Supporting Information

An Optimized Porous Rutile TiO_2 Nanorod Arrays for Enhancing Efficiency of Dye-Sensitized Solar Cells

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Figure S1. FE-SEM images of 1-D rutile TiO_2 NRAs prepared by hydrothermal method in a solution of 3 ml $TiCl_4$,30 ml DI water and 30 ml HCl (36.0~38.0w%) at 150 ℃ for different time; Film thickness versus the hydrothermal duration at 150 ℃ in a solution containing 3 ml $TiCl_4$, 30 ml DI water and 30 ml HCl (36.0~38.0w%).

Figure S2. FE-SEM image of 1-D single-crystal rutile TiO_2 NRAs prepared in a solution of 3 ml $TiCl_4$,30 ml DI water and 30 ml HCl (36.0~38.0w%) at 180 ℃ for 3 h.

Figure S3. FE-SEM images of rutile TiO_2 NRA films fabricated by hydrothermal in a solution of 3 ml $TiCl_4$,30 ml DI water and 30 ml HCl (36.0~38.0w%) at 150 ℃ for 12 h, followed by etching treatment in a solution of 20 ml DI water and 40 ml HCl (36.0~38.0w%) at 150 ℃ for 3h, 5h and 9h

Figure S4. FE-SEM images of etched rutile TiO_2 NRAs prepared by a secondary hydrothermal method with refreshed hydrothermal solutions.

Figure S5. FE-SEM images of ~ 21μm P25 NP film prepared by doctor-blade method on the $TiCl_4$-treated FTO substrate.

Figure S6. Photograph of the home-made Teflon-socket used for preparation of rutile TiO_2 NRAs.

Figure S7. XRD patterns of the FTO substrate, the FTO substrate with a compact TiO_2 layer and the glass substrate with a compact TiO_2 layer.

Figure S8. Comparison of SEM images of the rutile TiO_2 NRAs grown on the bare FTO substrate and the FTO substrate with a compact TiO_2 layer.

Figure S9. Photograph of the rutile TiO_2 NRA film on the FTO substrate fabricated by hydrothermal in a solution of 3 ml $TiCl_4$,30 ml DI water and 30 ml HCl (36.0~38.0w%) at 150 ℃ for 12 h, followed by different etching treatment.

Figure S10. UV-vis absorbance spectra of the photoanodes without dye-sensitizing

Figure S11. SEM images of the rutile TiO_2 NRAs etched under other conditions

Figure S12. SEM images of the rutile TiO_2 NRAs prepared by refreshing the hydrothermal solution for several times.

Figure S13. The electrochemical impedance spectra of the DSCs based on the ~ 20 μm rutile TiO_2 NRA photoanodes.

Figure S14. SEM images of the 1 h-etched rutile TiO_2 NRAs.

Figure S15. UV-vis absorbance spectra of the N719 dye-sensitized photoanodes with $TiCl_4$-treated FTO substrate as the baseline reference

Figure S16. IPCE spectra of the assembled DSCs based on rutile TiO_2 NRAs with different etching treatment; DSC-0, DSC-3, DSC-5, DSC-7 and DSC-9 are corresponding to the DSCs based on the rutile TiO_2 NRAs with 0, 3, 5, 7 and 9 h etching duration.

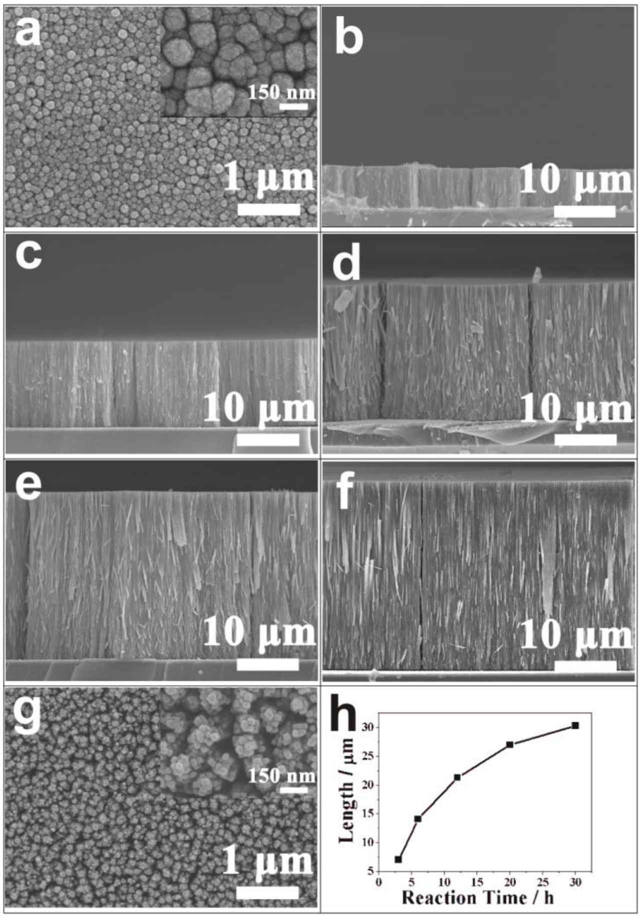

Figure S1. FE-SEM images of 1-D rutile TiO_2 NRAs prepared by hydrothermal method in a solution of 3 ml $TiCl_4$, 30 ml DI water and 30 ml HCl (36.0~38.0w%) at 150 ℃ for different time. a, b) TiO_2 NRAs prepared by hydrothermal for 3 h; image (a) and its inset show the top views of the as-prepared film; image (b) shows the cross-sectional view of the film. Images (c), (d), (e) and (f) corresponding to the rutile TiO_2 NRAs prepared by hydrothermal for 6 h, 12 h, 20 h and 30 h, respectively. Image (g) and its inset shows the top views of the TiO_2 NRAs prepared by hydrothermal for 30 h. h) Film thickness versus the hydrothermal duration at 150 ℃ in a solution containing 3 ml $TiCl_4$, 30 ml DI water and 30 ml HCl (36.0~38.0w%).

