Supporting Information

Open-ended TiO_2 nanotubes formed by two-step anodization and their application in dye-sensitized solar cells

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Experimental details

Fabrication of TiO2 nanotube (NT) array electrode.

Titanium (Ti) foils with a thickness of 0.25 mm were degreased by sonication in acetone and ethanol consecutively for five minutes. They were then rinsed with deionized (DI) water and dried in an oven at 100°C for 10 minutes. For the anodization process, the electrolyte used was 0.25 wt% ammonium fluoride (99+%, BDH) in anhydrous ethylene glycol (99.8%, GR Ph Eur international laboratory) at room temperature. The Ti foil served as the anode with platinum (Pt) the counter electrode. The anodization was performed for different hours at 50 V. After the anodization, a sonication process was used to remove bundles of clumped remnants on top of the TiO_2 NTs. The anodized substrate was then soaked in a water bath at 50°C for 1 h to remove the organic electrolyte. After that, the as-grown sample was heat treated at 270°C for 3 h while the anodized oxide layer was still amorphous (Fig. S5). A second anodization with the same anodization conditions as the first was conducted for another 2 h. Finally, a free-standing and open-ended TiO_2 NT array was obtained by dipping the as-grown sample into 37 wt% H_2O_2 solution and detaching it from the substrate or simply by prolonging the second anodization time until the first layer was fully detached from the Ti substrate and their SEM images are shown in Fig. S2. Subsequently, the open-ended TiO_2 NT layer was adhered to a FTO substrate by doctor-bladed NP paste. After annealing the assembly at 450°C for 3 h with heating and cooling rates of 1°C/min, the NT and FTO (with and without NR) were bonded togetherS2 to form the TiO_2 NT array electrode (Fig.S1).

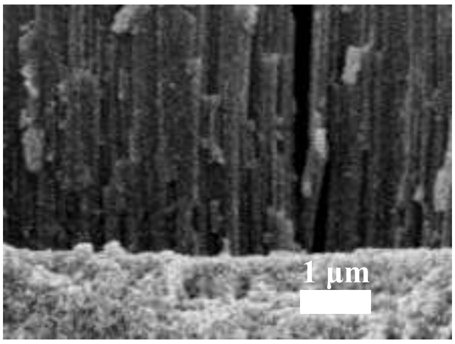

Fig. S1: SEM image of the NTs array attached on FTO after annealing.

