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Electronic Supplementary Information

For

Facile fabrication of aligned doubly open-ended TiO_2 nanotubes, via a selective etching process, for use in front-illuminated dye sensitized solar cells

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Contents

1. Experimental section:

Fabrication both end-opened TiO_2 nanotubes membrane

All anodization experiments were carried out at in ethylene glycol solution containing 0.25 wt% NH_4F and 0.3vol% at the room temperature. TiO_2 nanotube arrays were prepared by anodization of Ti foil (99.7%, 0.25 μm, Aldrich) in a two electrode electrochemical cell with a carbon sheets as the counter electrode. Before anodization, Ti foil was ultrasonically washed in acetone, ethanol, and D.I water. The anodization process was divided into two steps. At the first step, the Ti foil anodized at 60V for 120min, and resulting sample was ultrasonically washed by ethanol to remove electrolyte and debris of electrolyte, followed by annealing at 250^{o}C for 2hr. The annealed sample was anodized again in same anodizing condition in short time (5~10 min). After these two steps, anodized sample was immersed Ti foil in 33 wt% H_2O_2 solution. About 5 min later, TNTs film was separated from Ti foil, and closed bottom layer of TiO_2 nanotube was start to open with increase immersing time. After etching process, TiO_2 nanotube membrane was washed by ethanol, and dried in air condition.

Dye sensitized solar cell fabrication

Before attaching TiO_2 nanotube membrane on FTO substrate, 0.2M TIP solution was spin-coated on FTO to prevent charge recombination between electrolyte and FTO. As-prepared TiO_2 nanotube membrane was adhered onto FTO glass substrate using viscous TiO_2 nano-particles paste (ENB) which was printed onto FTO glass by doctorblade technique. Fixed TiO_2 nanotube and nanoparticles (TNT/NP) film was annealed at 550 ^{o}C for 30min, followed by immersing in 0.03Mm $(Bu_4N)_2Ru(dcbpyH)_{2}$-$(NCS)_2$ (N719 dye, Solaronix) solution for 24h. Afterward, the TiO_2 electrode was rinsed with acetonitirle in order to remove physically adsorbed dye. The dye-absorbed TiO_2 electrode were sandwiched together with a Pt-coated FTO glass counter electrode using 60 μm -thick-hot-melt spacer. The electrolyte, 0.03 M I_2, 0.6 M 1-butyl-3-methylimidazolium iodide iodide (BMII), 0.1 M guanidinium thiocyanate, 0.5 M LiI and 0.5 M 4-*tert*-butylpyridine in acetonitrile and valeronitrile (85:15), was introduced into the space between the sandwiched full cells.

Characterization

Scanning electron microscopy (SEM) measurement Field emission scanning electron microscope (FE-SEM, Hatachi S 4800) was utilized for morphological and structural characterization.

X-ray diffraction measurement X-ray diffraction analysis (XRD, Rigaku D/Max-2200/PC) was employed for crystal phase identification. The angle range examined was 20-80 degree at the θ-2θ scan mode.

Photoelectrochemical measurement The current-voltage characteristics were measured using a Keithley 2400 source meter under simulated AM 1.5G illumination (100 mW cm^{-2}) provided by a solar simulator (69920, 1 kW Xe lamp with an optical filter, Oriel) to determine the open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), fill factor (FF), and conversion efficiency (η). The incident light intensity was calibrated with reference to a Si solar cell equipped with an IR-cutoff filter (KG-5, Schott). The voltage step and delay time for the measurement were 10 mV and 40 ms, respectively.

Electron transport and life time measurement The time constants for the recombination and collection of the photo-injected electrons were determined by intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS) using a potentiostat (Complete CIMPS-1 systme, ZAHNERelektrik GmBH&CoKG). The spectra were recorded at light intensity that varied from 10 to 100 W/m^2. The photo-injected electron life and transport time was calculated from the middle frequency (f_{min}, $\tau = 1/2\pi f$). Charge collection (η_{cc}) efficiency was determined from following equation ($\eta_{cc} = 1 - (\tau_{trans}/\tau_e)$).

