Electronic Supplementary Information

Vertically Aligned Anatase TiO$_2$ Nanotubes On Transparent Conducting Substrates Using Polycarbonate Membranes

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**Experimental**

**Materials**

Fluorine-doped tin oxide (FTO) conducting glasses (TEC8, 8 ohms sq\(^{-1}\)) were from Pilkington. Track-etched polycarbonate (PC, diameter = 200 nm, thickness ~10 \(\mu\)m) membranes were from Whatman Co. Titanium chloride (TiCl\(_4\), 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\(_2\), 7 nm), poly(ethylene glycol dimethyl ether) (PEGDME, \(M_n = 500 \text{ g mol}^{-1}\)), iodine(I\(_2\)), 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%), N-methyl 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 \(\text{TiO}_2\) 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 H₂O 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 TiCl₄ 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/H₂O (20:80 wt. ratio) solution, followed by 0.1 ml of HCl/H₂O (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 p-toluenesulfonic acid monohydrate dissolved in 2.6 ml of H₂O was added. The solution was heated at 60 °C for 12 h yielding a non-aggregated transparent solution was made.

Preparation of TiO₂ 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 TiO₂ NTs.

Fabrication of DSSCs

All FTO glasses were washed sequentially with ethanol, acetone and ethanol. As-prepared TiO₂ NT photoanode was trimmed to an active area of 0.16 cm². Annealed TiO₂ 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 H₂PtCl₆ solution in IPA at 450 °C for 30 min. Quasi-solid state polymer electrolytes were prepared from PEGDME, MPII, SiO₂ and I₂ 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$_2$ photoelectrodes 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 × 8 in$^2$, 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$^{-2}$). Calibration was checked by a NREL-calibrated Si solar cell (PV Measurements Inc.). Intensity-modulated 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.
Frequency was set in the range of 10MHz to 0.01Hz.


**Fig. S1.** XRD pattern of TiO$_2$ NTs prepared by Pre-2 on the FTO substrates. * FTO peak. 2θ = 25.5, 38.0, 48.2, 54.3, 55.2 and 61.4° corresponding to (101), (004), (200), (105), (211) and (115) reflections of the anatase TiO$_2$ phase. Note that rutile TiO$_2$ phase appears at 2θ 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.