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Supplementary Information

Size effect of TiO_2 nanoparticles on the printable mesoscopic perovskite solar cell

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Experimental Section

The synthesis of the TiO_2 nanoparticles

The hydrothermal method of different sized TiO_2 nanoparticles was adapted from the literature[1]. The 15 nm sized TiO_2 nanoparticles was processed as follows: deionized water (300 mL) and concentrated nitric acid (1 mL) were added to a 500 mL round bottom flask. After the solution cooled down to 0℃ in ice bath, a mixture of glacial acetic acid （6 mL）and $Ti(OiPr)_4$ （30 mL） was added dropwise to the vigorously-stirred solution over 1.5 h. The mixture was heated to 80 ℃ and stirred for 3 h. After the colloidal solution cooled down to the room temperature, 300 mL colloidal solution was transferred into a titanium autoclave (Parr Instrument Company, 600 mL). The autoclave was heated to 200 ℃ and stirred for 12 h.

The preparation of the 20 nm TiO_2 nanoparticles is similar to above method except the temperature of autoclave is controlled to 250 ℃. For the 25nm and 30 nm TiO_2 nanoparticles, the solution of concentrated HNO_3 (1 mL) was replaced by the solution of glacial acetic acid (30 mL), the temperature of autoclave is controlled to 250 ℃ for 12h or 24 h respectively.

The assembling of the printable mesoscopic perovskite solar cell

The FTO glass substrates were firstly etched with a laser to form two detached electrode patterns before being cleaned ultrasonically for 10 minutes with detergent, deionized water and ethanol successively. Then, a TiO_2 dense layer was deposited on the patterned FTO glass substrates by aerosol spray pyrolysis at 450 ℃. After being cooled down to room temperature naturally, a mesoscopic TiO_2 layer was deposited

by screen printing with the TiO_2 nanoparticles slurry which were sintered at 500 ℃ for 30 min. Followed ZrO_2 space layer was printed on the top of the TiO_2 layer using a ZrO_2 paste, which acts as an insulating layer to prevent short circuit. Finally, about 10μm carbon CE was coated on the top of ZrO_2 space layer by printing carbon slurry and sintering at 400 ℃ for 25 min. After cooling down to room temperature naturally, the devices were laid horizontally and 4 μL of the $(5\text{-AVA})_x(MA)_{1-x}PbI_3$ precursor solution was dropped on the top of the mesoscopic carbon layer and then dried at 50 ℃.

Characterization

The X-ray Diffraction (XRD) spectra was used a D8 advance X-ray diffractor-meter with Ca Ka radiation (k=1.5418). The structure of carbon counter electrode based perovskite solar cell was observed using scanning electron microscopy (Nova NanoSEM450). Electrochemical impedance spectroscopy (EIS) of the cell was carried on a potentiostat (EG&G, M2273) under dark condition. Photocurrent density–voltage characteristics were measured with a Keithley 2400 source meter under illumination with an Oriel solar simulator composed of a 1000 W xenon arc lamp and AM 1.5 G filters. The illuminated active area was obtained with a black mask containing a circular hole of 0.13 cm^2.

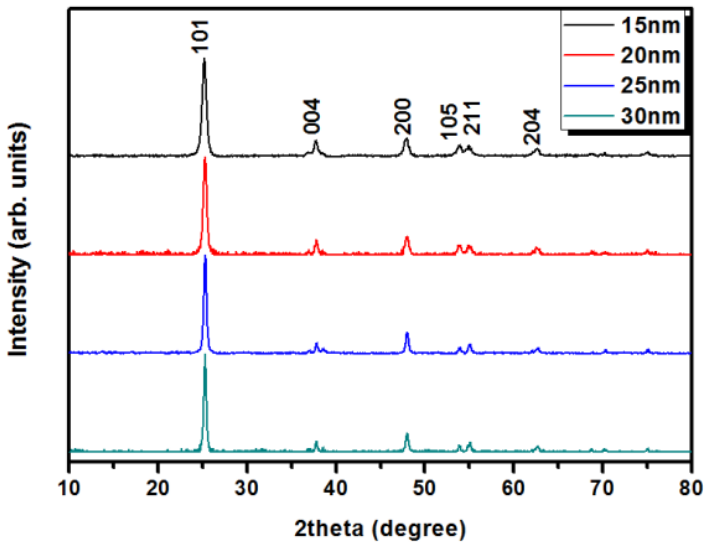

Figure S1. X-ray diffraction patterns of TiO_2 nanoparticles prepared by hydrothermal method.

