

## Electronic Supplementary Information

### Ultra-long Anatase TiO<sub>2</sub> Nanowire Arrays with Multi-layered Configuration on FTO Glass for High-efficiency Dye-sensitized Solar Cells

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#### Experimental Section

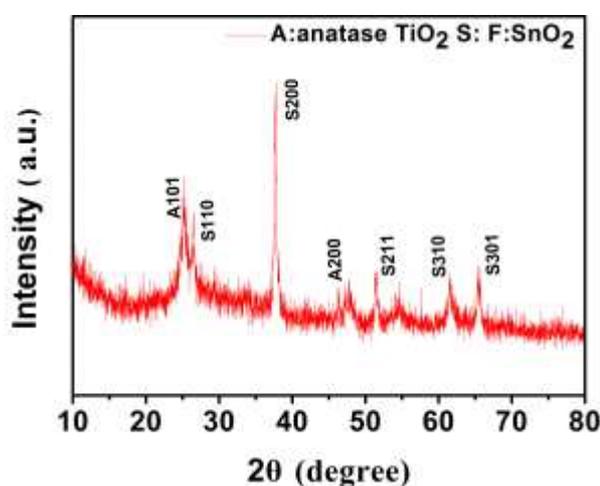
The synthesis of TiO<sub>2</sub> nanowire is modified according to the previous publication.<sup>1</sup> FTO glasses were ultrasonically cleaned in acetone, ethanol and deionized water each for 15 min, respectively. Then the synthesized TiO<sub>2</sub> colloid solution<sup>2</sup> was spin-coated onto the FTO glass, followed by annealing in air at 500 °C for 3h to obtain TiO<sub>2</sub>-coated FTO substrates. 0.35 g K<sub>2</sub>TiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub> was added to the mixture solvent containing 5 mL deionized water and 15 mL diethylene glycol (DEG). After vigorously stirring for 30 min, the mixture solution was transferred to a 50 mL Teflon-lined stainless steel autoclave. Then the coated substrates were placed at an angle against the wall of the Teflon-liner with the conducting side facing down. The hydrothermal synthesis was conducted at 180 °C for 9 h for the growth of the first-layer TiO<sub>2</sub> nanowire arrays. To increase the TiO<sub>2</sub> nanowire length, the as-prepared sample on FTO glass was repeatedly introduced to fresh solution baths every 9 h to grow second- and third-layer. It is worth noting, after each hydrothermal reaction, the autoclave was cooled to room temperature immediately using cool water and then the FTO glass was taken out and rinsed with deionized water, ethanol and then dried at room temperature, followed by annealing treatment at appropriate temperature (450, 500, 550 or 600 °C) for 30 min. The as-prepared anatase TiO<sub>2</sub> nanowire arrays on FTO glass were applied as photoelectrode for dye-sensitized solar cells. For comparison, 20 μm thick P25 based photoanode was prepared via screen-printing method and then used to fabricate dye-sensitized solar cells as well. The as-prepared TiO<sub>2</sub> were immersed into a 40 mM TiCl<sub>4</sub> aqueous solution at 70 °C for 30 min and washed with water and ethanol, then sintered at 520 °C for 30 min. After cooling down to 80 °C, the TiO<sub>2</sub> electrodes were putted into 0.5mM N719 dye (Ru[LL'-(NCS)<sub>2</sub>], L= 2,2'-bipyridyl-4,4'-dicarboxylic acid, L=2, 2'-bipyridyl-4,4'-ditetrabutylammonium carboxylate, Solaronix Co.) in acetonitrile/tert-butanol (1:1 v/v), and kept for 16 h at room temperature. The preparation process of Pt-coated FTO glass counter electrode and I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox electrolyte was similar to our previous report<sup>2</sup>. The active area of the dye-coated TiO<sub>2</sub> film was 0.16 cm<sup>2</sup>.

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- (1) W. Q. Wu, B. X. Lei, H. S. Rao, Y. F. Xu, Y. F. Wang, C. Y. Su, D. B. Kuang, *Sci. Rep.* 2013, **3**, 1352.
- (2) E. Scolan, C. Sanchez, *Chem.Mater.* 1998, **10**, 3217.