UV-Vis absorption measurements UV-Vis spectrophotometry (using an Optizen POP spectrophotometer) was used to measure adsorbed dye amount onto the TiO_2 films, and dye detached by immersing a 0.1 M KOH aqueous solution for 30 min, followed by measuring the absorbance of the resulting solution.

2. Figures

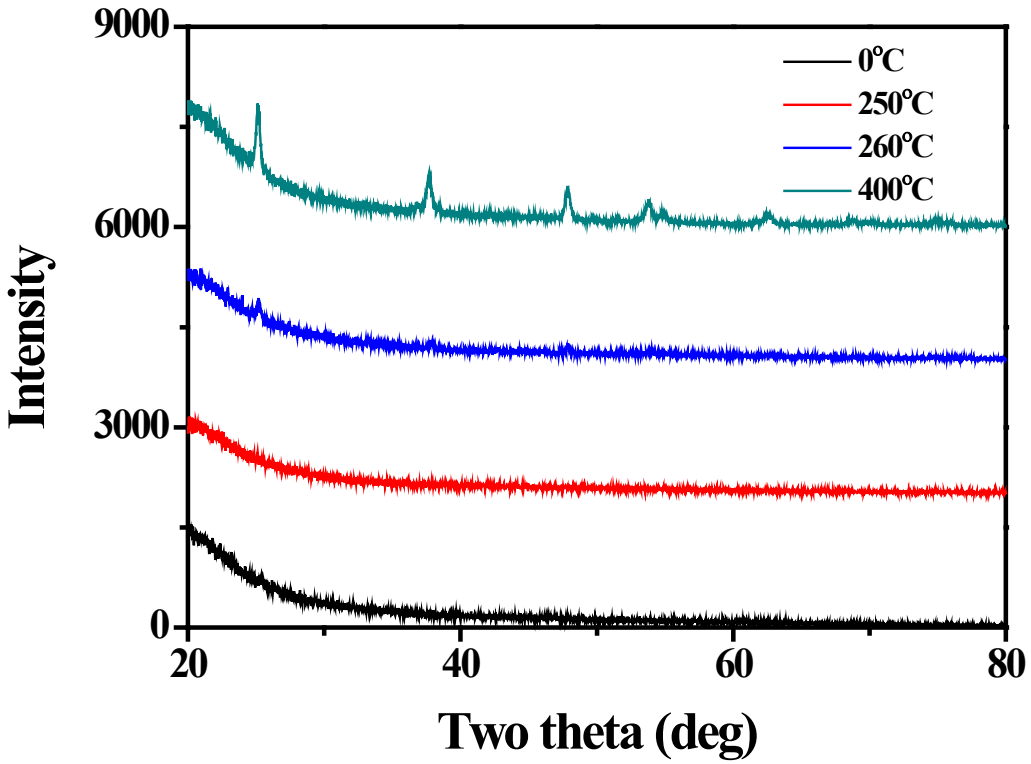

Figure S1. XRD patterns of freestanding NT membrane with increasing temperature. As shown in spectra, crystal phase of un-annealed NT (0 °C). This amorphous phase remained until 250 °C, and the antase peaks appeared at 260 °C. The anatase peak was clearly observed at 400 °C.

