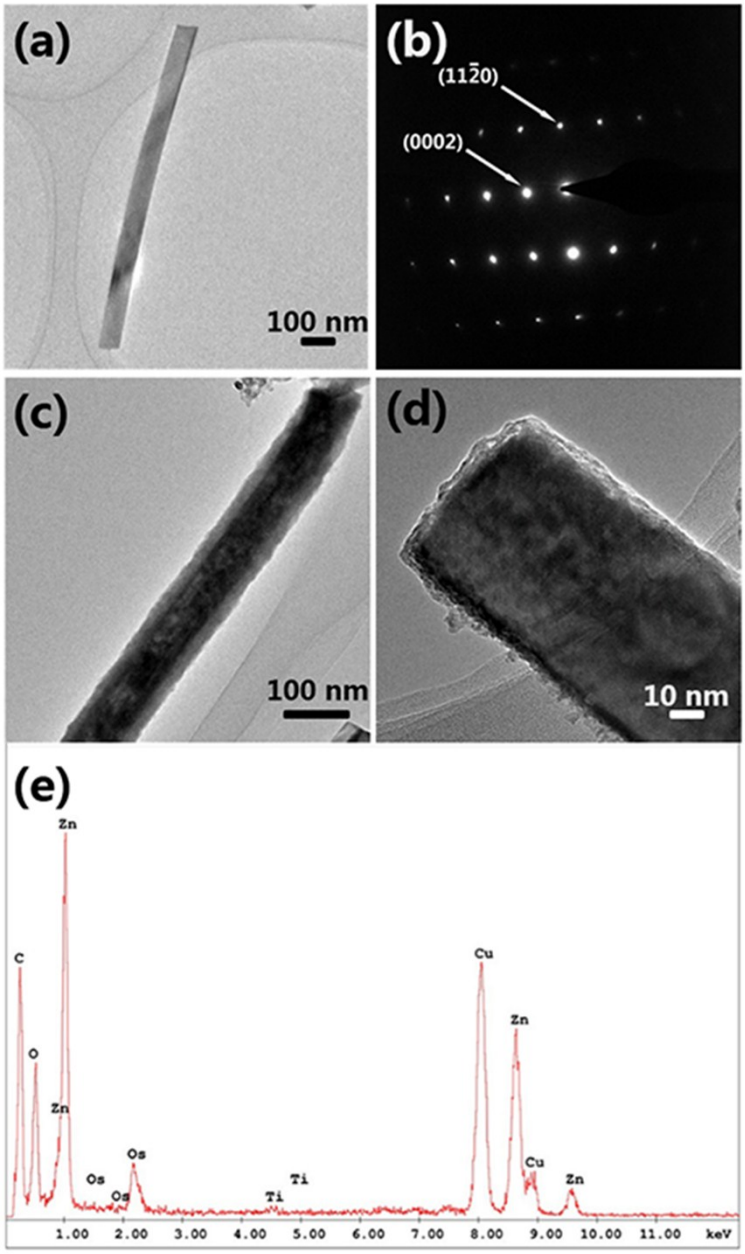

Figure S1. (a) The TEM image of ZnO NR; (b) The corresponding SAED pattern of the ZnO NR; (c) The TEM image of ZnO/TiO_2 NR; (d) The TEM image of ZnO/TiO_2 NR of higher magnification; (e) The EDS pattern of the ZnO/TiO_2 NR.