## Characterization:

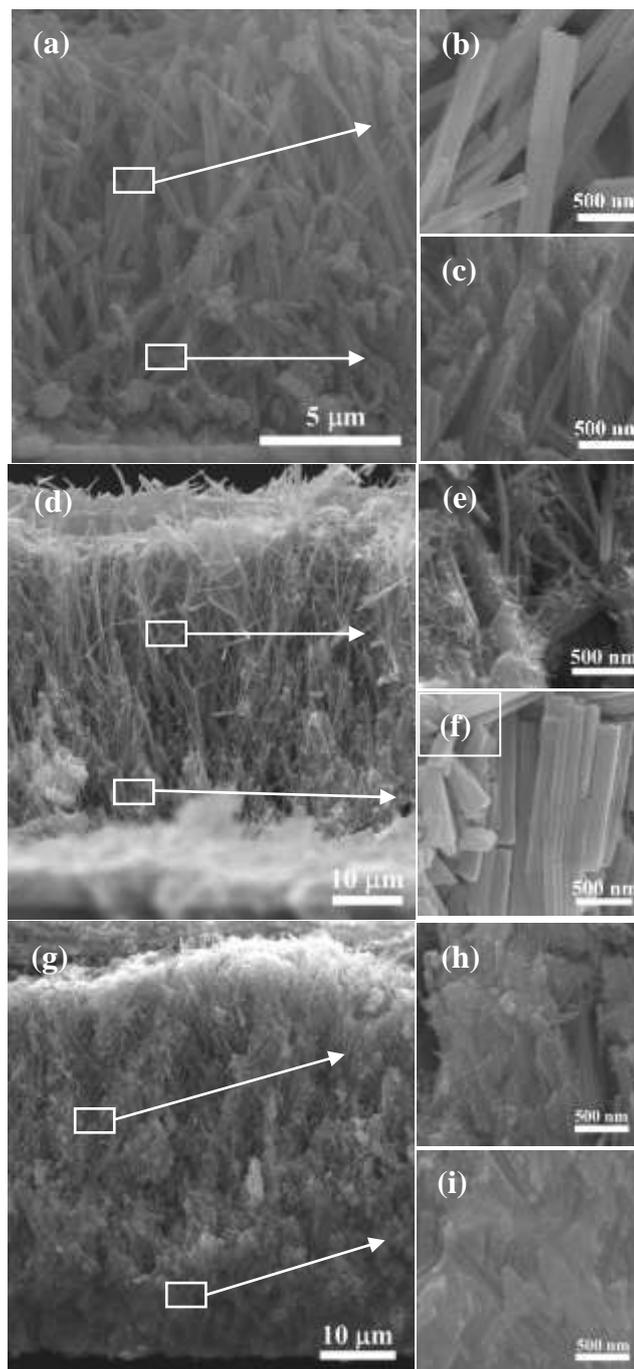
The phase purity of the as-prepared samples was examined by X-ray diffraction (XRD, Bruker D8 Advance). The Field emission scanning electron microscopy (FE-SEM, JSM-6330F) were performed to characterize the morphological structure. The diffuse reflectance spectra of TiO<sub>2</sub> nanowire arrays and P25 based film were measured on a UV/Vis-NIR spectrophotometer (UV-3150) to evaluate their reflectance performance. The absorption spectra of N719 dye-desorption solutions from the TiO<sub>2</sub> films (dye-absorbed TiO<sub>2</sub> film was immersed into 0.1 M NaOH aqueous solution) were also measured on a UV/Vis-NIR spectrophotometer (UV-3150) to measure the adsorped dye amount of TiO<sub>2</sub> films. The photocurrent density-photovoltage (*J-V*) characteristics were carried out using a Keithley 2400 source meter under simulated AM 1.5 G illumination (100 mW cm<sup>-2</sup>) provided by a solar light simulator (Oriel, Model: 91192). The incident light intensity was calibrated with a NREL-calibrated Si solar cell. The Spectral Products DK240 monochromator was employed for the IPCE measurement as a function of wavelength from 400 to 800 nm. The electrochemical impedance spectroscopy (EIS) measurements were performed with a Zennium electrochemical workstation (ZAHNER) with the frequency range from 10 mHz to 1 MHz. The magnitude of the alternative signal was 10 mV. The impedance measurements were carried out under forward bias of -0.80 V in the dark condition or under illumination (LED light source, 100 W m<sup>-2</sup>) at open circuit.



