Electronic Supplementary Information

Photosynthesis-inspired Bifunctional Energy-Harvesting Devices That Convert Light and Salinity Gradient into Electricity

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1. Experimental Section

1. 1 Materials and reagents

All chemical reagents were used without further purification. Nafion 117 membrane [a copolymer of tetrafluoroethylene and perfluoro (4-methyl-3, 6-dioxa-7-octene-1-sulfonic acid)] and Ti sheet (99.7%) were purchased from Sigma-Aldrich. Sodium sulfate and hydrofluoric acid were purchased from Beijing Chemical Works. Pt wire was purchased from Trillion Metals Co., Ltd. Deionized water was used for all of the experiments.

1. 2 Fabrication of the energy-harvesting device

The photosynthesis-inspired energy-harvesting device was composed of a custom-built two-chamber electrochemical cell, which was divided into two regions of anode and cathode. A quartz window was embedded on anode side of electrochemical cell for the transmission of UV light. The anode and cathode region was filled with Na_2SO_4 aqueous with a high and low concentration respectively, which were separated by a cation-selective membrane (Nafion 117). The light-active anode was a TiO_2 electrode consisting of nanotubular arrays (NTAs), which was prepared by a well-established anodization route in a fluoride-contained aqueous electrolyte [1-3]. Briefly, a commercially Ti sheet with a thickness of 0.25 mm (99.7%, Aldrich) was anodized at a voltage of 20 V for 20 min in 0.5% HF aqueous solution. The voltage was supplied by a direct-current power source (Beijing Dahua Co., Ltd). After naturally dried in the air, the anodized Ti sheet was annealed at 450 °C for 3 h to achieve the anatase crystallization. The cathode was a chemically inert Pt electrode, which was used to relay the light-induced electrons in the circuit.

1. 3 Characterization

The crystallization of TiO_2 NTAs was characterized with a Shimadzu XRD-6000 X-ray diffraction meter (XRD) at a diffraction angle between 20 º and 80 º. The surface and cross-sectional morphologies were studied using a FEI Quanta FEG 250 environmental scanning electron microscope (SEM).

1. 4 Electric measurement

The energy conversion performance of the device from light energy and salinity gradient was characterized by measuring the current-voltage (*I-V*) and current-time (*I–t*) curves using a CHI660E electrochemical potentiostat (Shanghai Chenhua Instrument Company) at two-electrode configuration. The short-circuit current density (I_{sc}) and open-circuit voltage (V_{oc}) were read from the intercept of *I-V* curve on the current and voltage axes respectively. The incident light was 365-nm parallel light with an irradiance of 5.7 mW/cm^2 from a super-high pressure mercury lamp (CHF-XM500, Beijing Trusttech Co. Ltd, China). The salinity gradient was provided by two Na_2SO_4 aqueous electrolytes with different concentrations. The power output of the devices was obtained from the *I-V* curves. The power output (*P*) at a certain voltage was calculated by multiplying voltage (*V*) and the corresponding current (*I*), *i. e.* $P=I \times V$. The maximal power output (P_{max}) was obtained by reading the peak value from the plot of power output vs. voltage (from 0 to V_{oc}).

The diffusion potential across the cation-selective membrane (E_{diff}) formed by the diffusion of Na_2SO_4 electrolytes from high to low concentration was obtained from the *I-V* curves measured by a Keithley 6487 picoameter (Keithley Instruments, Cleveland, OH) using two Ag/AgCl electrodes. The side of high-concentration Na_2SO_4 electrolyte was defined to be an anode region. The E_{diff} was read from the intercept of *I-V* curve on the voltage axis.

2. Supplementary Figure

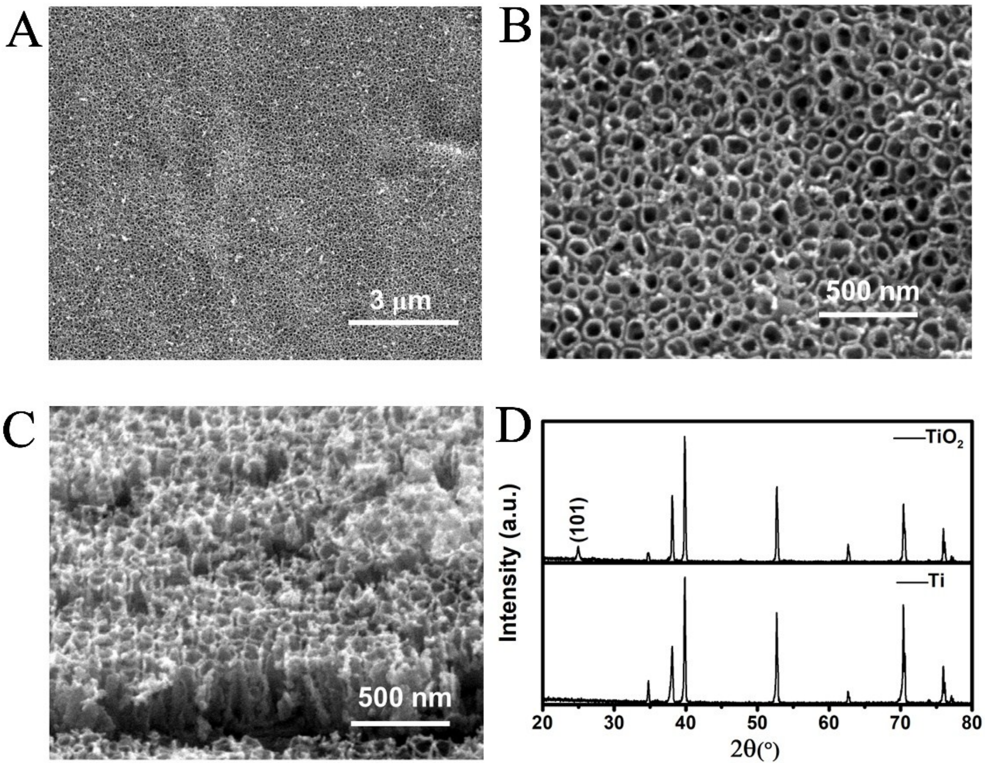

Fig. S1 (A, B) The top-viewed SEM image of TiO_2 nanotubular arrays (NTAs) at a low (A) and high (B) magnification. (C) The Cross-sectional SEM image. (D) XRD patterns of TiO_2 NTAs and Ti substrate. The large-scale, uniform and well-defined TiO_2 NTAs show an average internal diameter of ~72.5 nm and a wall thicknesses of ~14.9 nm. The length of TiO_2 NTAs is ~250.6 nm. TiO_2 NTAs demonstrated an anatase crystallization.

3. References:

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[3] Z. Liu, V. Subramania, M. Misra, *J. Phys. Chem. C* 2009, 113*,* 14028–14033.