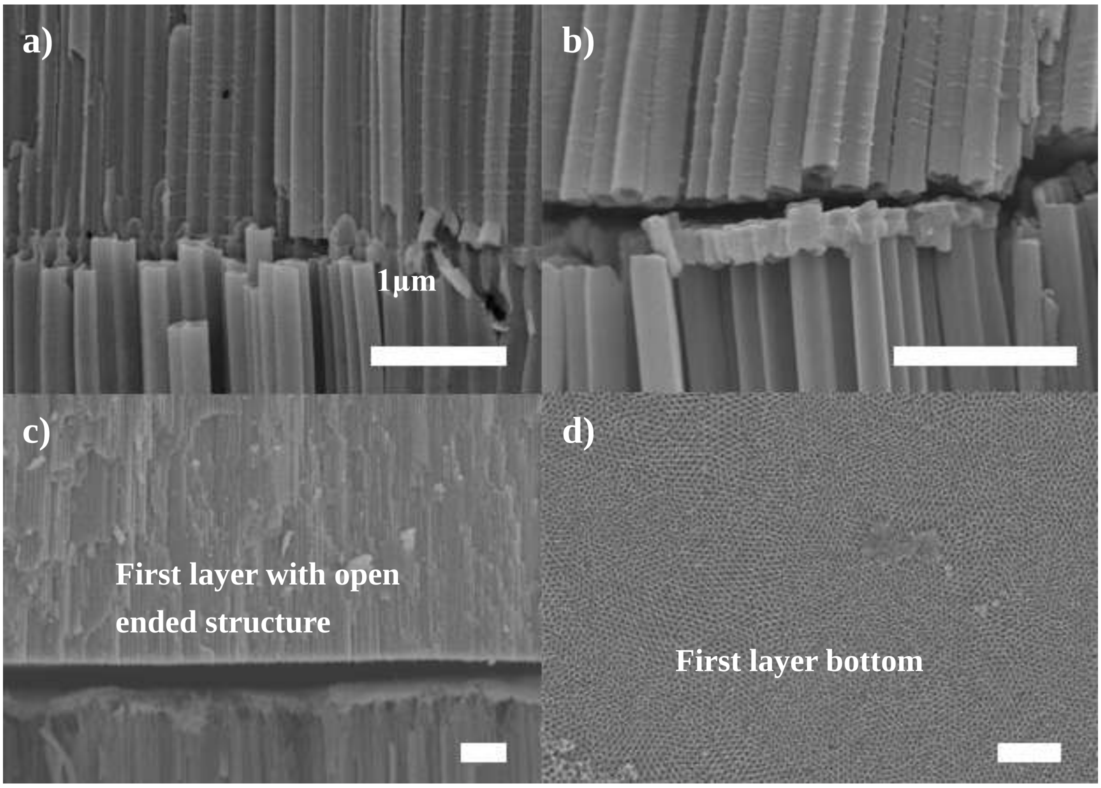

Fig. S2: SEM images of time sequence of second anodization (a) shorter time, (b) longer second anodization, (c) prolonged second anodization until separation of the first and second layers occurs, (d) bottom surface of a free-standing open-ended NT layer after separation of the two layers, showing a flat surface with a large scale. The scale bars indicated in all the diagrams are 1 µm.

Synthesis of TiO_2 nanorods. TiO_2 nanorods (NRs) were grown on FTO substrate. The substrate was ultrasonically cleaned sequentially in acetone, ethanol, and DI water for 5 min each and was finally oven dried at 100°C for 10 min. To prepare the precursor solution, 1 mL of Titanium (IV) butoxide (reagent grade, 97%) was added dropwise to a 1:1 mixture of DI water and concentrated (35%) hydrochloric acid (HCl) to obtain a clear transparent solution. Subsequently 0.8 mL titanium n-butoxide was added into 60 mL of the above precursor solution and it was treated hydrothermally in an autoclave at 150°C for 12 h with the FTO substrate placed vertically in the solution. Rutile TiO_2 NRs could be synthesized on the FTO substrate.[S3]

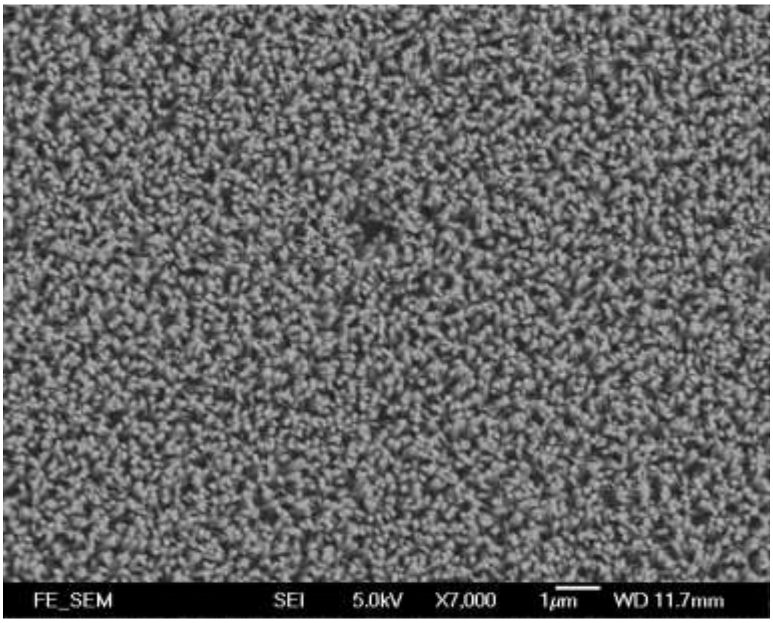

Fig. S3: SEM image of TiO_2 NRs after hydrothermal growth.