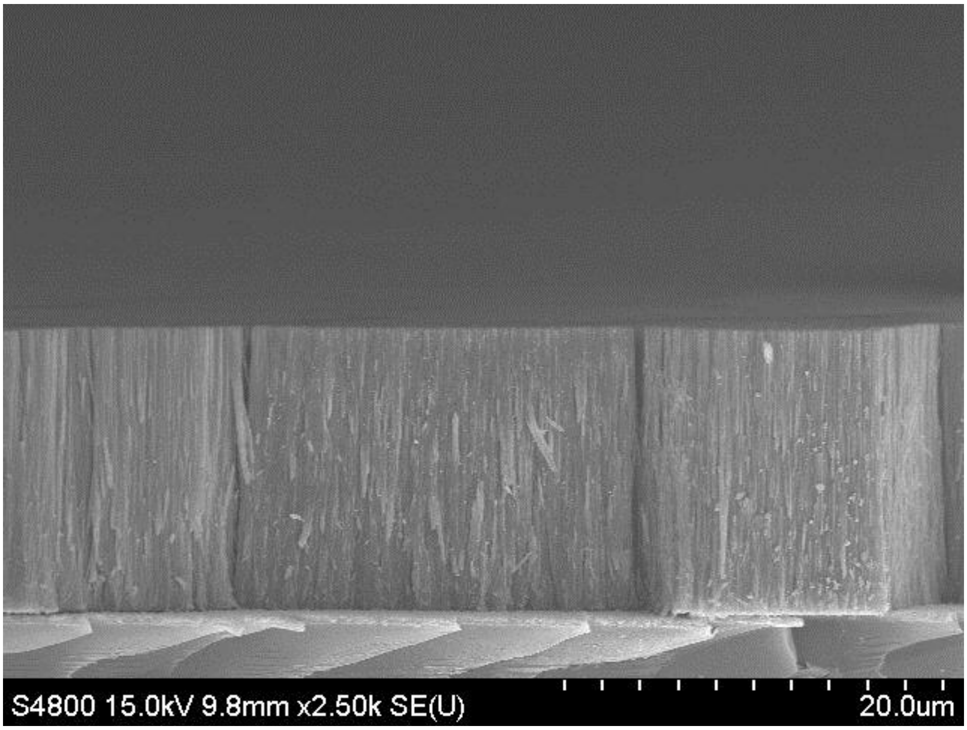

Figure S2. FE-SEM image of 1-D single-crystal rutile TiO_2 NRAs prepared in a solution of 3 ml $TiCl_4$,30 ml DI water and 30 ml HCl (36.0~38.0w%) at 180 ℃ for 3 h. It can be seen from the cross-sectional view of the film that around 15-μm-thick TiO_2 NRAs has been achieved and the film maintains an excellent adhesion with the FTO substrate.

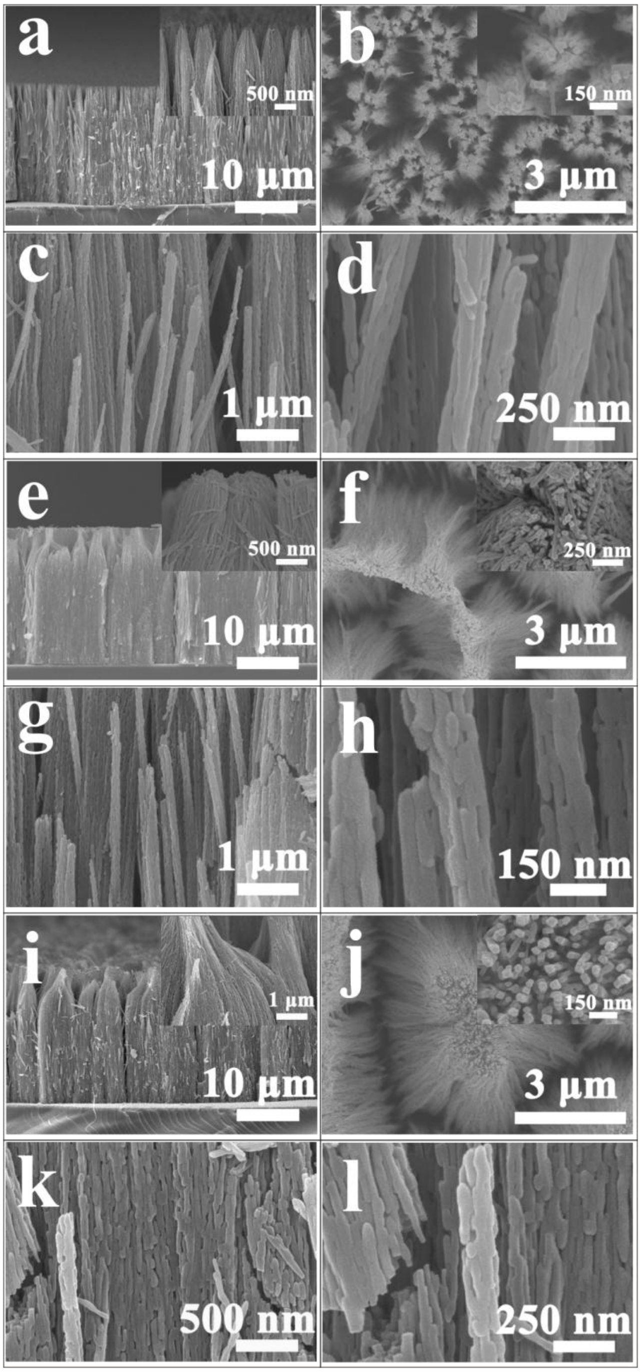

Figure S3. FE-SEM images of rutile TiO_2 NRA films fabricated by hydrothermal in a solution of 3 ml $TiCl_4$,30 ml DI water and 30 ml HCl (36.0~38.0w%) at 150 ℃ for 12 h, followed by etching treatment in a solution of 20 5 ml DI water and 40 ml HCl at 150 ℃for different time. (a), (b), (c) and (d) 3-h-etched films; (e), (f), (g) and (h) 5-h-etched films; (i), (j), (k) and (l) 9-h-etched films; (a), (e) and (i) show the cross-sectional views of the films etched for 3, 5 and 9 h, respectively, while (b), (f) and (j) show the top views of the corresponding films. Insets show the enlarged FE-SEM images of the corresponding samples.

