## **Electronic Supplementary Information**

# Vertically Aligned Anatase TiO<sub>2</sub> Nanotubes On Transparent Conducting Substrates Using Polycarbonate Membranes

Sung Yeon Heo,<sup>a</sup> Dong Jun Kim,<sup>a</sup> Harim Jeon,<sup>a</sup> Bumsuk Jung,<sup>b</sup> Yong Soo Kang,<sup>c</sup>

Jong Hak Kim<sup>a,\*</sup>

<sup>a</sup> Department of Chemical and Biomolecular Engineering, Yonsei University, 262

Seongsanno, Seodaemun-gu, Seoul 120-749, South Korea

<sup>b</sup>Department of Environmental Engineering and Energy, Myongji University, Yongin,

Kyeonggido 499-728, South Korea

<sup>c</sup> WCU Program Department of Energy Engineering, Hanyang University, Seoul 133-

791, South Korea

<sup>\*</sup>To whom correspondence should be addressed:

Tel: +82-2-2123-5757; Fax: +82-2-312-6401

E-mail: jonghak@yonsei.ac.kr

### **Experimental**

#### Materials

Fluorine-doped tin oxide (FTO) conducting glasses (TEC8, 8 ohms sq<sup>-1</sup>) were from Pilkington. Track-etched polycarbonate (PC, diameter = 200 nm, thickness ~ $10 \mu \text{m}$ ) membranes were from Whatman Co. Titanium chloride (TiCl<sub>4</sub>, 99%), titanium isopropoxide (TTIP, 97%), titanium n-butoxide (TNB, 97%), poly(vinyl chloride) (PVC,  $M_n = 55000 \text{ g/mol}$ , poly(oxyethylene methacrylate) (POEM,  $M_n = 475 \text{ g mol}^{-1}$ ), 1,1,4,7,10,10-hexamethyltriethylene tetramine (HMTETA, 99%), copper chloride (CuCl, 99%), hydrogen chloride solution (HCl, 37%), fumed silica (SiO<sub>2</sub>, 7 nm), poly(ethylene glycol dimethyl ether) (PEGDME,  $Mn = 500g \text{ mol}^{-1}$ ), iodine(I<sub>2</sub>), 1-methyl-3-propyl imidazolium iodide (MPII), p-toluenesulfonic acid monohydrate (98.5%) and benzyl alcohol (99.8%) were from Sigma-Aldrich. Ethanol (99.7%), n-butanol (99.8%), acetonitrile (100%), isopropyl alcohol (IPA, 99.5%), tetrahydrofuran (THF, 100%), Nmethyl pyrrolidone (NMP, 99.5%) and methanol (99.5%) were from J.T. Baker. Acetylacetone (99%) and toluene (99.8%) were from Dae Jung. Ruthenium dye (N719) was from Solaronix. Paste (18 NR-T) with TiO<sub>2</sub> nanoparticles (NP) was from Dyesol-Timo. All solvents and chemicals were of reagent grade and were used as received.

#### Preparation of three types of precursor solutions

TTIP solution was prepared by successive addition of TTIP, HCl and H<sub>2</sub>O at a volume ratio of 2:1:1. The solution was aged at room temperature for 30 min and diluted five times with ethanol. Pre-1 solution was prepared by dropwise addition of 1.5 mL of TiCl<sub>4</sub> to the 10 mL of toluene with magnetic stirring. The solution was poured into 50 mL of benzyl alcohol and stirred for 1 hour. After heating in an oven at 70 °C for 12 hours, the resulting white solution was precipitated by centrifugation at 12,000 rpm for 30 min. Added to 0.4 g of precipitates was 2 ml of THF/H<sub>2</sub>O (20:80 wt. ratio) solution, followed by 0.1 ml of HCl/H<sub>2</sub>O (37:63 wt. ratio) solution to increase homogeneity. Pre-2 solution was prepared by mixing 4 ml of acetylacetone and 3 ml of butanol. Then, 5 ml of TNB was slowly dropped into 7 ml of prepared solution, and 0.055 g of ptoluenesulfonic acid monohydrate dissolved in 2.6 ml of H<sub>2</sub>O was added. The solution was heated at 60 °C for 12 h yielding a non-aggregated transparent solution was made.

