# Electronic Supplementary Information

## Light-regulated Ion Transport through Artificial Ion Channels Based on $TiO_2$ Nanotubular Arrays

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***Experiments***

Self-organized $TiO_2$ nanotubular arrays were prepared by three-step electrochemical anodization in an electrolyte consisting of 0.25 wt% ammonium fluoride (Xilong Chemical Factory) and 2 vol% Milli-Q water in ethylene glycol (Xilong Chemical Factory).[1, 2] A platinum foil with a size of 1 cm×1 cm served as a counter electrode. The voltage was provided by a DC power supply (HB17601SL2A, Shanghai Meitian Wiring Co., Ltd). To obtain regular $TiO_2$ nanotubes, Ti foil (99.7%, Adrich) was firstly anodized at 60 V for 1 h, and subjected to ultrasonication in 1 M HCl (Beijing Chemical Factory) to remove the anodized layer completely. The textured Ti surface was then anodized in the same electrolyte at 60 V for another 2 h, followed by calcined at 500 °C under ambient air for 3 h to induce $TiO_2$ crystallization. Finally, crystallined $TiO_2$ nanotubes were anodized at 12 V until the nanotubular arrays separated from the metallic substrate completely. In combination with the protons formed by the anodization, the fluoride ions in the electrolyte could dissolve the bottom side of $TiO_2$ nanotubular arrays locally. The morphologies of $TiO_2$ nanotubular arrays were studied using a FEI Quanta FEG 250 environmental scanning electron microscope (SEM).

The ion transport properties of artificial ion channels based on $TiO_2$ nanotubular arrays were characterized by measuring ionic current. $TiO_2$ nanotubular arrays were mounted on a polyvinyl chloride (PVC) holder by gluing its perimeter on a 0.5 cm diameter opening in the holder using epoxy resin (Fig S5). The holder was then placed as a separator wall in a double chamber cell with a quartz window. Potassium chloride (Beijing Chemical Factory) aqueous solution with variable concentration (0.1, 0.5, 1, 2.5 and 5 mM) was chosen as electrolyte. A Keithley 6487 picoammeter (Keithley Instruments, Cleveland, OH) was used to measure the ion current. Ag/AgCl electrodes were used to apply a transmembrane voltage across the nanotubular arrays because of their high sensitivity and good stability. The base side of nanotubular arrays was defined to be positive. Correspondingly, the ionic current flowing from the base to tip side was defined to be positive. The light resource 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 irradiance of the UV light was determined to be 11.5 mW/cm$^2$ measured with a power meter (UV-A, Photoelectric Instrument Factory of Beijing Normal University). The UV light was irradiated on the base side.

For control experiment, ionic currents without $TiO_2$ nanotubular arrays or through artificial ion channels based on a track-etched polyethylene terephthalate (PET) porous membrane were also investigated (Fig. S2). However, no photo-responses were detected in these two systems, demonstrating the light-regulated ion transport in our system was really induced by $TiO_2$ nanotubular arrays

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

[2] Z. Liu, Q. Zhang, T. Zhao, J. Zhai and L. Jiang, *J. Mater. Chem.* 2011, **21**, 10354 .