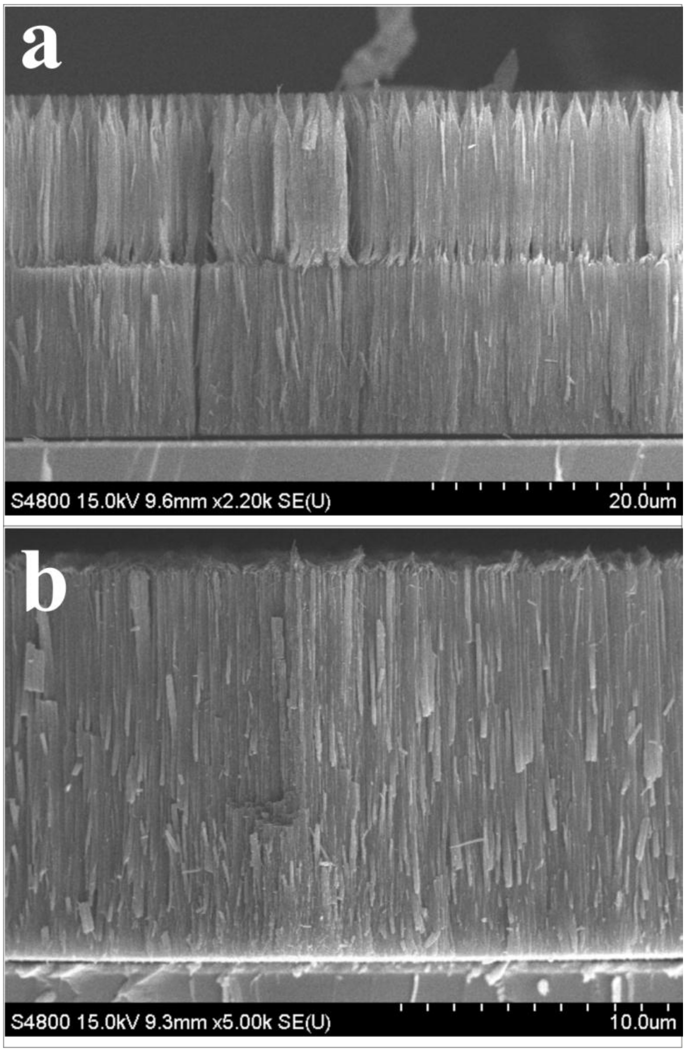

Figure S4. FE-SEM images of rutile TiO_2 NRAs grown on the $TiCl_4$-treated FTO substrate in a solution of 2 ml $TiCl_4$, 30 ml H_2O and 30 ml HCl (36.0~38.0w%) at 150 ℃ for 10 h and the hydrothermal process was repeated once by refreshing the hydrothermal solution under the same condition, then followed by a etching treatment process using HCl as the etching agent. After etching treatment, the interface between the two rutile TiO_2 NRA layers can be clearly seen from image (a) and the upper layer was easily detached from the under layer in some part of the film, as shown in image (b).

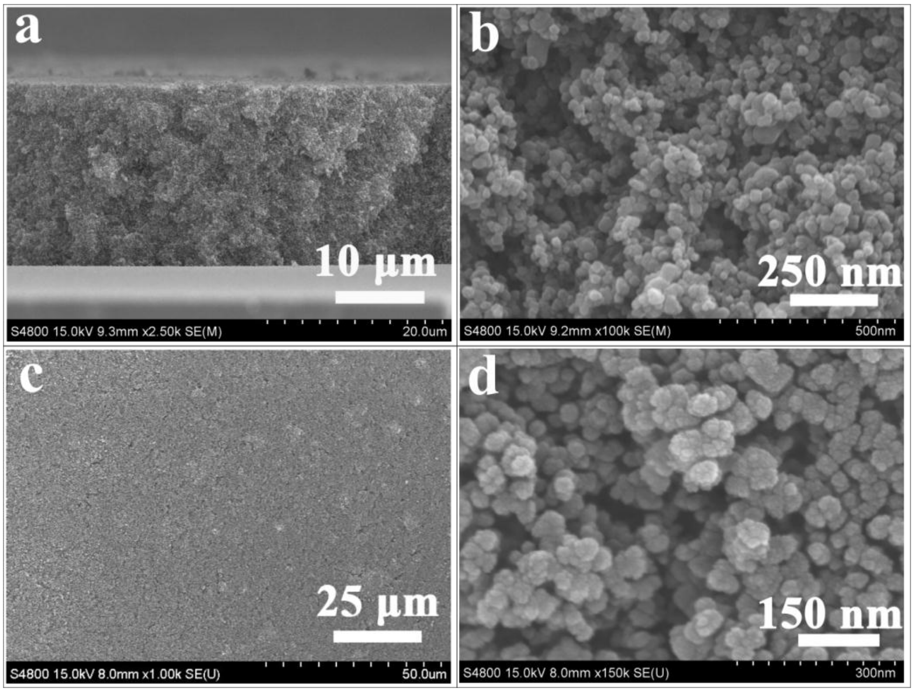

Figure S5. FE-SEM images of ~ 21μm P25 NP film prepared by doctor-blade method on $TiCl_4$-treated FTO substrate. (a) Cross-sectional image of the as-prepared P25 film. (b) Enlarged view of TiO_2 nanoparticle (NP) from the cross-sectional image. (c) Top view of the P25 film. (d) Magnified image of top morphology, indicating that the diameter of TiO_2 NPs is in the range of 20~50 nm.