#### Preparation of TiO<sub>2</sub> NT on the FTO substrate

The PC membrane was immersed in the different precursor solutions for 5 h. Strong attachment of PC membrane to the FTO substrate was achieved by introducing a thin adhesion layer based on a PVC-*g*-POEM graft copolymer. PVC-*g*-POEM was

synthesized *via* atom transfer radical polymerization (ATRP) following the previously reported procedure [1-3]. Then, 0.15 g of PVC-*g*-POEM was dissolved in 4.5 mL of THF, followed by the addition of 1.8 mL of TTIP/HCl solution. This solution was coated onto the FTO substrate using a spin coater at 1500 rpm for 30 sec. Before the PVC-*g*-POEM/TTIP/HCl was dried completely, the as-immersed PC membrane was removed and attached to the adhesion layer. Finally, samples were calcined at 500 °C for 2 h to remove the template and crystallize the TiO<sub>2</sub> NTs.

#### **Fabrication of DSSCs**

All FTO glasses were washed sequentially with ethanol, acetone and ethanol. Asprepared TiO<sub>2</sub> NT photoanode was trimmed to an active area of 0.16 cm<sup>2</sup>. Annealed TiO<sub>2</sub> NTs were immersed in N719 dye solution (13 mg in 50 g of ethanol) at 50 °C for 2 h. Counterelectrodes were prepared *via* thermal decomposition of 7 mM H<sub>2</sub>PtCl<sub>6</sub> solution in IPA at 450 °C for 30 min. Quasi-solid state polymer electrolytes were prepared from PEGDME, MPII, SiO<sub>2</sub> and I<sub>2</sub> dissolved in acetonitrile and dropped on the photoelectrode. The photoanode and counter electrode were superposed and pressed by clipping to achieve slow evaporation and a thin electrolyte layer. Cells were placed in a vacuum oven for a day for complete evaporation of the solvent. Cells were then sealed with an epoxy resin.

#### Characterization

The morphology and structure of  $TiO_2$  were investigated using a field-emission scanning electron microscope (FE-SEM, SUPRA 55VP, Germany, Carl Zeiss) and energy-filtering transmission electron microscope (EF-TEM, LIBRA 120, Germany, Carl Zeiss). Dyes were desorbed by immersing the dye-adsorbed TiO<sub>2</sub> phtoelectrodes in 0.1M NaOH solution. The amounts of desorbed dye were analyzed using a UV-visible spectrophotometer (Shimadzu) in the range of 200 to 1100 nm. Photovoltaic performances were measured using a Keithley Model 2400 and a 1000W xenon lamp (Oriel, 91193). The light was homogeneous up to an  $8 \times 8$  in<sup>2</sup>, and its intensity was calibrated with a Si solar cell (Fraunhofer Institute for Solar Energy System, Mono-Si + KG filter, Certificate No. C-ISE269) at a 1 sun illumination (100mW cm<sup>-2</sup>). Calibration was checked by a NREL-calibrated Si solar cell (PV Measurements Inc.). Intensitymodulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS) were measured using an electrochemical workstation equipped with a frequency response analyzer under a modulated light emitting diode (635 nm) driven by a source supply, providing both DC and AC components of the illumination.

5

Frequency was set in the range of 10MHz to 0.01Hz.

- [1] S. H. Ahn, J. H. Koh, J. A. Seo and J. H. Kim, Chem Commun, 2010, 46, 1935-1937.
- [2] S. H. Ahn, H. Jeon, K. J. Son, H. Ahn, W. G. Koh, D. Y. Ryu and J. H. Kim, J Mater Chem, 2011, 21, 1772-1779.
- [3] S. H. Ahn, W. S. Chi, J. T. Park, J. K. Koh, D. K. Roh and J. H. Kim, Adv Mater, 2012, 24, 519-522.

**Fig. S1**. XRD pattern of TiO<sub>2</sub> NTs prepared by Pre-2 on the FTO substrates. \* FTO peak.  $2\theta = 25.5$ , 38.0, 48.2, 54.3, 55.2 and  $61.4^{\circ}$  corresponding to (101), (004), (200), (105), (211) and (115) reflections of the anatase TiO<sub>2</sub> phase. Note that rutile TiO<sub>2</sub> phase appears at 2 $\theta$  values of 27.5°, 36.2°, 41.4° and 54.5°, corresponding to (110), (101), (111) and (211) crystal planes, respectively (ICDD-JCPDS database, NO. 77-0441).



**Fig. S2**. Cross-section SEM image of  $TiO_2$  photoelectrode fabricated with Pre-2, followed by infiltration of nanoparticles.

