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Supporting Information

Sub-100 nm TiO_2 Tubular Architectures for Efficient Solar Energy Conversion

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Characterization Methods

Morphological and Structural Characterization. A Zeiss SEM Ultra 60 field emission scanning electron microscope (FESEM) with an In-Lens detector was used to study the morphology of the samples. A Thermo Scientific K-alpha XPS spectrometer with an Al anode was used for the XPS measurements, with the spectra charge-referenced to O1s at 532 eV. The crystalline phases were detected and identified using Alpha-1 Panalytical XRD instrument with a Cu Kα radiation at $\lambda = 1.540598$ Å at a scan step (2θ) of 0.004°. A Shimadzu UV-3101PC UV-Vis-NIR spectrophotometer was used for the optical characterization of the films. Raman measurements were performed on a Raman microscope (ProRaman-L Analyzer) with an excitation laser beam of wavelength 532 nm.

Photoelectrochemical Measurements. The photoelectrochemical properties were investigated in 1M KOH solution using a three-electrode configuration with sub-100 nm TiO_2 tube array photoanodes, saturated Ag/AgCl as a reference electrode, and platinum foil as a counter electrode. A scanning potentiostat (CH Instruments, model CHI 760D) was used to measure dark and illuminated currents at a scan rate of 10 mV/s. Sunlight was simulated with a xenon ozone-free lamp (Newport) and AM 1.5 G filter at 100 mW/cm^2

Electrochemical Impedance Spectroscopy (EIS) Measurements: EIS measurements were done using Biologic SV-200 potentiostat for both long nanotubes and the sub-100nm structures. The EIS measurements were performed in 1 M KOH electrolyte at room temperature (22±2 °C) under dark conditions. A three-electrode electrochemical cell was used with the nanotubes as the working electrode, Platinum as the counter electrode and Calomel as the reference electrode. The applied voltage was swept from -0.7 V to 0.6 V, while the frequency ranged from 100 mHz to 1000 KHz.

Solar Cell Assembly and Testing: While in a dry nitrogen environment all samples were immersed in $TiCl_4$ solution at room temperature, then rinsed in ethanol and annealed at 400 ◦C for 45 min (see details below). The N719 dye was subsequently infiltrated into the nanotubes using anhydrous ethanol as a solvent. The annealed nanotube samples were immediately immersed overnight in 0.4 mM solutions of the dye. Liquid-junction solar cells were assembled by infiltrating the dye-coated TiO_2 electrode with redox electrolyte containing lithium iodide (LiI, 0.1M), diiodine (I_2 0.01M), tert-butyl pyridine (TBP, 0.4M), butylmethylimidazolium iodide (BMII, 0.6M), and guanidinium thiocyanate (GuNCS, 0.1M) in a mixture of acetonitrile and methoxy propionitrile (v/v=15:1). Conductive glass slides, sputter-coated with 100 A^0 of Pt, were used as the counter electrode. The working (nanotubes) and counter (Pt) electrodes were spaced by a 25 μm thick SX-1170 spacer. Photocurrent density and the photovoltage of the dye-sensitized solar cells were measured with active sample areas of 0.4 cm^2 using AM1.5 simulated sunlight produced by a 50W Oriel Solar Simulator (100 mW cm^{-2}), calibrated with a NREL-certified silicon solar cell, and a CHI 660C potentiostat

For $TiCl_4$ treatments, the TiO_2 nanotubes were immersed in 0.2 M aqueous solutions of $TiCl_4$ and then treated at 80 ˚C for 30 min. Subsequently, the samples were washed with DI water and rinsed with ethanol to remove any excess $TiCl_4$, and finally dried in a nitrogen jet. After the treatment, TiO_2 nanotube samples were annealed again at 400 ˚C for 45 min to crystallize attached nanoparticles.

Dye desorption measurements were carried out by immersing the samples in 5 ml of 10 mM KOH for 30 min. The concentration of fully desorbed dye was measured spectroscopically using UV/VIS spectrophotometer and calculated the amount of dye adsorption on the TiO_2 nanotube layer using Beers–Lambert law.

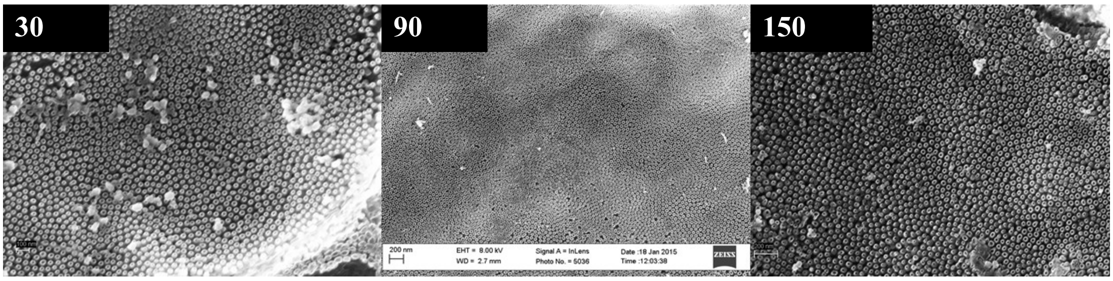

Figure S1. SEM images of the sub-100 nm TiO_2 tubes formed at different anodization times.