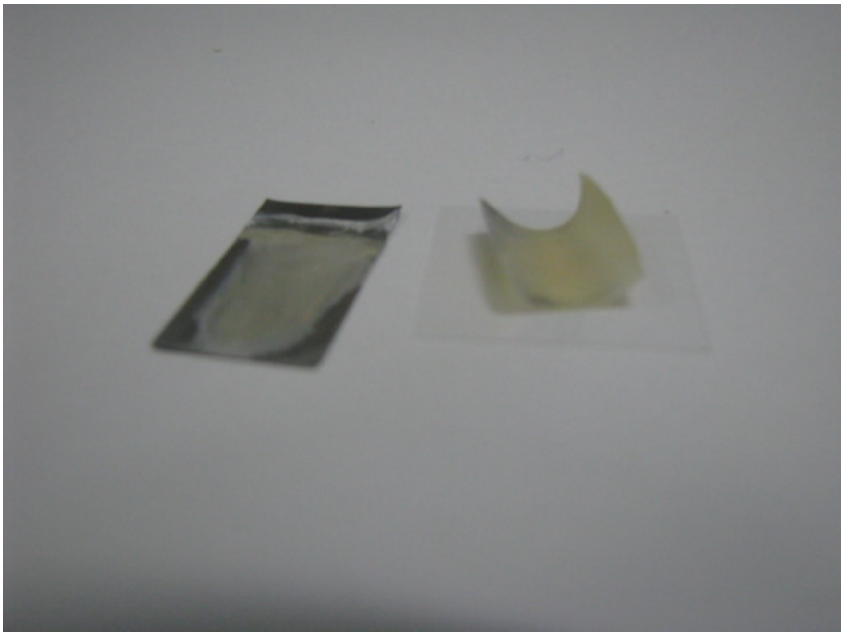

Figure S2. Digital photograph of the un-annealed NT membrane detached from the Ti foil. While un-annealed NT membrane frequently curled or rolled at the air drying condition, annealed NT membrane until 250 ^{o}C did not show these problems as shown in Figures 2(a).

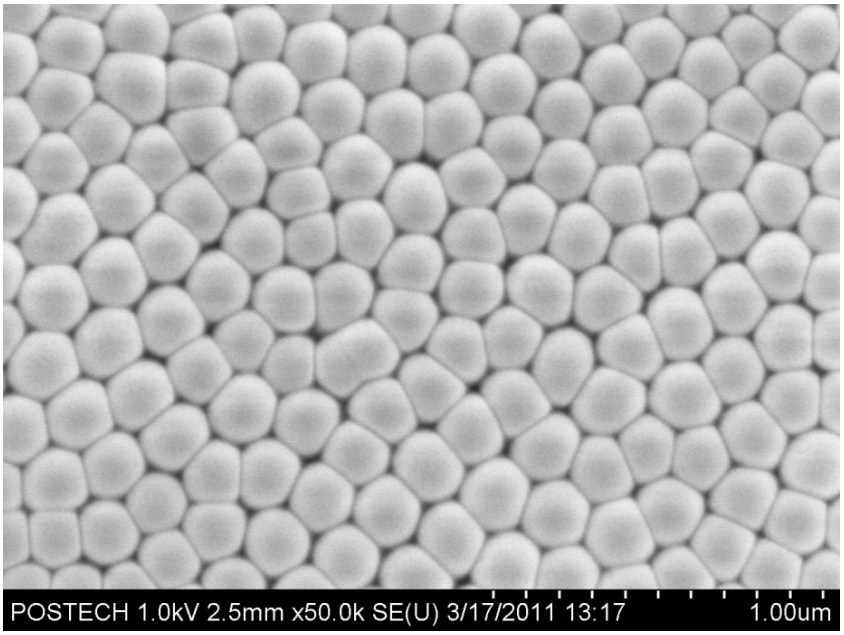

Figure S3. SEM images of bottom layer of the crystallized (annealed 400 ^{o}C) NT membrane after detaching from Ti foil. Because crystallized (anatase phase) NT was chemically stable, additional etching process not occurred during 2nd anodization, thus bottom layer of NT remained closed.