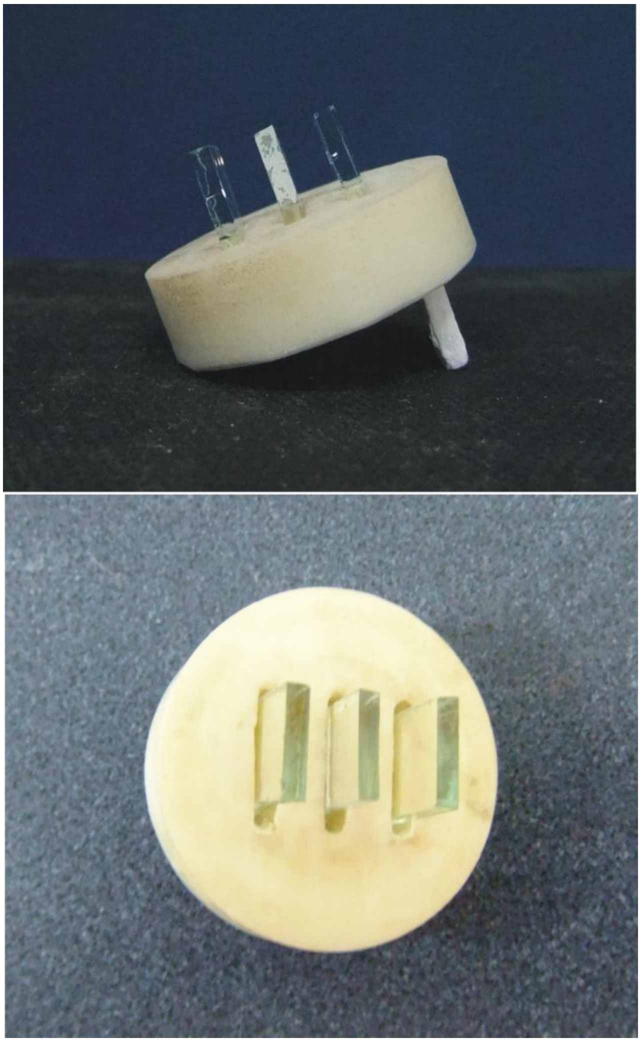

Figure S6. Photograph of the home-made Teflon-socket used for preparation of rutile TiO_2 NRAs. There are mainly three advantages introduced by the socket. First, FTO substrates can be firmly fixed on the socket so that falling down to the bottom of the autoclave can be avoided, while in previous report, the FTO substrate is simply place against the inner wall of the autoclave with its conductive side facing down. Second, the inserted portion of FTO substrate was wrapped with Teflon tape so as to protect the conductive side inserted in the socket from being deposited by rutile TiO_2 NRAs and preserve its conductivity. Third, three pieces of FTO substrates can be used at each hydrothermal experiment and as it has been confirmed in our experiment, these three samples have almost a similar film thickness and diameter in the same hydrothermal condition regardless of a little height difference.

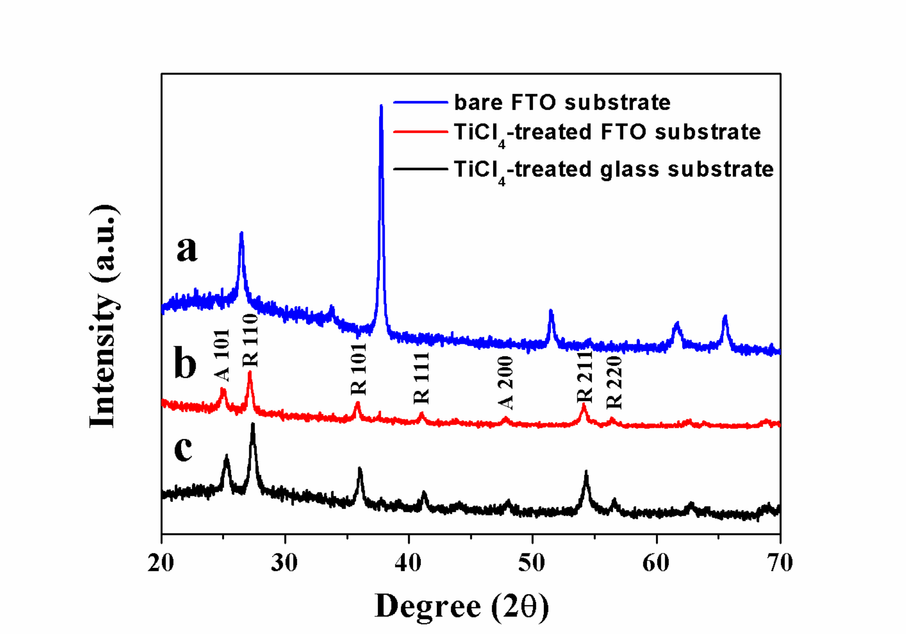

Figure S7. XRD patterns of the FTO substrate (a), the FTO substrate with a compact TiO_2 layer (b) and the glass substrate with a compact TiO_2 layer (c). "A" is denoted as anatase TiO_2, while "R" is denoted as rutile TiO_2. In order to identify the phase of the compact TiO_2 layer, the FTO substrate and the glass substrate were immersed in an aqueous solution of 0.2 M $TiCl_4$ and then kept at 70 ℃ for 12 h. The samples were annealed at 550℃ for 1h before the XRD measurements. We found that only the XRD peaks corresponding to the FTO substrate could be observed if the FTO substrate was deposited for only 30 min, because the compact TiO_2 layer that was deposited only for 30 min was too thin to be detected. Therefore, the deposition duration was prolonged to 12 h in this experiment.