**Fig. S1.** XRD patterns of photoanode based on as-prepared TiO<sub>2</sub> nanowire arrays prepared at 180 °C for 9 h on FTO glass.

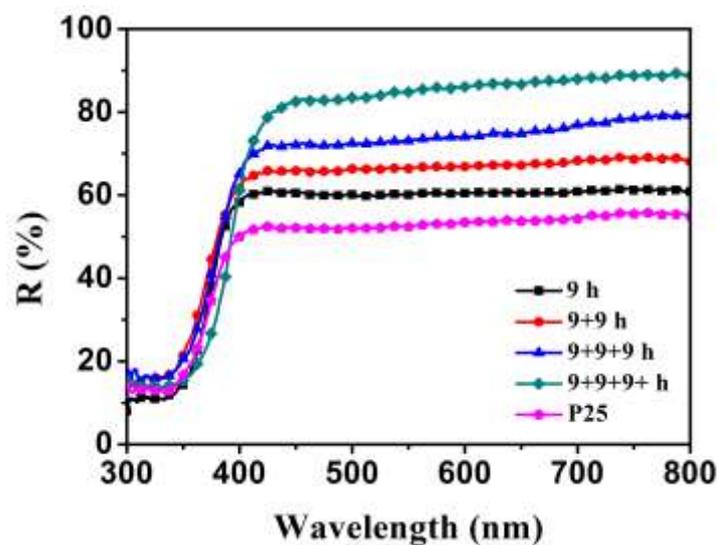
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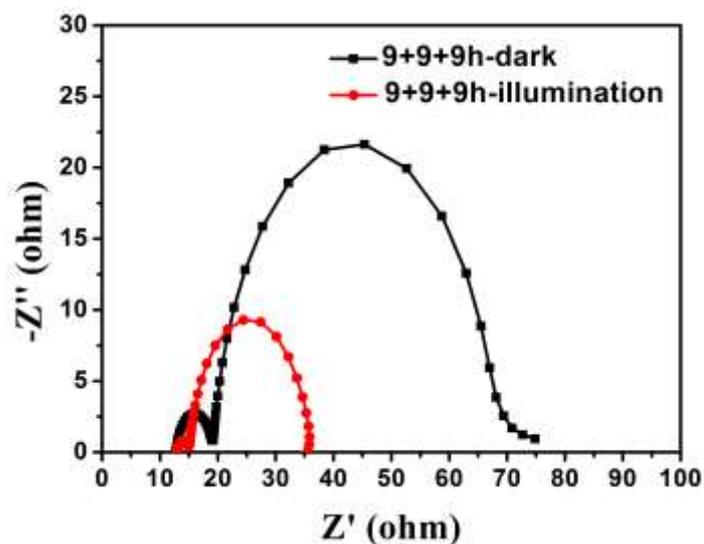


**Fig. S2.** SEM images of TiO<sub>2</sub> nanowire arrays obtained by hydrothermal growth at 180 °C after 1 cycles (a, b, c), 2 cycles (d, e, f) and 4 cycles (g, h, i), respectively. Each hydrothermal cycle is carried out for 9 h.

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**Fig. S3.** Diffuse reflectance spectra of the TiO<sub>2</sub> nanowire arrays photoanodes prepared at different times of hydrothermal reaction cycle and P25 nanoparticles photoanode.

