Supporting Information for:

Photocurrent Generation in a Light-harvesting System with Artificial Multifunctional Nanochannels

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Experimental Section

Fabrication of Nanochannels: Self-standing TiO_2 nanochannels were prepared using three-step electrochemical anodization.[1] Firstly, Ti foil (99.7%, Adrich) was pre-anodized at 60 V voltage provided by A DC power supply (HB17601SL2A, Shanghai Meitian Wiring Co., Ltd) for 1 h, and subsequently ultrasonically treated in 1 M HCl to remove the anodized layer completely. Then, Ti foil with textured surface was anodized at 60 V for another 2 h, followed by annealed at 450 ºC under ambient air for 3 h to induce TiO_2 crystallization. Finally, a free-standing membrane consisting of crystallized TiO_2 nanochannels was peeled off from Ti substrate by a third anodization at 12 V. The side of TiO_2 nanochannels detached form Ti substrate (tip side) was opened locally. The electrolyte used in each step was ethylene glycol (Xilong Chemical Factory) containing 0.25wt% ammonium fluoride (Xilong Chemical Factory) and 2vol% Milli-Q water.

Pt nanoparticles were deposited on the side of TiO_2 nanochannels with small pore diameter (tip side) using an ion sputtering coator (SBC-12, KYKY Technology Co., Ltd) with discharged current of 2 mA. Pt NPs size could be regulated by sputtering

time. The tip side of TiO_2 nanochannels faced the deposition flux zone to ensure single-sided surface platinization during ion sputtering.

Characterization: The morphologies of TiO_2 nanochannels were observed by a FEI Quanta FEG 250 environmental SEM and a JEOL JSM-7500F field-emission scanning electron microscope (FESEM). An INCA Energy 250 energy spectrum analyzer was used to confirm the modification of Pt NPs on the tip side of TiO_2 nanochannels. The average diameters of Pt NPs were estimated from the TEM images measured using a JEOL-2100 transmission electron microscope (TEM).

Photocurrent measurement: During the measurement, Pt NPs decorated TiO_2 nanochannels with geometric area of 0.2 cm^2 was mounted between two chambers of the electrochemical cell with a quartz window. The light source was provided by a super-high pressure mercury lamp with 365-nm parallel light output (CHF-XM500, Beijing Trusttech Co. Ltd, China) obtained by a band-pass filter. The light irradiance was 8.4 mW cm^{-2} measured with a power meter (UV-A, Photoelectric Instrument Factory of Beijing Normal University). Potassium chloride aqueous solution (1 mM, pH=6.05) was chosen as the electrolyte. The circuit was connected by two Ag/AgCl electrodes with anode facing to base side of nanochannels. A Keithley 6487 picoammeter (Keithley Instruments, Cleveland, OH) was used to measure the current-time (I-t) curves under discontinuous UV illumination. The open-circuit voltage was recorded by a CHI660D electrochemical workstation (Shanghai Chenhua Apparatus Co., China). Photocurrent and photovoltage were defined to be the absolute value of maximum photo-generated current and voltage calculated from I-t and U-t curves.

Supporting Figures S1-S7

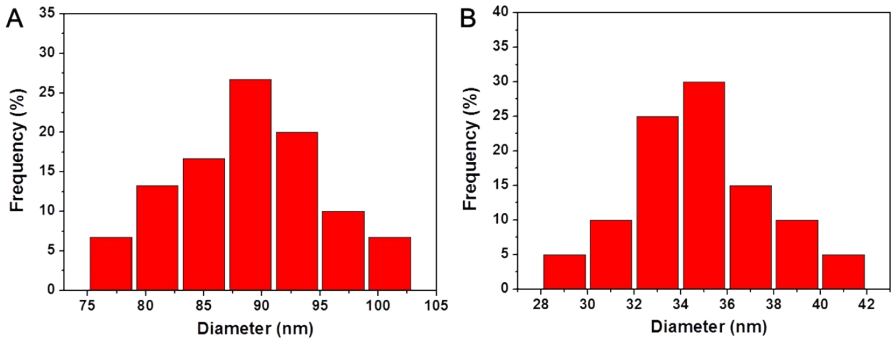

Figure S1. Pore size distribution histograms of base side (A) and tip side (B) of TiO_2 nanochannels. The average diameter of base side is determined to be ~89 nm with a distribution from 77 nm to 101 nm and that of the tip side is ~35 nm with a distribution from 29 nm to 41 nm.