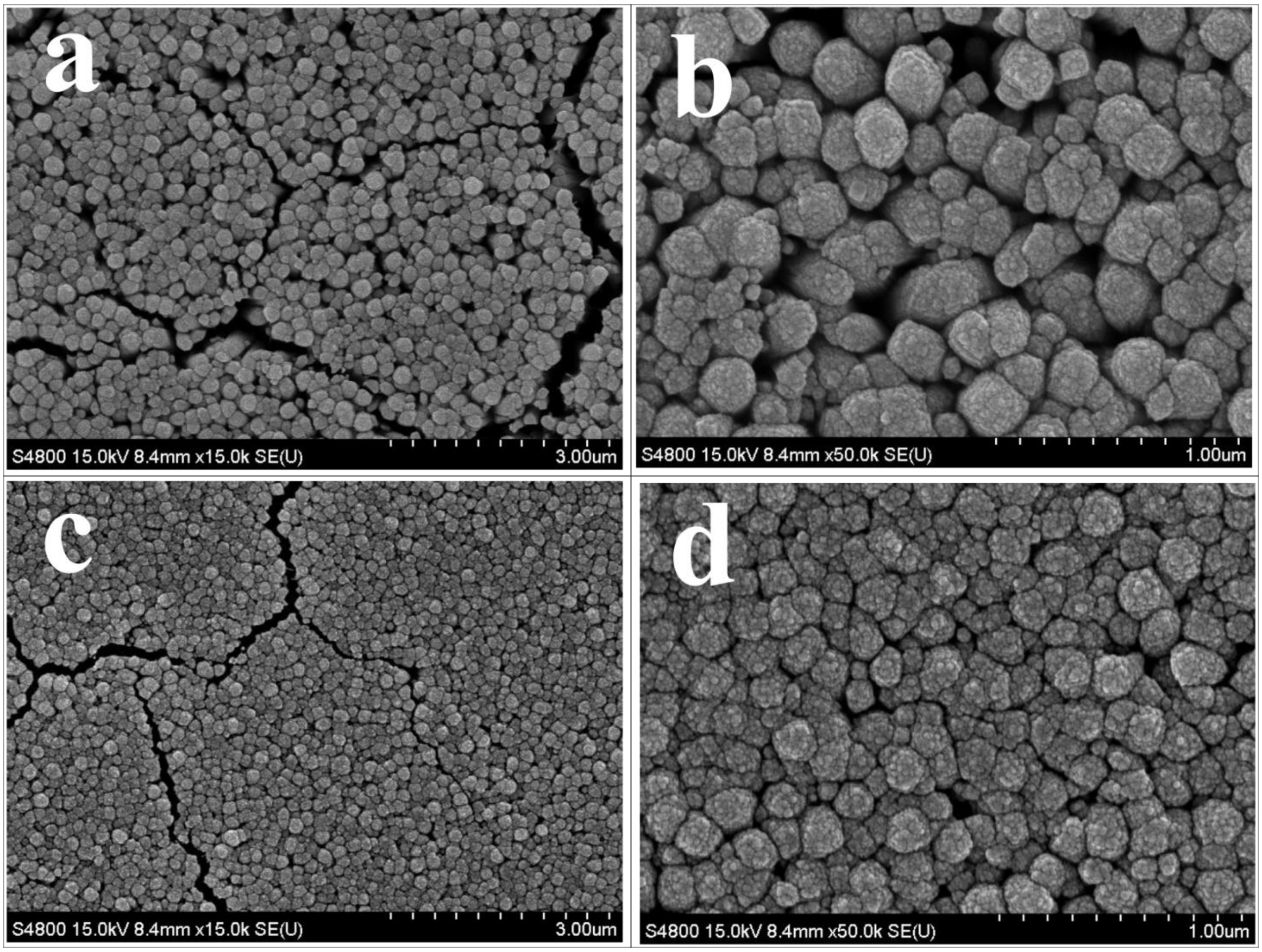

Figure S8. SEM images of the rutile TiO_2 NRAs grown on the (a) (b) bare FTO substrate and (c) (d) FTO substrate with a compact TiO_2 layer. From the top morphology of the rutile TiO_2 NRAs, it could be observed that the diameter of the nanorods grown directly on the bare FTO substrate is in the range of 100-230 nm while the diameter of the nanorods grown on the $TiCl_4$-treated FTO substrate (e.g. pre-treated a compact TiO_2 layer) is around 150 nm. Moreover, the nanorods for the latter sample is much more densely aligned and uniformly distributed in the diameter. The samples were prepared in a hydrothermal solution of 1 ml $TiCl_4$, 30 ml concentrated HCl (36.0~38.0w%) and 30ml DI water and kept for 6 h at 150 ℃. As for the FTO substrate with a compact TiO_2 layer, the preparation process is the same to the description in the Experimental section of the manuscript.

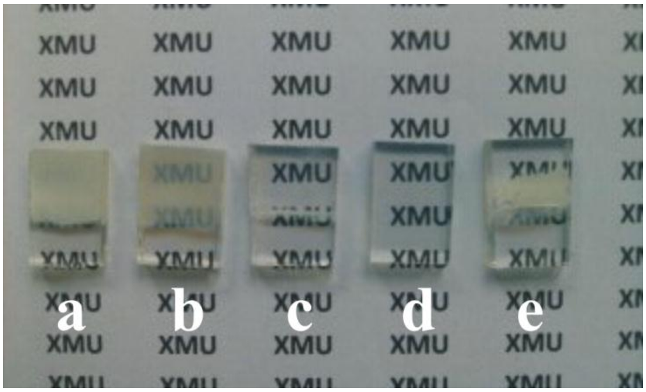

Figure S9. Photograph of the rutile TiO_2 NRA film on the FTO substrate fabricated by hydrothermal in a solution of 3 ml $TiCl_4$,30 ml DI water and 30 ml HCl (36.0~38.0w%) at 150 ℃ for 12 h, followed by (a) annealed at 450 ℃ for 2 h, (b) without any post-treatment, (c) etching treatment in a solution of 10 ml DI water and 50 ml HCl at 150 ℃ for 7 h, (d) etching treatment in a solution of 60 ml HCl at 150 ℃ for 7 h and (e) etching treatment in a solution of 20 ml DI water and 40 ml HCl at 150 ℃ for 9 h.

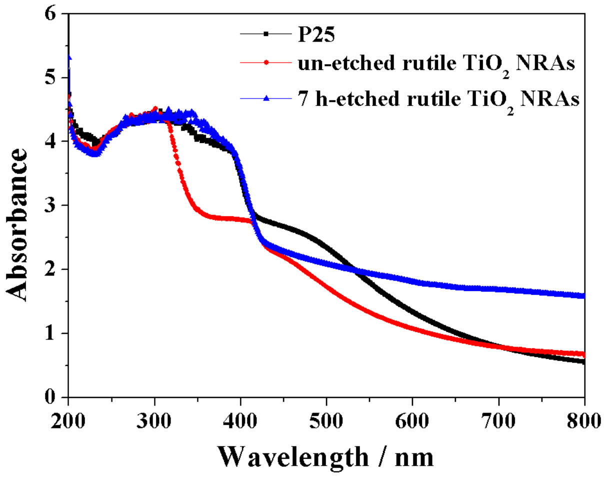

Figure S10. UV-vis absorbance spectra of the photoanodes without dye-sensitizing: P25 (the black curve), un-etched rutile TiO_2 NRAs with the thickness around 20 μm (the red curve) and 7 h-etched rutile TiO_2 NRAs with the thickness around 20 μm (the blue curve). All the samples were annealed at 450 ℃ for 2 hours before the measurements.