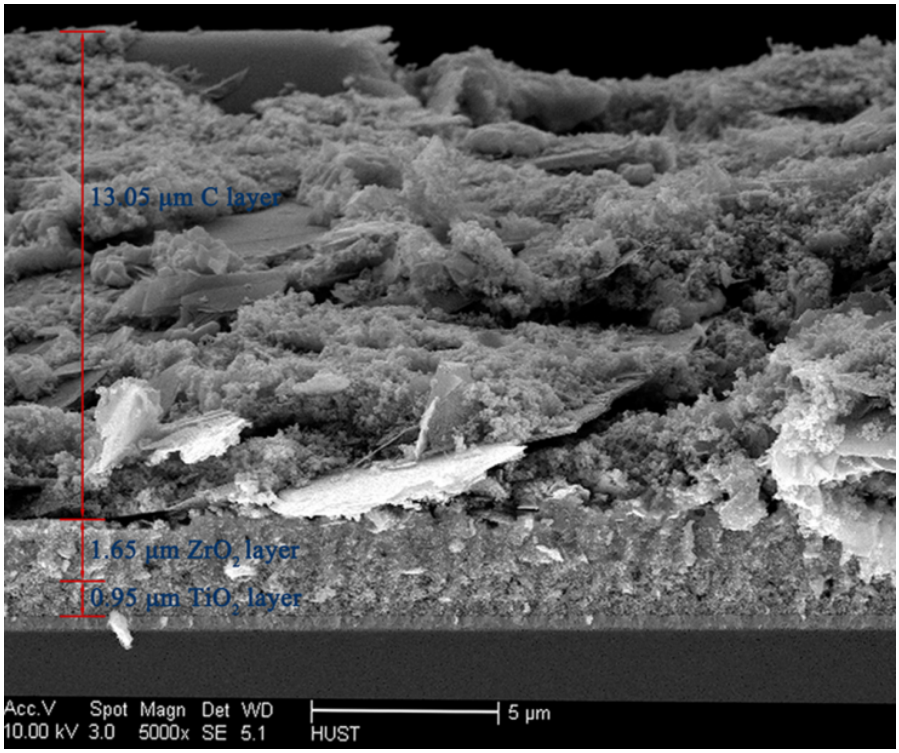

Figure S2. Cross-sectional SEM image of the carbon electrode based perovskite mesoscopic solar cells.

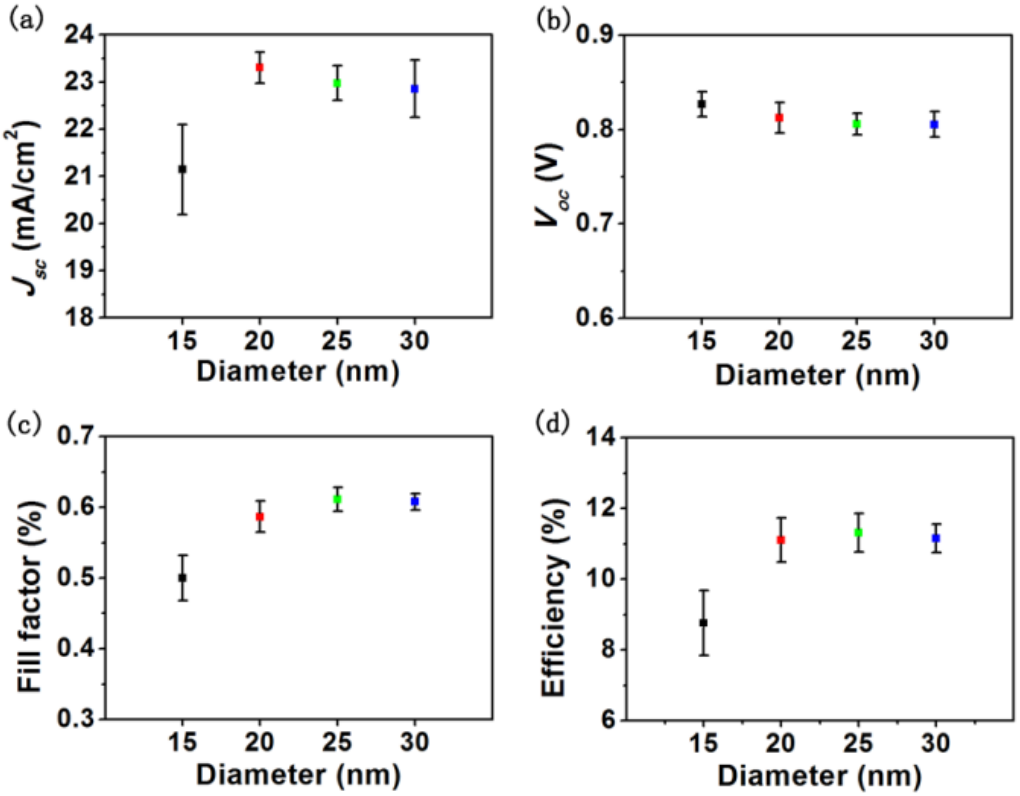

Figure S3. Size effects on the key photovoltaic performance parameters. (a) Short-circuit current density (J_{sc}), (b) Open circuit voltage (V_{oc}), (c) fill factor (*FF*), and (d) power conversion efficiency.