Fabrication of DSSC. The open-ended TiO_2 NT array electrode was soaked in a dye-containing solution (0.3 mM N719 in ethanol) and was kept at 60°C for 18 h. The sample was then rinsed with pure ethanol in order to remove non-chemisorbed dye before the assembly of the solar cell. The cell was assembled by sandwiching between two electrodes (TiO_2 NT array electrode and a platinum-coated conductive oxide glass (Solaronix) counter electrode) a spacer layer (SX1170–25, Solaronix) to fix the separation. The space layer was 60 µm in thickness for TiO_2 layers thicker than 25 µm; otherwise it was 25 µm in thickness. The electrolyte (DMPII 1.0 M, LiI: 0.1 M, I_2: 0.12 M, 4-TBP: 0.5M) was infiltrated by placing an electrolyte droplet in the cavity of the device active area. In this study, four types of photoanode were fabricated for comparison, P25/FTO (commercial P25 particles on FTO), NT(C)/NP/FTO (close-ended NTs on FTO attached by hydrothermal TiO_2 NPs), NT(O)/NP/FTO (open-ended NTs on FTO attached by hydrothermal TiO_2 NPs), and NT(O)/NP/NR/FTO (open-ended NTs on FTO with NRs on the surface, attached by hydrothermal TiO_2 NPs). To further improve the performance of the DSSCs, $TiCl_4$ treatment was used by immersing the whole photoanode into a 0.2M $TiCl_4$ solution for 10 min at ~50°C, followed by rinsing with deionized water and annealing at 450°C for 3 h in air (heating/cooling rate of 1°C/min).

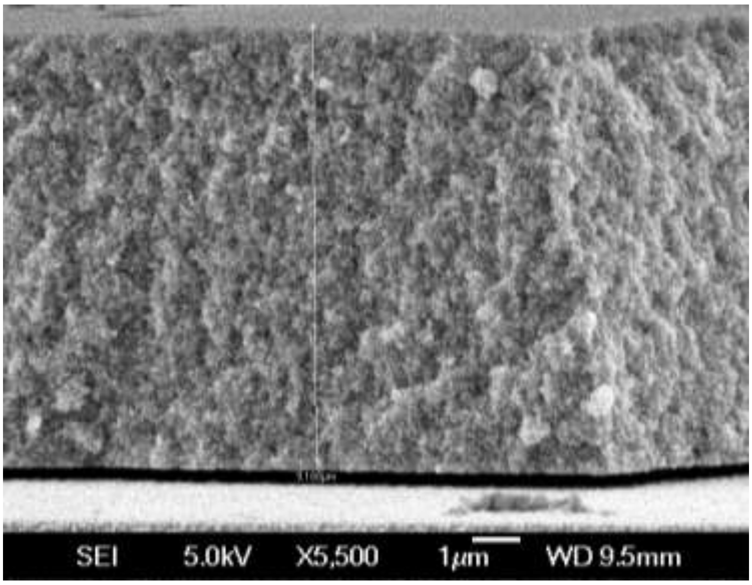

Fig. S4: SEM image of a layer of TiO_2 NP photoanode.

Current-voltage (I-V) characterization. I-V characteristics were measured using a Keithley 2400 sourcemeter. For white-light efficiency measurements (at 100 $mWcm^{-2}$), a Newport 91160 solar light simulator with an AM1.5G filter was used. All the measurements were performed in air. The active area of DSSCs was 0.2 cm^2.

Dye Desorption Measurement:

The dye (N719) adsorbed on the TiO_2 electrode was detached in aqueous 0.1 M NaOH for 24 hours, and the absorption intensity of the dye solution was measured by a UV-vis spectrophotometer (UV-2550).