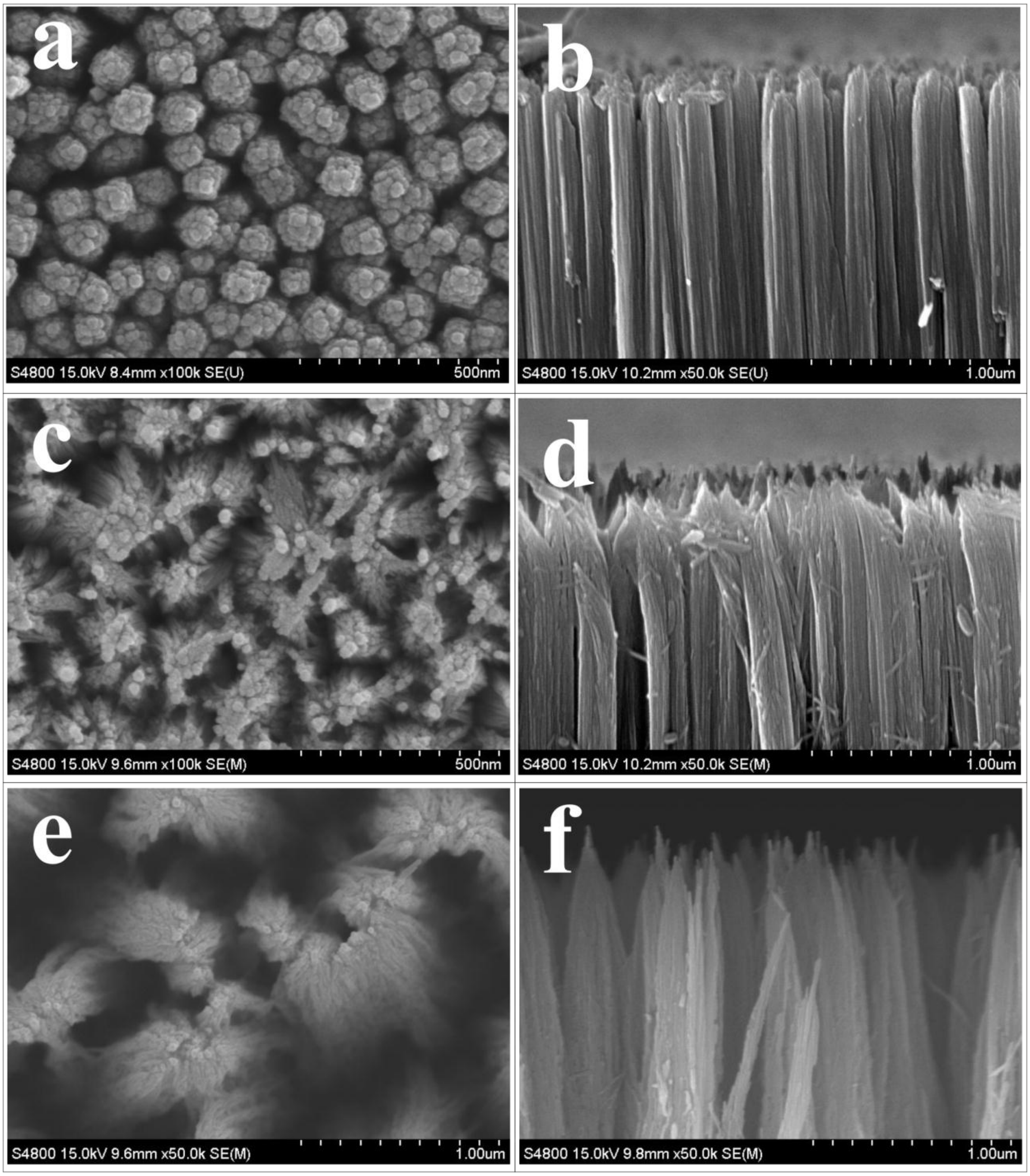

Figure S11. SEM images of the rutile TiO_2 NRAs etched under other conditions: (a) (b) saturated NaCl solution at 150 ℃ for 7 h; (c) (d) 4 mol/L sulfuric acid aqueous solution at 150 ℃ for 3 h and (e) (f) 4 mol/L sulfuric acid aqueous solution at 150 ℃ for 7 h. The rutile TiO_2 NRAs used for these experiments were prepared on $TiCl_4$-treated FTO substrates by hydrothermal in a solution of 3 ml $TiCl_4$,30 ml DI water and 30 ml HCl (36.0~38.0w%) at 150 ℃ for 12 h. The as-prepared samples were non-annealed before the SEM observation.

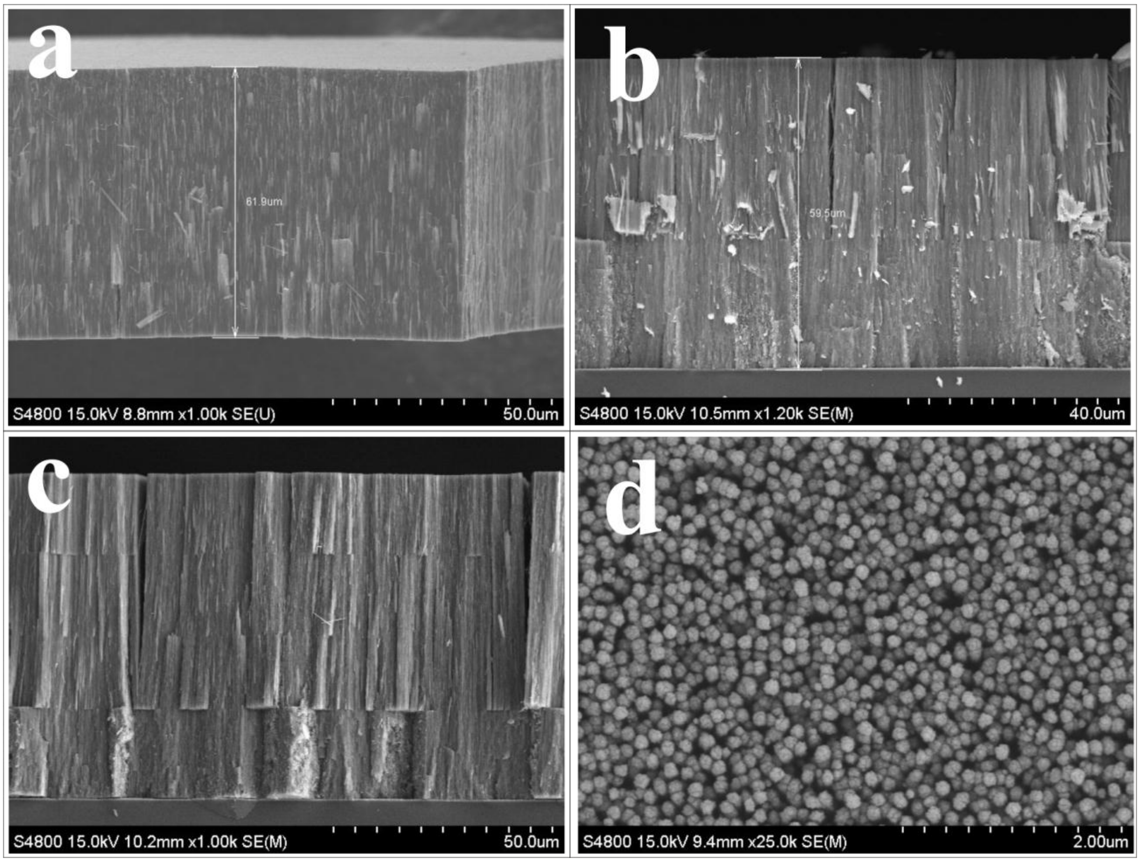

Figure S12.SEM images of the rutile TiO_2 NRAs prepared by refreshing the hydrothermal solution for several times. (a) ~62 μm rutile TiO_2 NRAs prepared in a solution of 3 ml $TiCl_4$,30 ml DI water and 30 ml HCl (36.0~38.0w%) at 150 ℃ for 10 h, followed by refreshing the hydrothermal solution for three times with the same hydrothermal duration for each stage (i.e. 10 h); (b) ~ 59.5 μm rutile TiO_2 NRAs prepared by refreshing the hydrothermal solution for two times. First, ~ 25 μm rutile TiO_2 NRAs was annealed at 450 ℃ for 2 h. Then the sample was used for further hydrothermal reaction in a solution of 3 ml $TiCl_4$,30 ml DI water and 30 ml HCl (36.0~38.0w%) at 150 ℃ for 10 h and the hydrothermal reaction was continued for another 10 h after refreshing the hydrothermal solution. (c), (d) ~ 74μm rutile TiO_2 NRAs prepared by refreshing the hydrothermal solution for three times. First, ~ 20 μm rutile TiO_2 NRAs on the $TiCl_4$-treated FTO substrate was annealed at 450 ℃ for 2 h. Then, the sample was used for further hydrothermal in a solution of 3 ml $TiCl_4$, 30 ml DI water and 30 ml HCl (36.0~38.0w%) at 150 ℃ for 10 h, followed by refreshing the hydrothermal solution for another two times with each stage lasting for 12 h. Image (a), (b) and (c) are the cross-sectional view of the as-prepared films and image (d) is the top-morphology of the ~ 74 μm rutile TiO_2 NRAs.

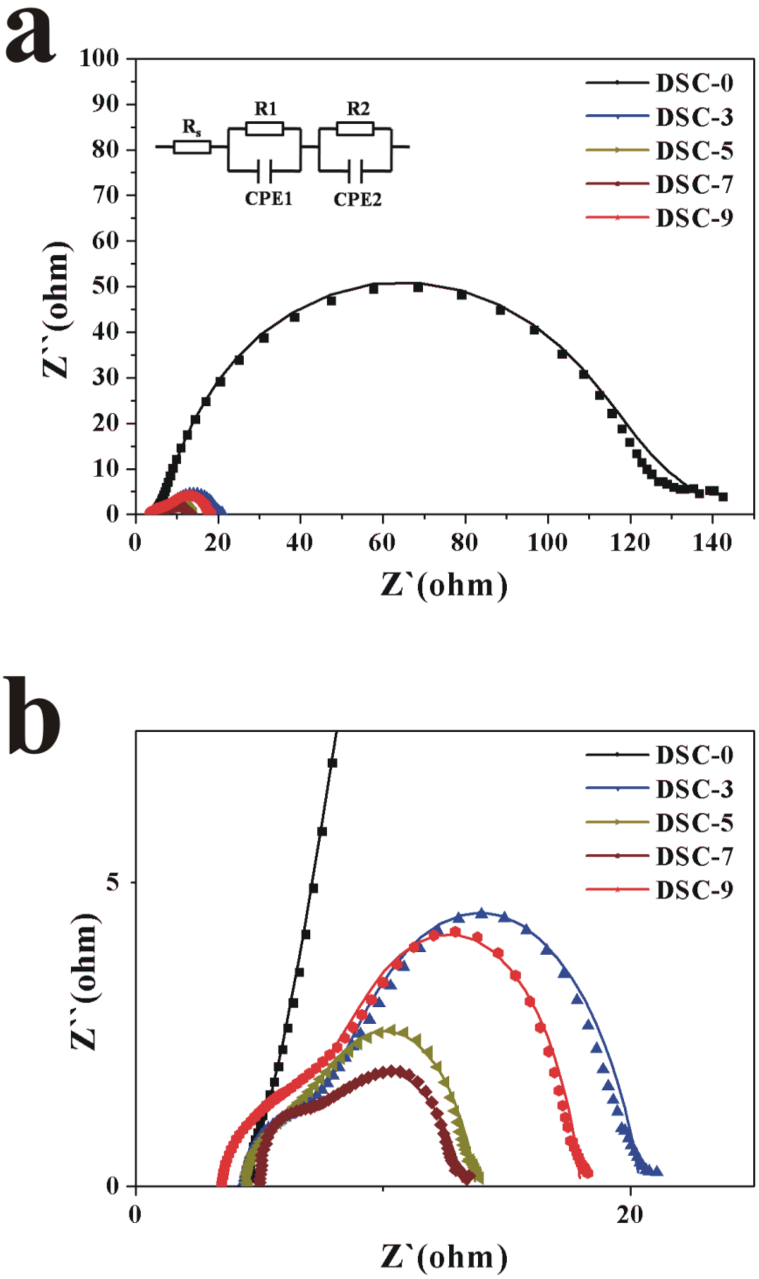

Figure S13. (a) The electrochemical impedance spectra of the DSCs based on the ~ 20 μm rutile TiO_2 NRA photoanodes. DSC-0, DSC-3, DSC-5, DSC-7 and DSC-9 are corresponding to the DSCs assembled by the rutile TiO_2 NRAs with 0 h, 3 h, 5 h, 7 h and 9 h etching treatment, respectively. An active area of 0.14 cm^2 was used for EIS measurements. The inset image of (a) shows the equivalent circuit used for fitting. The dot lines are measured curves of the DSCs while the continuous solid lines are the corresponding fitted curves calculated by the ZSimpWin software according to the given equivalent circuit. Figure (b) shows the enlarged Nyquist plots of the DSC-3, DSC-5, DSC-7 and DSC-9. The equivalent circuit is composed of two constant phase elements (CPE) and three resistances (R). Rs, R1 and R2 are corresponding to the sheet resistance of substrate, charge transfer resistance of the counter electrode and recombination resistance, respectively.

Table 1. Resistance values calculated from the fitted EIS spectra using a ZSimpWin software.

Sample	**Rs (ohm)**	**R1 (ohm)**	**R2 (ohm)**

DSC-0	4.25	43.77	94.12
DSC-3	4.25	3.65	12.51
DSC-5	4.42	2.55	6.8
DSC-7	4.92	2.21	6.13
DSC-9	3.37	4.48	10.51

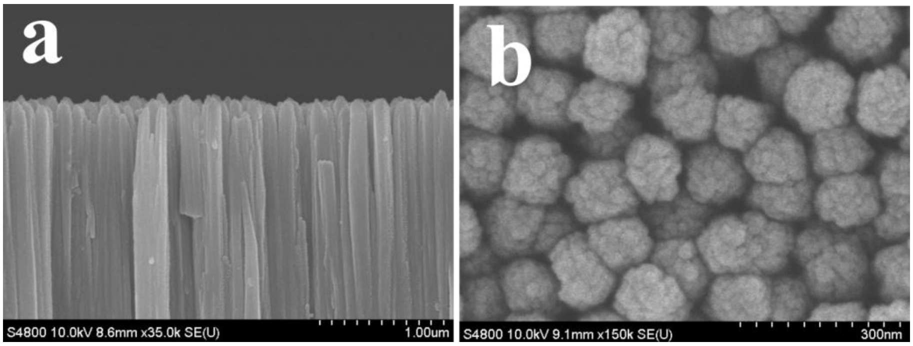

Figure S14. SEM images of the enlarged cross-sectional view of 1 h-etched rutile TiO_2 NRAs (a) and the top morphology (b); The rutile TiO_2 NRAs used for assembly of the DSC was prepared in a solution of 3 ml 5 $TiCl_4$,30 ml DI water and 30 ml HCl (36.0~38.0w%) at 150 ℃ for 12 h, followed by etching treatment in a solution containing 20 ml DI water and 40 ml HCl (36.0~38.0w%) at 150 ℃ for 1 h. The as-prepared sample was annealed at 450 ℃ for 2 h before assembled into DSCs.

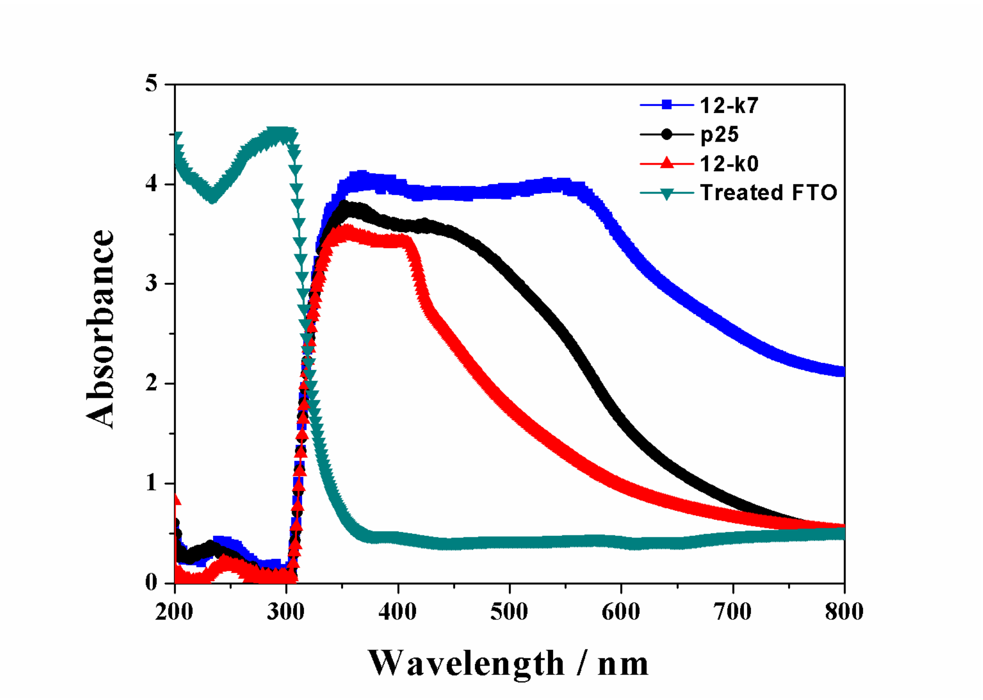

Figure S15. UV-vis absorbance spectra of the N719 dye-sensitized photoanodes: P25 (the black curve), un-etched rutile TiO_2 NRAs with the thickness around 20 μm (the red curve) and 7 h-etched rutile TiO_2 NRAs with the thickness around 20 μm (the blue curve). All the samples were annealed at 450 ℃ for 2 hours before dye-sensitizing. The sample corresponding to the green curve is the $TiCl_4$-treated FTO substrate, which is used as the baseline reference and annealed at 450 ℃ for 2 hours before the measurement. The only difference between the spectra provided here and the Fig 5b in the manuscript is that the baseline used for the latter is blank (ie. the baseline curve was obtained when no sample was fixed in the sample holder of the UV-Vis-NIR spectrophotometer).

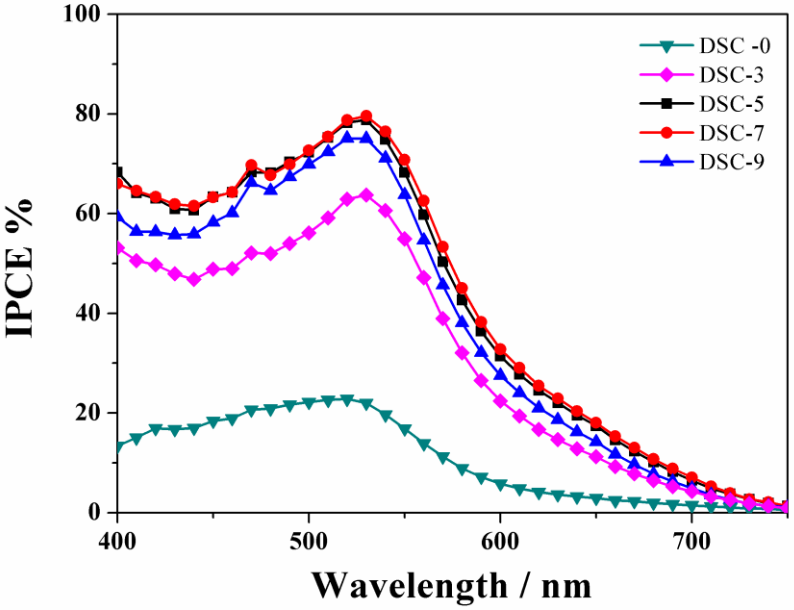

Figure S16. Incident photon-to-current efficiency (IPCE) spectra of the assembled DSCs based on rutile TiO_2 NRAs with different etching treatment; DSC-0, DSC-3, DSC-5, DSC-7 and DSC-9 are corresponding to the DSCs based on the rutile TiO_2 NRAs with 0, 3, 5, 7 and 9 h etching duration. IPCE spectra were measured on an Oriel QE/IPCE Measurement Kit (Newport) with 150-300W Oriel Solar Simulators.