Electronic Supplementary Information

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

Huihui Ren, Tianliang Xiao, Qianqian Zhang, and Zhaoyue Liu*
School of Chemistry, Beihang University, Beijing 100191, P. R. China.

E-mail: liuzy@buaa.edu.cn.

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-dioxaocta-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$_2$SO$_4$ 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 ° and 80 °. 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$_2$SO$_4$ 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$_2$SO$_4$ 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$_2$SO$_4$ electrolyte was defined to be an anode region. The $E_{diff}$ was read from the intercept of $I$-$V$ curve on the voltage axis.
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: