

## Supplementary Information

### Detailed methods

The scattering layer (polydispersed TiO<sub>2</sub> nanoparticles) with thickness of (2±1) μm was in situ electrospayed on top of TiO<sub>2</sub> nanofiber(~60 nm) layer with thickness of (10±1) μm. The method of preparation of the TiO<sub>2</sub> nanofiber layer was similar to our previous work<sup>1</sup>. First, TiO<sub>2</sub> nanofibers were directly electrospun onto a fluorine-doped SnO<sub>2</sub> conducting(FTO) glass from a precursor solution containing polyvinylpyrrolidone(PVP, M<sub>w</sub>=1,300,000, 1 g), titanium isopropoxide(TIP, 1.2 g), acetic acid (1 g) and ethanol (30 mL). All the materials are purchased from Sigma-Aldrich, and used as them purchased without purification. An electric potential of 70 kV was applied to the rotating electrode which was spaced 19 cm from the collector. The resulting composite nanofiber(PVP/TiO<sub>2</sub>) layer was exposed to moisture for about 5 hours to allow complete hydrolysis and then calcinated at 450°C for 2 hours. After calcination, this layer was peeled off from the original FTO glass and transferred to another FTO glass that has been pre-coated with an ultra-thin TiO<sub>2</sub> paste. The TiO<sub>2</sub> nanofiber photoanode was obtained after calcinating at 450°C for 2 hours. Subsequently, TiO<sub>2</sub> nanoparticles were electrospayed from the same nozzle-less device onto the TiO<sub>2</sub> nanofibers photoanode from a precursor solution containing PVP (M<sub>w</sub>=10,000, 1.5 g), TIP (3 g), acetic acid (2 g) and ethanol (30 mL). An electric potential of 50-70 kV was applied in the electrospaying. Finally, the resulting TiO<sub>2</sub> nanofiber photoanode with a scattering layer made up of nanoparticles was obtained after calcinating at 450°C for 2 hours. In order to compare the

effectiveness of the novel scattering layer with the traditional one, TiO<sub>2</sub> nanoparticles with monodispersed diameter of 200 nm was coated on a nanofiber photoanode with the same thickness of (2±1) μm. The resulting photoanode was further treated with an aqueous solution of TiCl<sub>4</sub> (40 mM) at 60°C for 15 min and then sensitized in a solution of 0.3 mM Ru based dye (N719) solution in absolute ethanol at 55°C for 24 hour. The soaked photoanode was washed with ethanol to remove unanchored dye molecules and subsequently dried in vacuum furnace at room temperature. Pt-sputtered FTO glass was used as the counter electrode. The counter electrode and dye anchored TiO<sub>2</sub> photoanode were assembled into a sandwich prototype with surlyn (DuPont, 25 μm). Finally, the electrolyte, made of 0.6 M 1-methy-3-propylimidazolium iodide(PMII), 0.05 M LiI, 0.05 M I<sub>2</sub>, and 0.5 M 4-tert-butyl pyridine(TBP) in acetonitrile, was injected into the sandwich-like device. The current density versus voltage (*J-V*) characteristics was measured by a Keithley 2400 source meter under illumination of AM1.5G 100 mW / cm<sup>2</sup> from a solar simulator ABET SUN 2000.