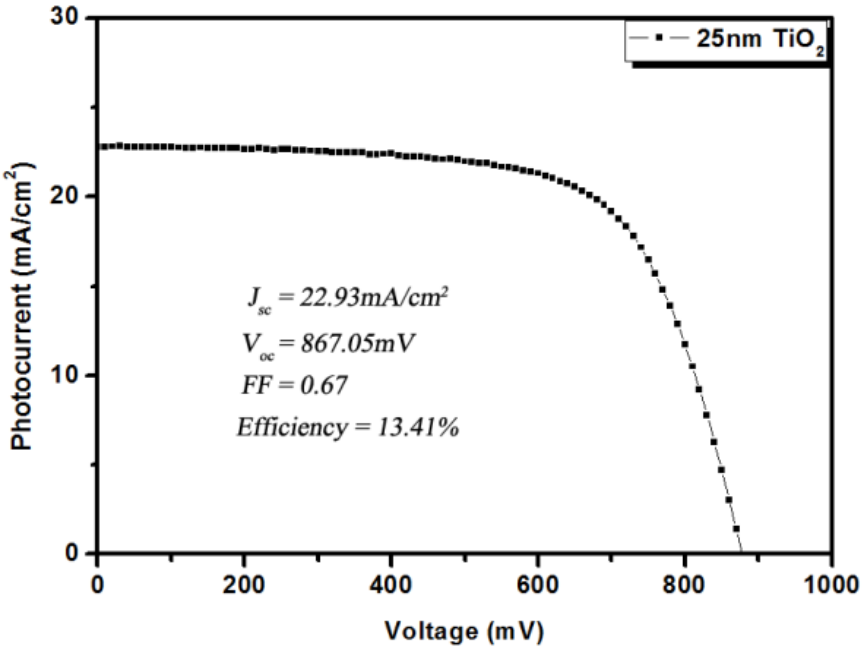

Figure S4. Photocurrent density versus applied potential curves of mesoscopic perovskite solar cells.

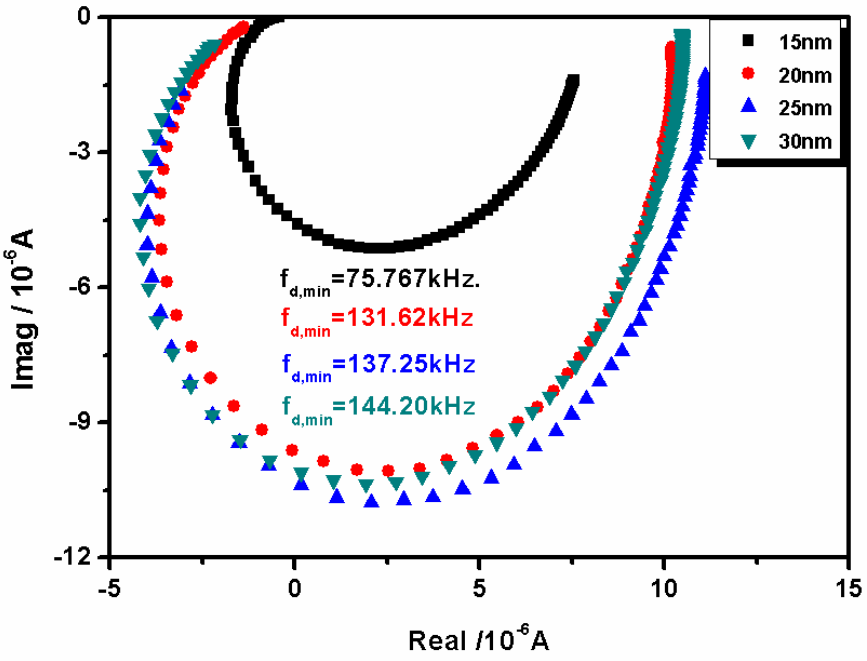

Figure S5. IMPS plots of carbon electrode based mesoscopic perovskite solar cells with different sized TiO_2 nanoparticles.

1 N. R. Neale and A. J. Frank, *Journal of Materials Chemistry*, 2007, **17**, 3216.