Stepped light-induced transient measurements of photocurrent and voltage (SLIM-PCV). In this study, the SLIM-PCV were performed with a bias white light and a small pulse of red light to probe the devices' transient photovoltage and photocurrent.[S4] A red light laser was the red light source to induce a small voltage change around the V_{oc} condition of the devices under AM1.5G simulated solar light illumination (power=100 mW/cm^2). During the experiment, this V_{oc} condition was achieved by tuning the simulator light intensity, shining it on the cell during the measurement, and then measuring the voltage decay under zero current condition. By turning the red light on and off, a transient curve could be obtained [S4,S5] by fitting a single exponential V_{oc} decay curve to obtain the electron lifetime.[S6] This exponential decay characteristic can be derived in the following way:

$$n_c = n_{co}\, e^{eV_{ph}/kT} \qquad (1)$$

where n_c and n_{co} are the concentrations of electron at the conduction band when the light is on, leading to a photovoltage V_{ph}. e, k, and T are electron charge, Boltzmann's constant, and temperature, respectively. [S6]

For small perturbation of photovoltage induced by an external light source:

$$n_c\left(V_{ph} + \Delta V\right) = n_{co}\, e^{e(V_{ph}+\Delta V)/kT} \cong C\left(1 + \frac{e\Delta V}{kT}\right) \qquad (2)$$

Therefore:

$$\Delta n_c \cong C'\Delta V \qquad (3)$$

Similarly for the continuity equation:

$$\frac{\partial \Delta n_c}{\partial t} = -\frac{\Delta n_c}{\tau} \qquad (4)$$

Combining (3) and (4) and then integrating both sides:

$$\Delta V = C'' e^{-t/\tau}$$

where C, C′, and C″ are constants and τ is electron lifetime.

From the derivation shown, the electron lifetime determined by this method (single exponential decay) is valid only when the perturbation of photovoltage is small enough to have the approximation of (3).[S4] The concentration of dye is independent of electron lifetime. The function of dye here is to inject the photoexcited electron into the conduction band of TiO_2 to tune the quasi-Fermi level, and thus tune the V_{oc} level. The electron lifetime determined here is at the same light intensity, which is the electron lifetime at the operation (1 sun) condition.

Crystal structures

The XRD measurement was performed on 20-μm-long TiO_2 NT samples to study the phase transition at different annealing temperatures (Fig. S5). The NT sample heat treated at 270°C was still amorphous, similar to the as-anodized sample without any heat treatment. For the sample heat treated at 450°C, only anatase phase could be detected.

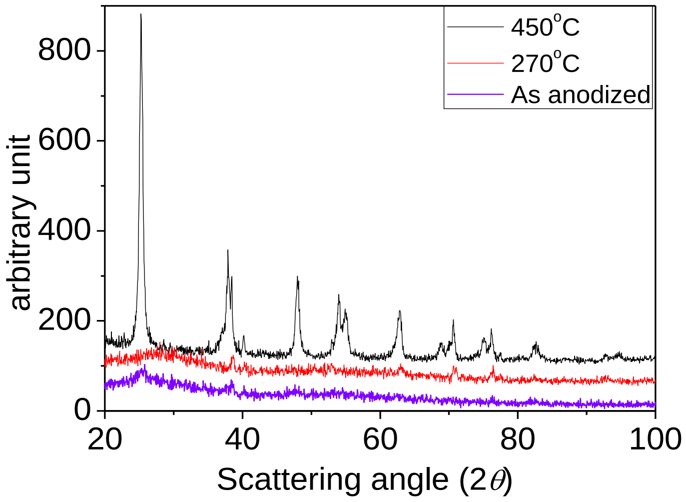

Fig. S5: XRD patterns of the TiO_2 NT samples after different heat treatments. Anatase (A) peaks could be observed when the NT sample was annealed at 450°C.

I-V characteristics for NT/NP/FTO with various NT lengths

Fig. S6 shows the IV characteristics of DSSCs with various lengths of open-ended NTs. It can be seen that J_{sc} first increases with increasing length of NT. When the NT length exceeds 28 μm, J_{sc} starts to decrease with increasing NT length. This effect might be attributed to increased electron recombination with a longer pathway before reaching the electrode.