***Figures in Electronic Supplementary Information***

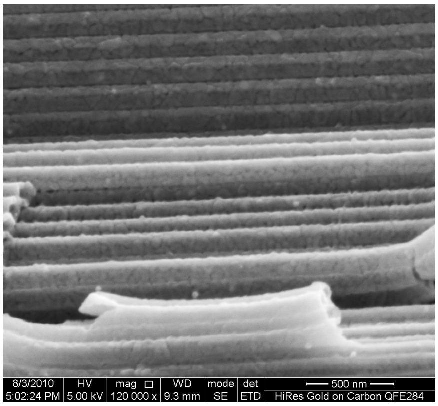

**Fig. S1** Magnified cross-sentional SEM images of self-standing $TiO_2$ nanotubular arrays

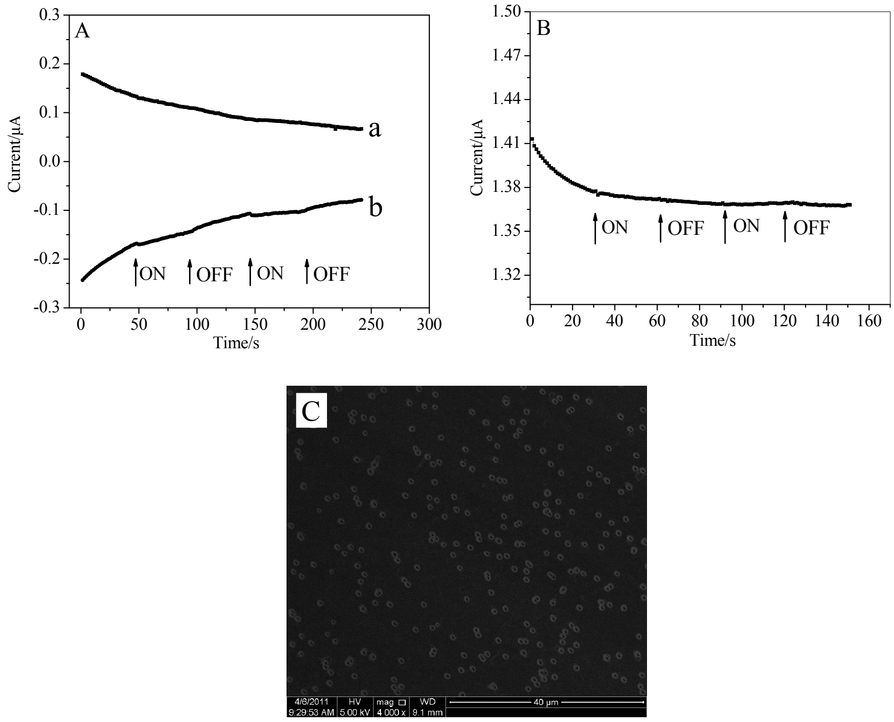

**Fig. S2** (A) Ionic current-time curves of control experiment without $TiO_2$ nanotubular arrays at (a) +0.2 V and (b) -0.2 V transmembrane voltages when the UV irradiance is switched on (ON) and off (OFF) alternately. The electrolyte is 1 mM KCl aqueous solution. (B) Ionic current-time curves of control experiment with artificial ion channels based on PET porous membrane at +1 V transmembrane voltage when the UV irradiance is switched on (ON) and off (OFF) alternately. The electrolyte is 1 mM KCl aqueous solution. (C) SEM image of the track-etched polyethylene terephthalate (PET) porous membrane.

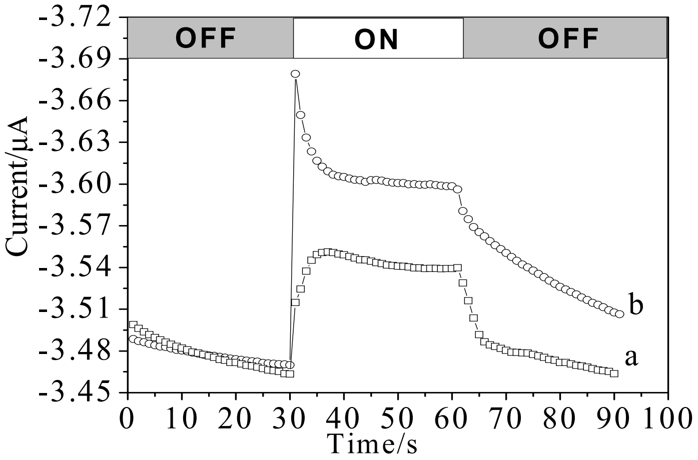

**Fig. S3** Ionic current-time traces of $TiO_2$ artificial ion channels at a transmembrane voltage of -0.2 V (a) without and (b) with adding of $CH_3OH$ (10 vol%) into 1 mM KCl electrolyte when UV is switched on (ON) and off (OFF) alternately. The UV light is irradiated on the base side of ion channels.