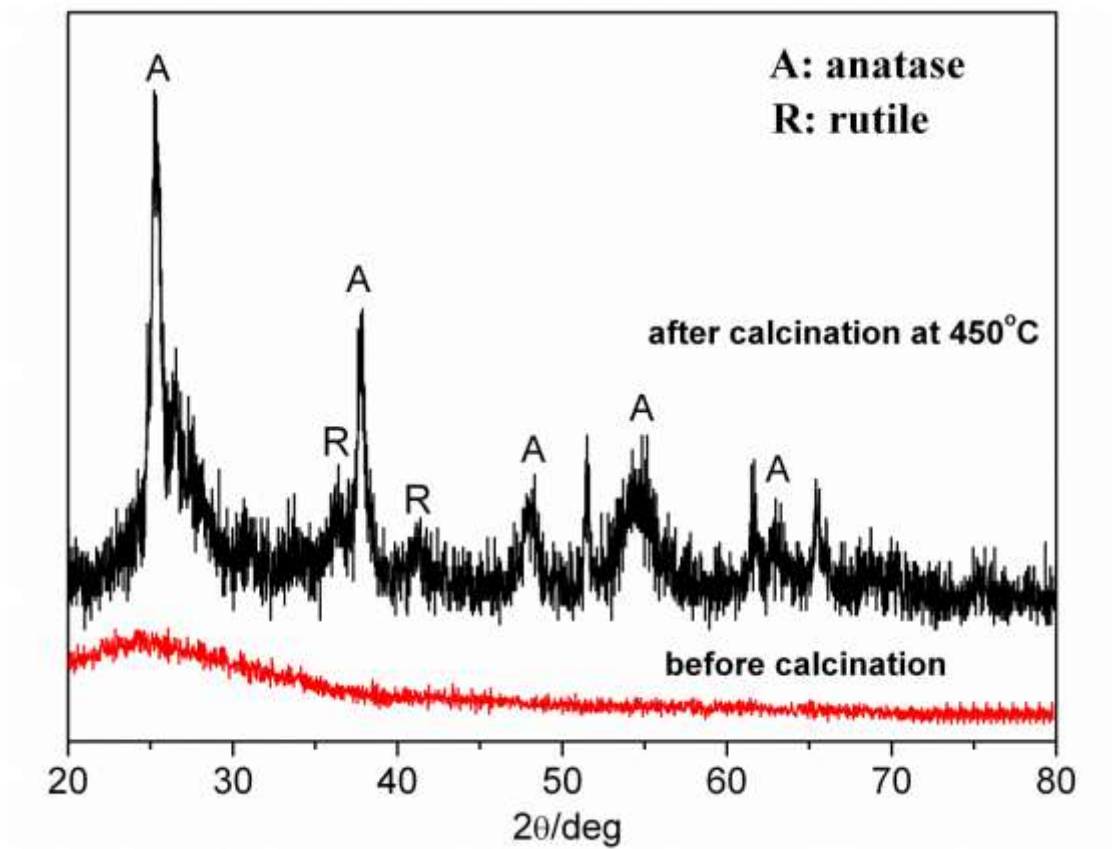


Fig S1. XRD patterns of electrospun  $\text{TiO}_2$  before and after calcination

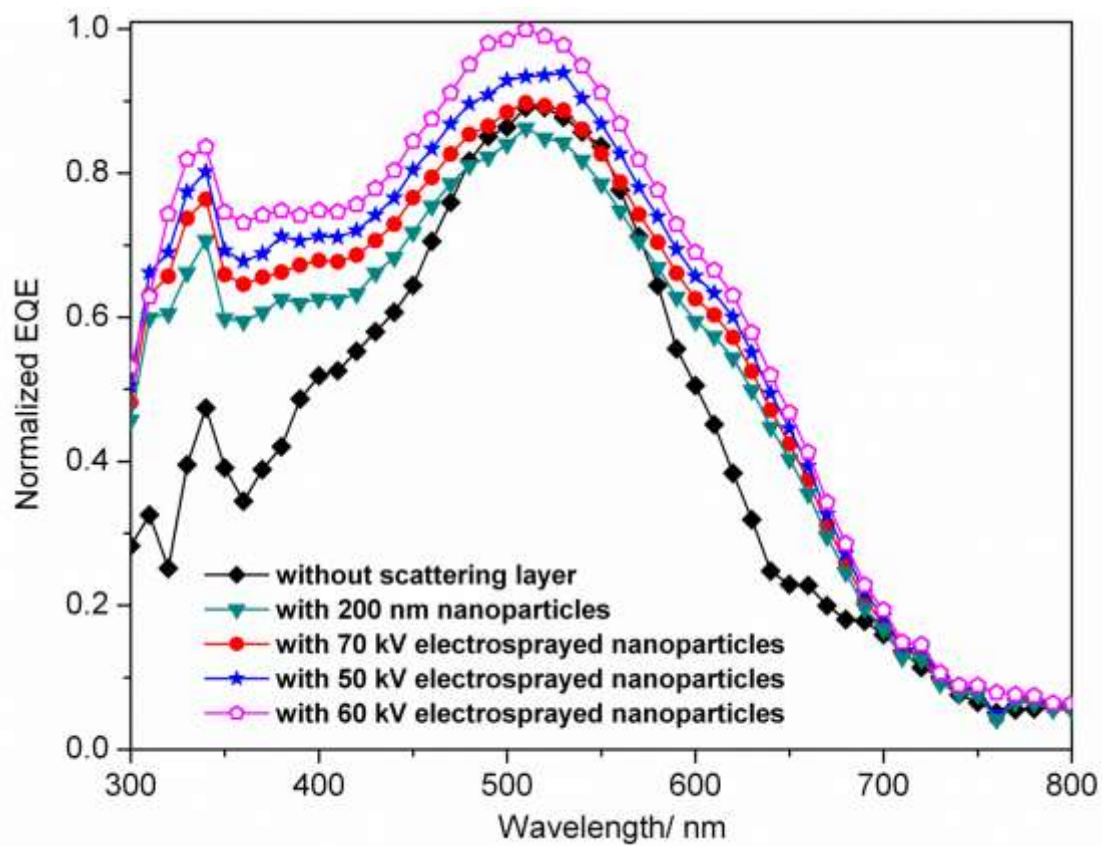


Fig. S2 The normalized EQE spectrum of DSSC devices with and without scattering layer

Reference

- [1] Yang, L.; Leung, W. W.-F., *Adv Mater* 2011, **23**, 4559