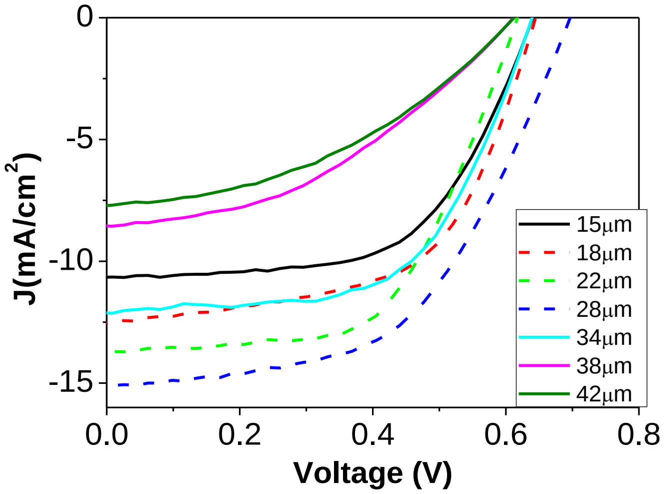

Fig. S6: Current density-potential characteristics NT(O)/NP/FTO DSSCs with different lengths of open-ended TiO_2 NTs.

NT length (μm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	*Eff* (%)
15	10.56	0.64	060	4.06
18	12.53	0.64	0.58	4.67
22	13.72	0.62	0.58	4.95
28	15.38	0.69	0.52	5.57
34	12.35	0.64	0.58	4.53
38	8.57	0.61	0.40	2.11
42	7.73	0.61	0.41	1.93

Table S1: Summary of photovoltaic performance of NT(O)/NP/FTO DSSCs with different lengths of open-ended TiO_2 NTs.

Electron lifetime measurement of NP/NR/FTO

The electron lifetime for a NP-NR cell, under the front and back side illumination is shown in Fig. S7. Since the thickness of NP and NR are only 2 μm respectively, which are much shorter than the samples examined in this study as shown in Fig. 3. Therefore the diffusion process for iodide and tri-iodide in this cell are better, and hence enhance the electron lifetime compared with the cells with thicker NP and NT layers, i.e. ~ 0.11s and ~0.04 s for NT(O)(8 μm)/NP/FTO and NP(9 μm)/FTO under front side illumination (see Fig. 3). Due to the shorter length of the TiO2 layer, For the NP-NR cell, the electron lifetime under front side illumination (~0.14 s) is only slightly lower than the electron lifetime under back side illumination (~0.15 s) (see Fig. S7).

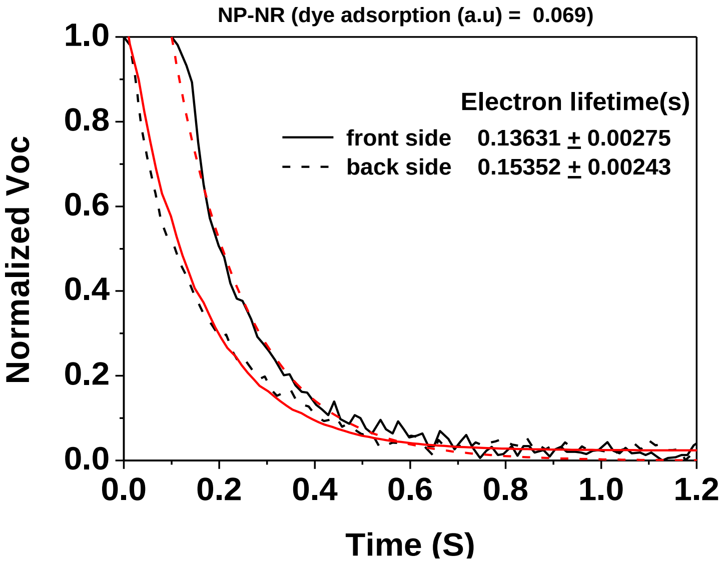

Fig. S7: Photovoltage decay of the cells in the open circuit condition for front and back side illumination). Note that V_{oc} is around 0.58 V. The electrode consists of NP-NR (without NTs).

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