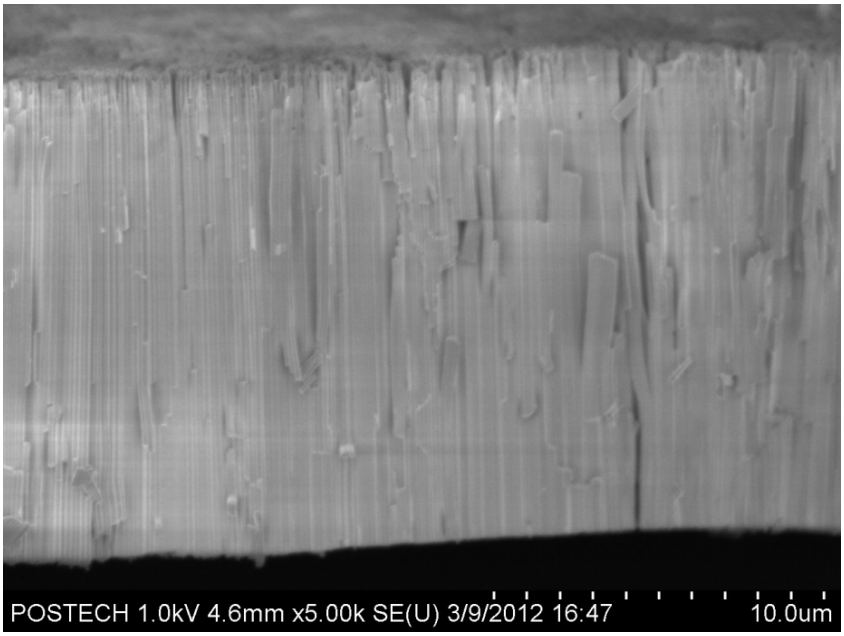

Figure S4. Cross-section SEM images of the NT membrane used in DSCs. Thickness of this membrane was about 14 μm fabricated from 120min anodization.

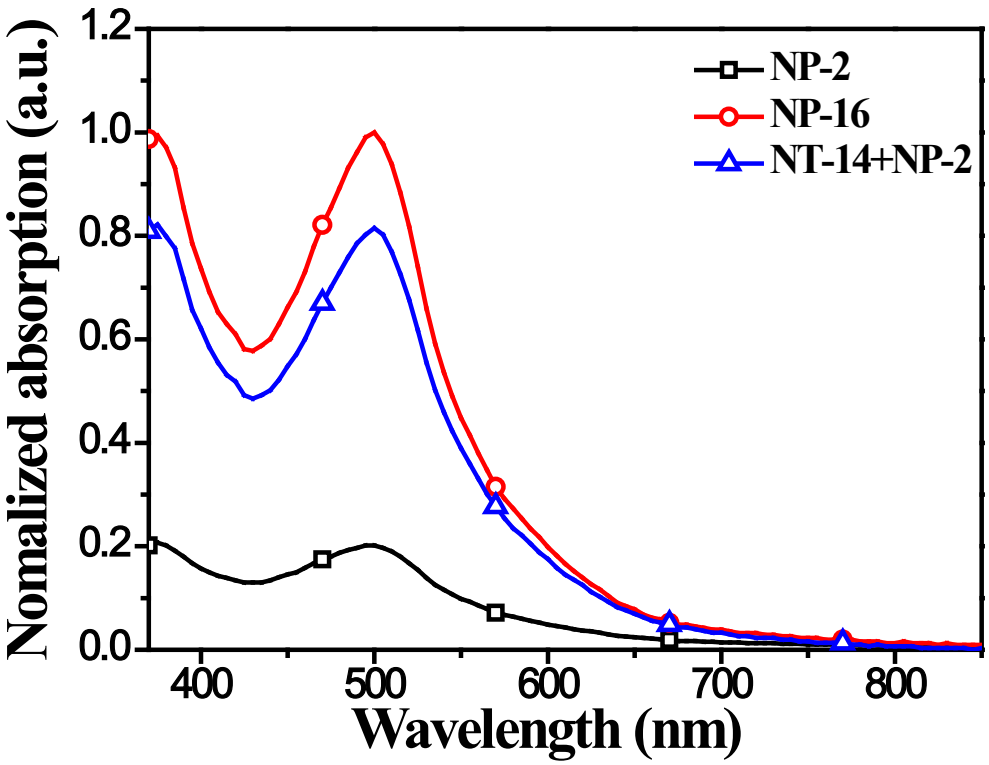

Figure S5. UV-Vis absorption spectra of dye detached solution from the corresponding TiO_2 nanotubes and nanoparticles film. Dye was detached by immersing a 0.1 M KOH aqueous solution for 30 min. Thicknesses of NP2 and NP16, NT14 corresponded to 2, 16, 14μm respectively, and dimension of cell was 0.48cm^2.