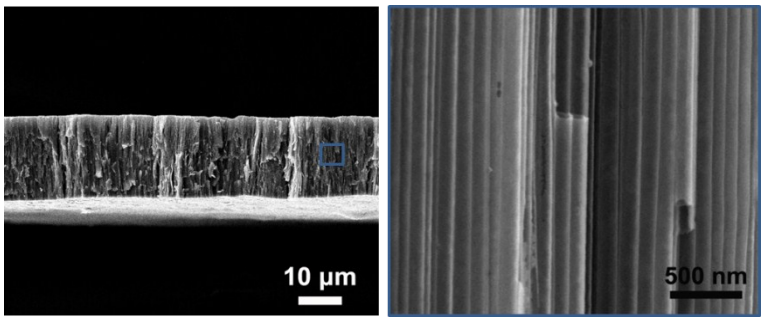

Figure S2. Cross-sectional SEM images of Pt NPs decorated TiO_2 nanochannels. Blue box indicates the magnified image. Nanochannels length, namely, the thickness of TiO_2 porous membrane is determined to be ~26.5 µm.

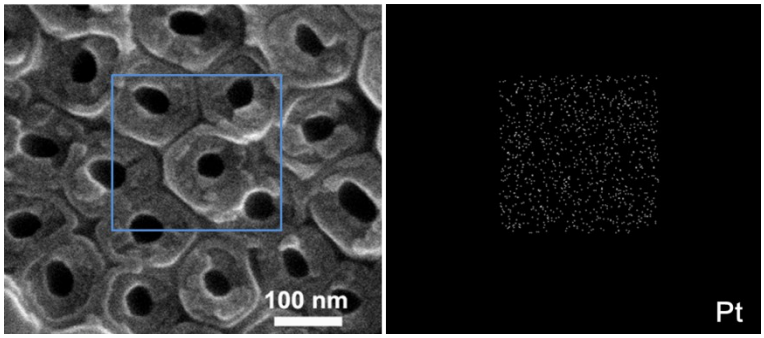

Figure S3. Pt element mapping of TiO_2 nanochannels with Pt NPs deposited on the tip side.

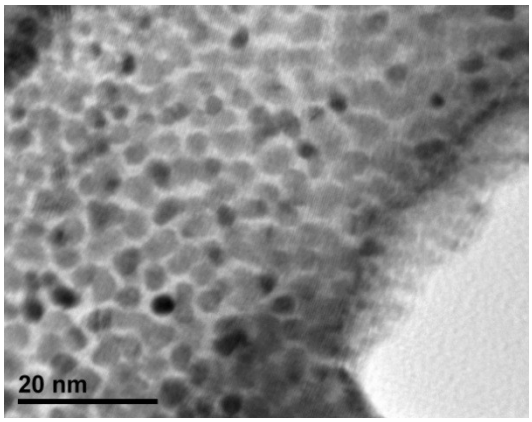

Figure S4. TEM image of Pt NPs with deposition time of 200s. Pt NPs are well distributed with little aggregation.

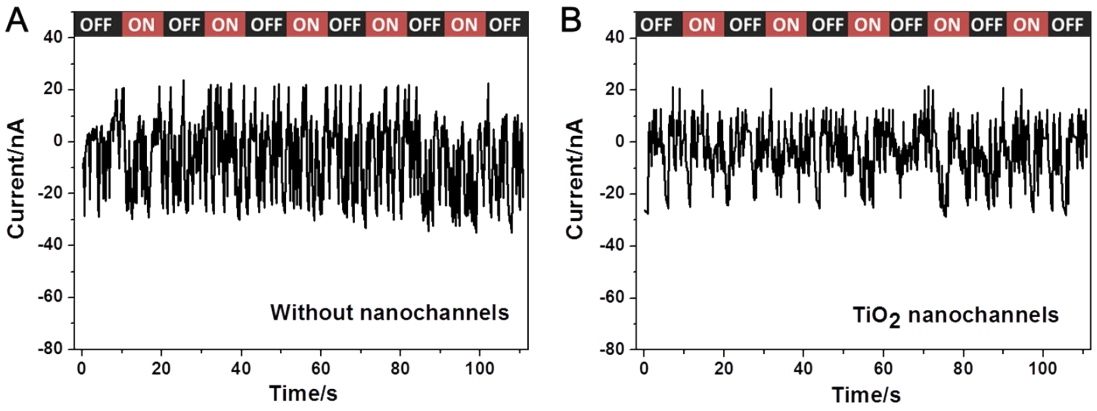

Figure S5. Photocurrent evolution in light-harvesting systems without nanochannels (A) and with TiO_2 nanochannels (B) under alternating UV light on-off irradiation.