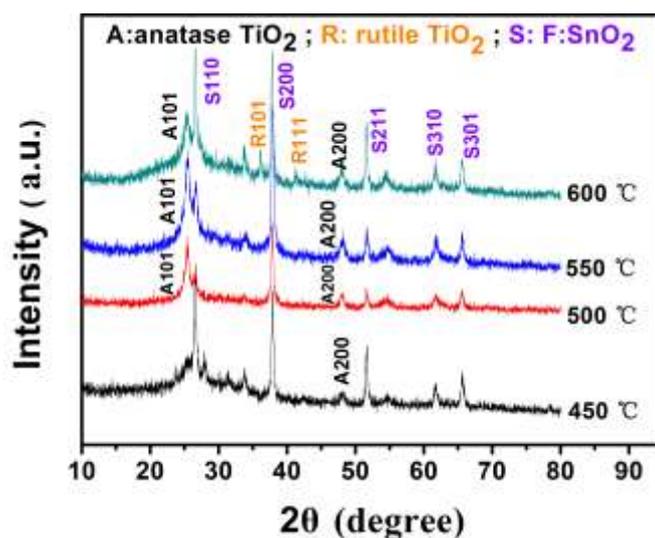


**Fig. S4.** EIS of DSSCs based on the TiO<sub>2</sub> NWs prepared at 180 °C for 3 times of hydrothermal cycles measured in dark at a forward bias of -0.80 V (black curve) or under 100 W m<sup>-2</sup> light illumination at open circuit potential (red curve).

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**Table S1.** Detailed simulative value of recombination resistance ( $R_2$ ) and electron lifetime value ( $\tau_r$ ) from EIS spectra calculated by equivalent circuit as shown in Fig.3 and Fig. S4.

DSSCs	$R_2$ (ohm)	$\tau_r$ (s)
9 h	186.5	0.170
9+9 h	81.18	0.138
9+9+9 h-dark	51.81	0.119
9+9+9 h-illumination	20.66	0.053
9+9+9+9 h	43.04	0.094
P25	23.82	0.085



**Fig. S5.** XRD patterns of photoanode based on as-prepared  $\text{TiO}_2$  nanowire arrays prepared at 180 °C for 9 h on FTO glass followed by further calcination process at 450 °C, 500 °C, 550 °C or 600 °C for 30 min.

Figure S5 indicates that the as-prepared nanowires samples are indexed as pure anatase  $\text{TiO}_2$  when the calcinations temperature risen from 450 °C to 550 °C. It is worth noting that the crystallinity was improved along with the increased calcinations temperature. However, when the temperature was up to 600 °C, the rutile  $\text{TiO}_2$  phase began to appear, and the samples are indexed as mixed crystal including anatase and rutile  $\text{TiO}_2$ . In order to investigate the effect of cystallinity on the photoanode's

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photovoltaic performance, we fabricated the DSSCs with such 15  $\mu\text{m}$  long  $\text{TiO}_2$  nanowires photoanode (9h samples) which was calcinated under different temperatures. The photovoltaic parameters are summarized in Table S2.

**Table S2.** Detailed Photovoltaic Parameters ( $J_{sc}$ ,  $V_{oc}$ ,  $FF$ , and  $\eta$ ) of DSSCs based on  $\text{TiO}_2$  photoanodes (15  $\mu\text{m}$ ) prepared at 180  $^\circ\text{C}$  for 9 h under different calcination temperatures.

DSSCs	$J_{sc}/$ $\text{mA cm}^{-2}$	$V_{oc}/$ $\text{mV}$	$\eta/\%$	$FF$
9h-450 $^\circ\text{C}$	10.35	839	5.51	0.63
9h-500 $^\circ\text{C}$	11.25	876	6.02	0.62
9h-550 $^\circ\text{C}$	12.10	873	6.71	0.64
9h-600 $^\circ\text{C}$	8.76	850	5.25	0.71

The results shows that when the crystallinity of samples was improved, both photocurrent density and voltage were increased, leading to enhanced power conversion efficiency. And the DSSCs based on  $\text{TiO}_2$  under 550  $^\circ\text{C}$  calcination achieved the best efficiency of 6.71% with  $J_{sc}$  of 12.10  $\text{mA cm}^{-2}$  and  $V_{oc}$  of 873 mV which can be ascribed to its high crystallinity. However, further increased the calcinations temperature to 600  $^\circ\text{C}$ , the  $J_{sc}$  decreased significantly, leading to a markedly decline of efficiency to 5.25%. This is mainly because temperature over 600  $^\circ\text{C}$  will result in the fact that quite a portion of anatase  $\text{TiO}_2$  would transform to rutile phase, which is not beneficial to the DSSCs application.