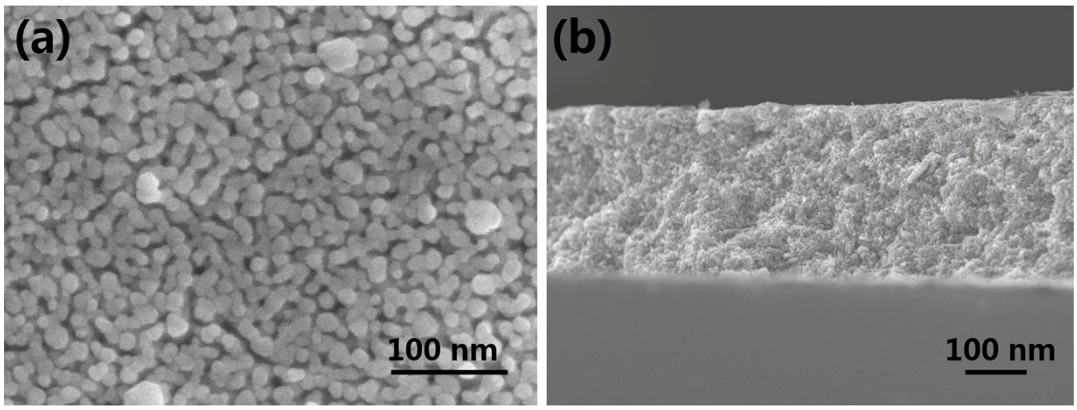

Figure S2. The plain and cross-section images of ZnO seed layer.

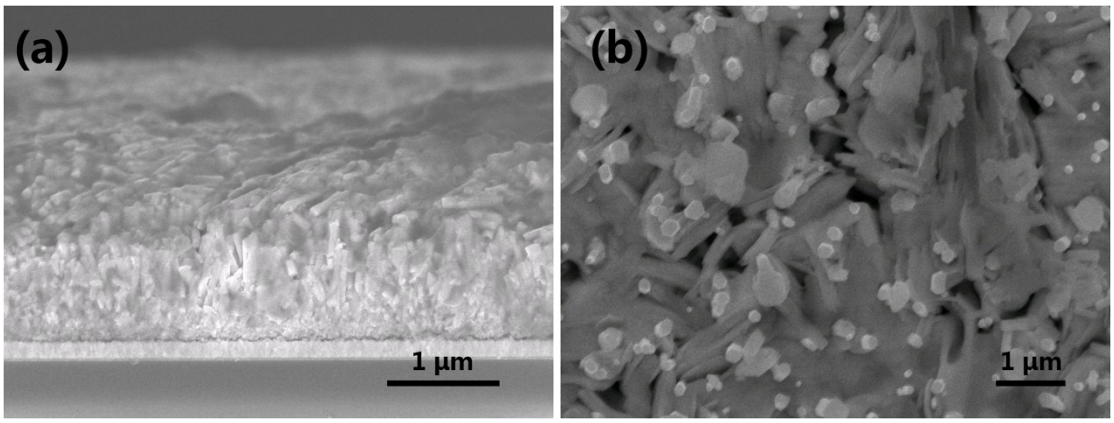

Figure S3. Cross-sectional (a) and plane view (b) SEM image of the ZnO NR/Perovskite.

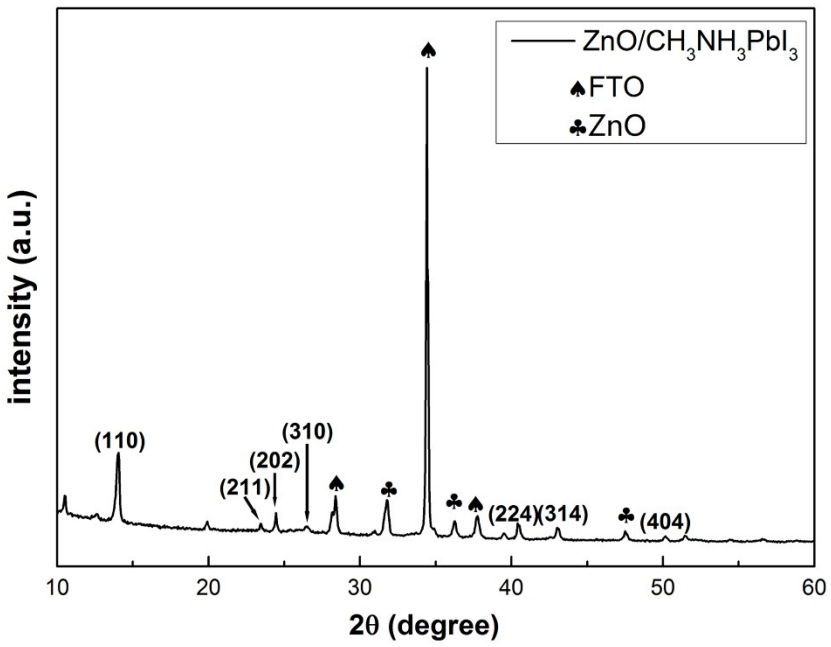

Figure S4. The XRD pattern of ZnO/perovskite.