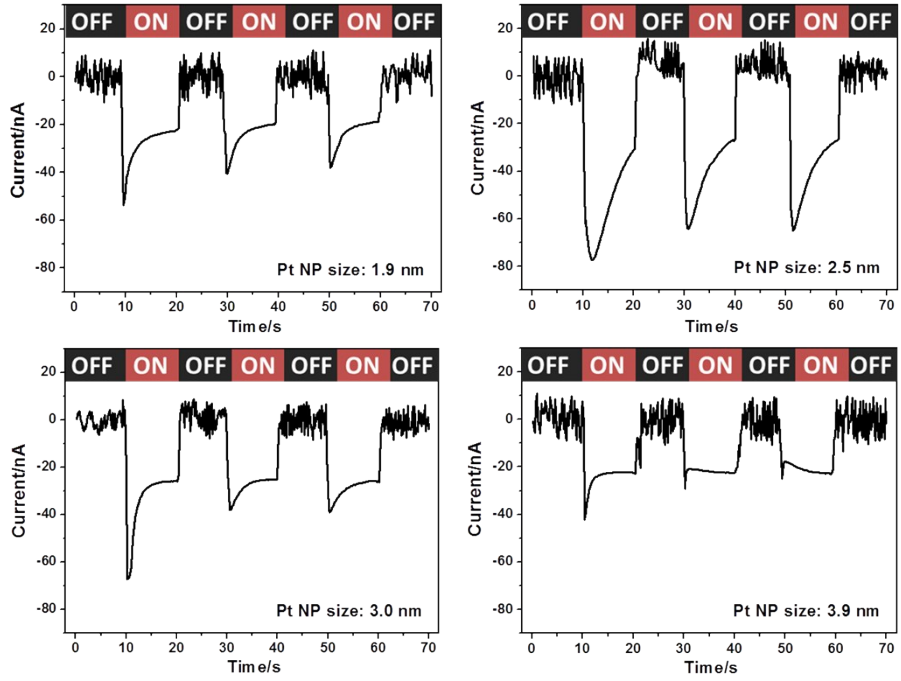

Figure S6. Photocurrent generation in a series of light-harvesting systems with different Pt NP size under dark/light switch.

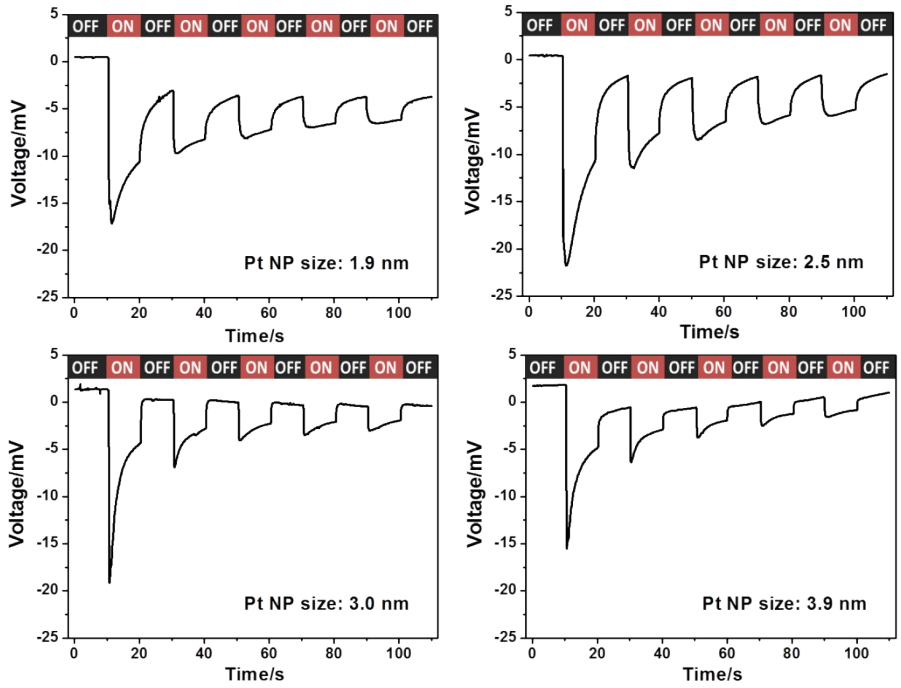

Figure S7. Open-circuit voltage evolution in a series of light-harvesting systems with different Pt NP size under dark/light switch.

Reference

1 Q. Chen and D. Xu, *J. Phys. Chem. C*, 2009, **113**, 6310.