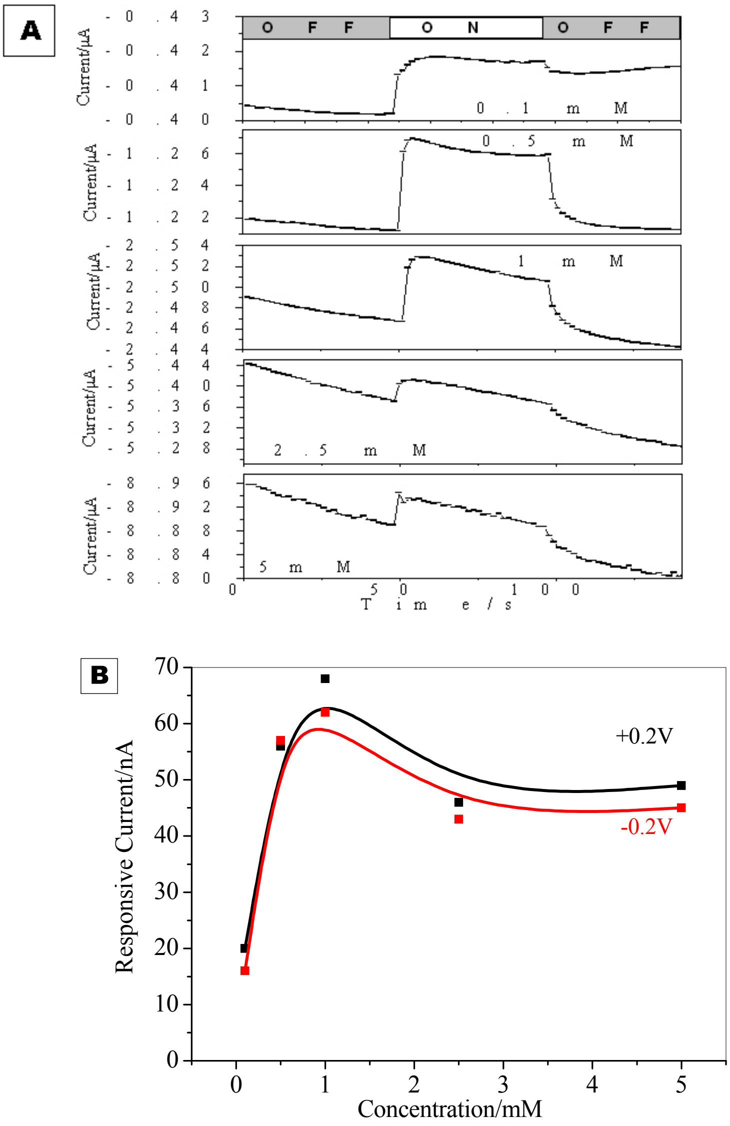

**Fig. S4 (A)** Ionic current-time traces of $TiO_2$ artificial ion channels at -0.2 V voltage in KCl electrolyte with concentration of 0.1 mM, 0.5 mM, 1 mM, 2.5 mM and 5 mM. The UV light is irradiated on base side. (B) The comparison of the responsive currents ($I_R$) dependence on the concentration of KCl electrolyte at +0.2 V and -0.2 V transmembrane voltages.

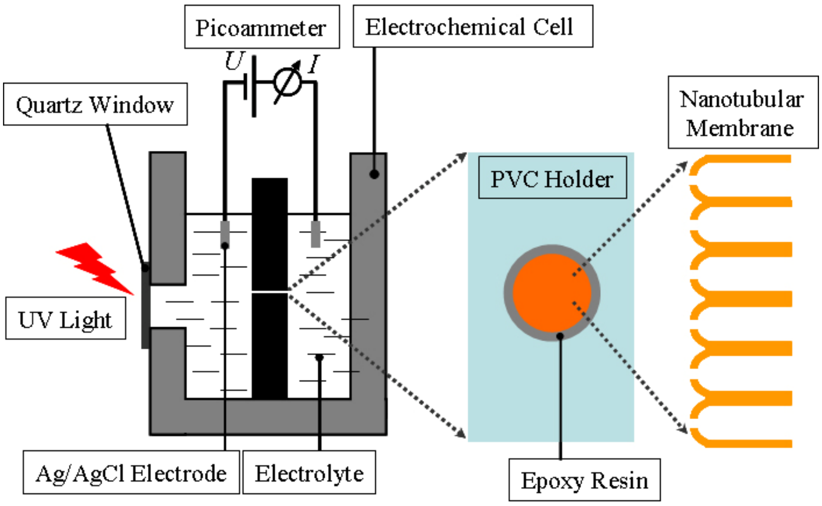

**Fig. S5** Schematic diagram of the home-made double-chamber electrochemical cell with quartz window for the measurements of ionic current.