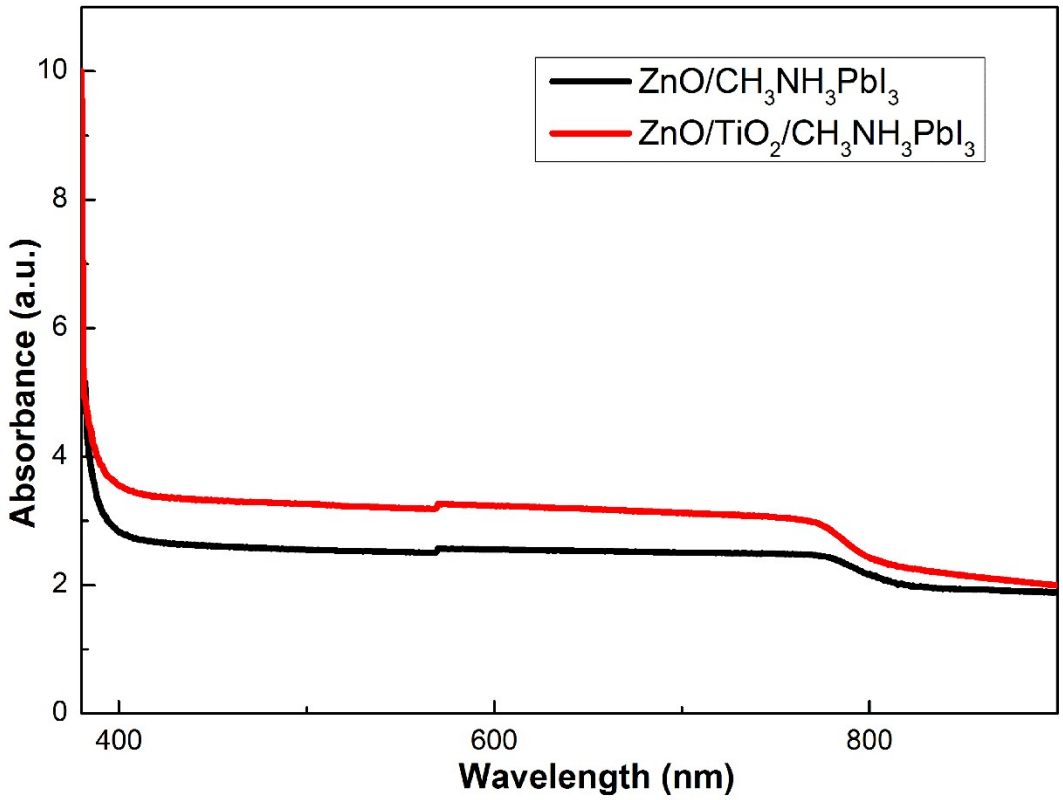

Figure S5. The UV-vis absorption spectra of the ZnO/perovskite and ZnO/TiO_2/ perovskite.

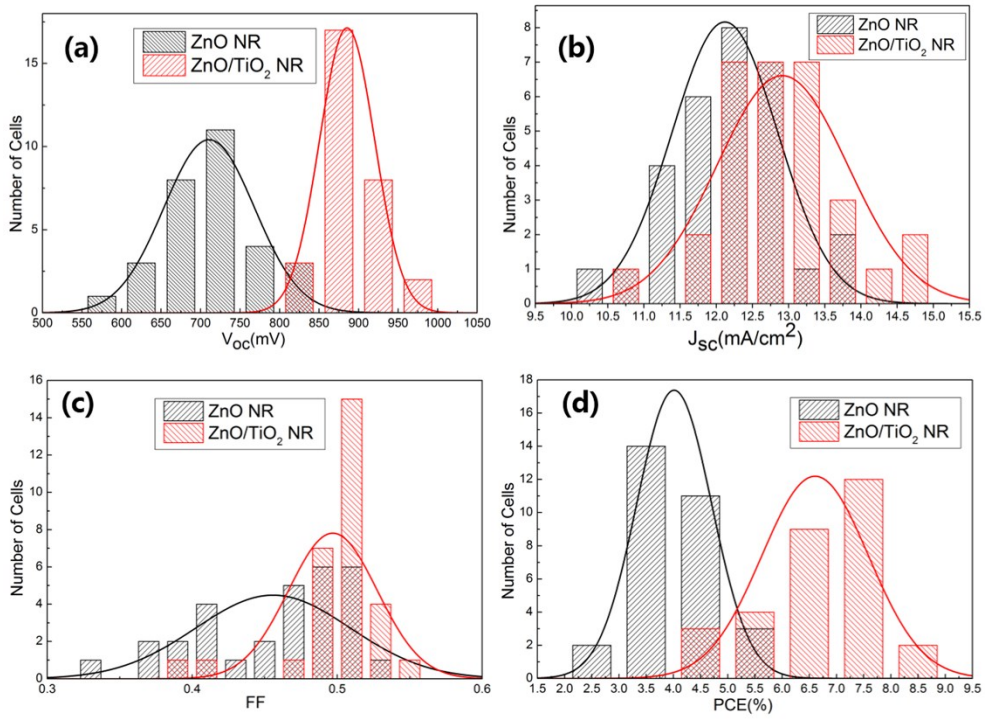

Figure S6. The overall distributions of performance parameters for 30 devices.

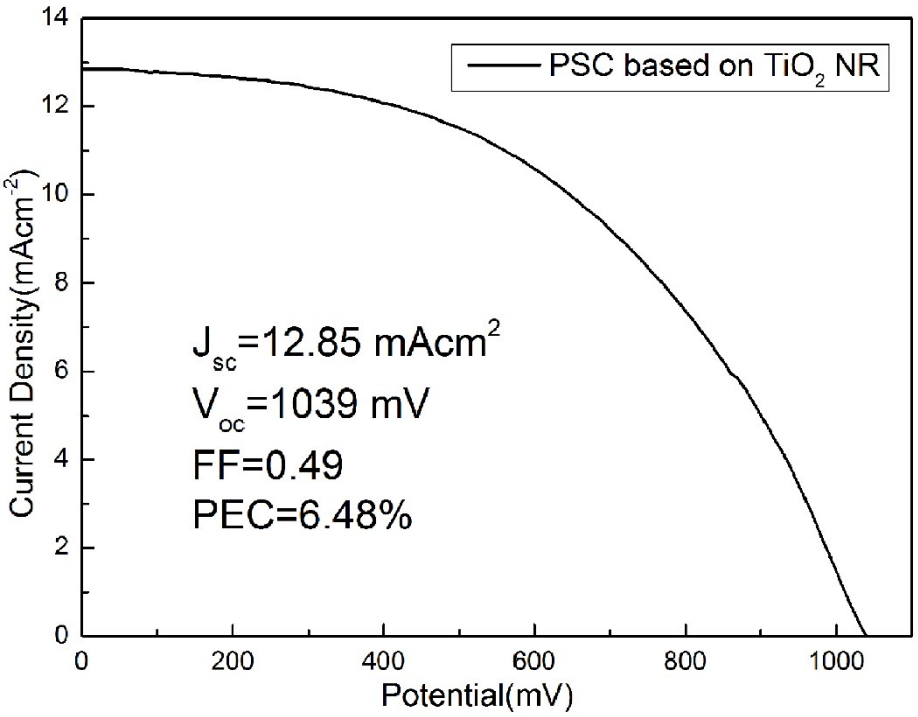

Figure S7. J-V curves of the PSC based on TiO_2 NR array.

Table S1. Photovoltaic parameters of the PSCs based on ZnO NR and ZnO/TiO_2 NR, respectively.

Samples	J_{sc}(mA·cm^{-2})	V_{oc}(mV)	FF	PCE(%)
ZnO NR	14.19	843.16	0.46	5.56
ZnO/TiO_2 NR	14.82	960.39	0.58	8.24

Table S2. Resistivity Values of PSC based on ZnO NR, TiO_2 NR and ZnO/TiO_2 NR, respectively.

Samples	**R_s(Ω)**	**R_{ct1}(NR/Perovskite) (Ω)**	**R_{ct2}(Perovskite/CE) (Ω)**
ZnO NR	273.6	739.3	1984
ZnO/TiO_2 NR	352.4	1251	1995
TiO_2 NR	34	1884	2443