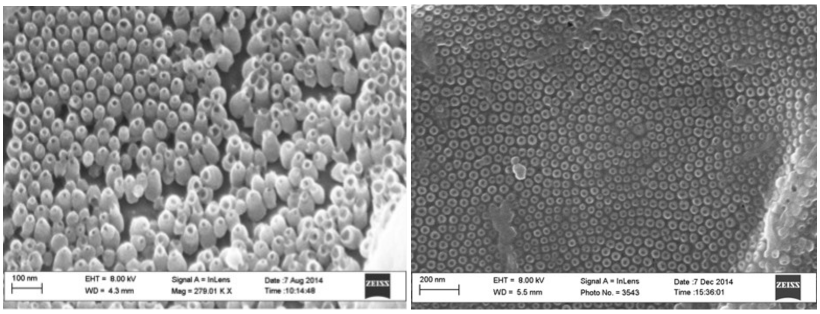

Figure S2. SEM images of the TiO_2 nanotubes fabricated in PVP-free electrolytes

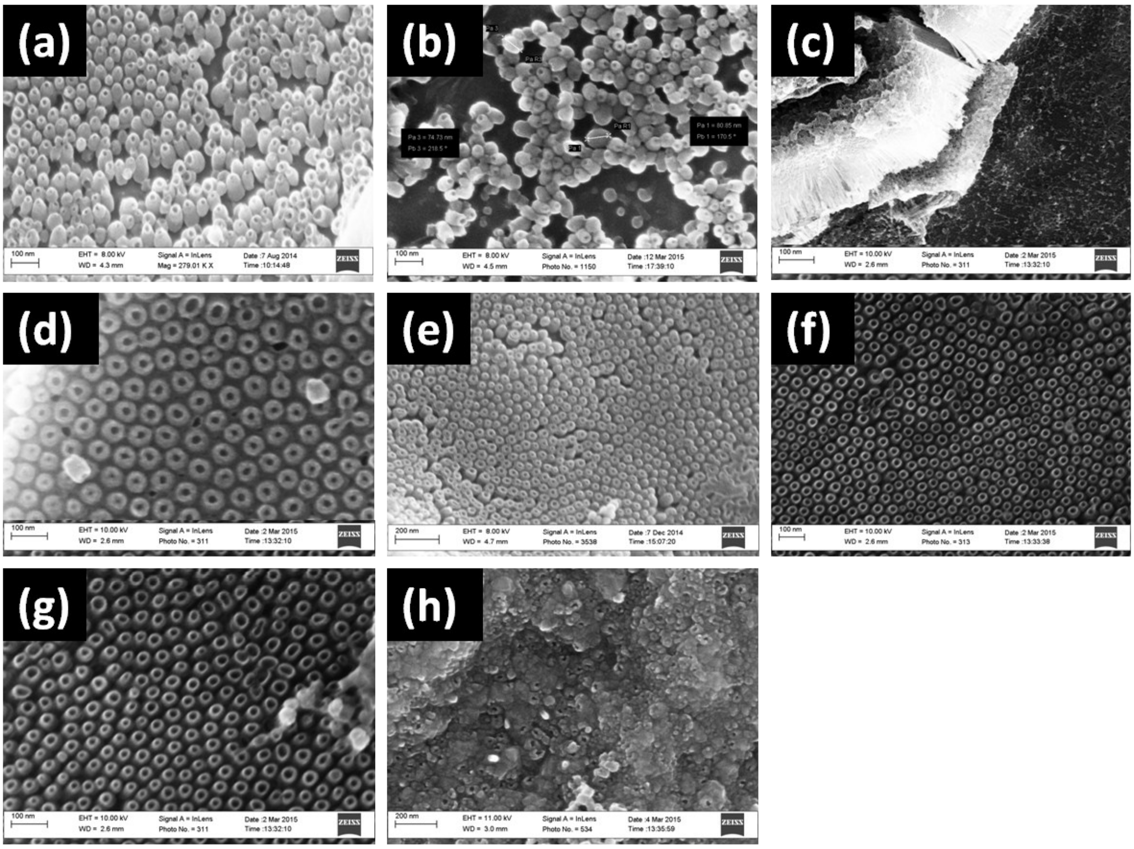

Figure S3. SEM images of the sub-100 nm TiO_2 tubes: (a, b) as-anodized, (c) the nanotubes obtained after 5 min of anodization, (d) annealed at 350°C, (e) annealed at 400°C, (f) annealed at 450°C, (g) annealed at 500°C, and (h) annealed at 600°C.

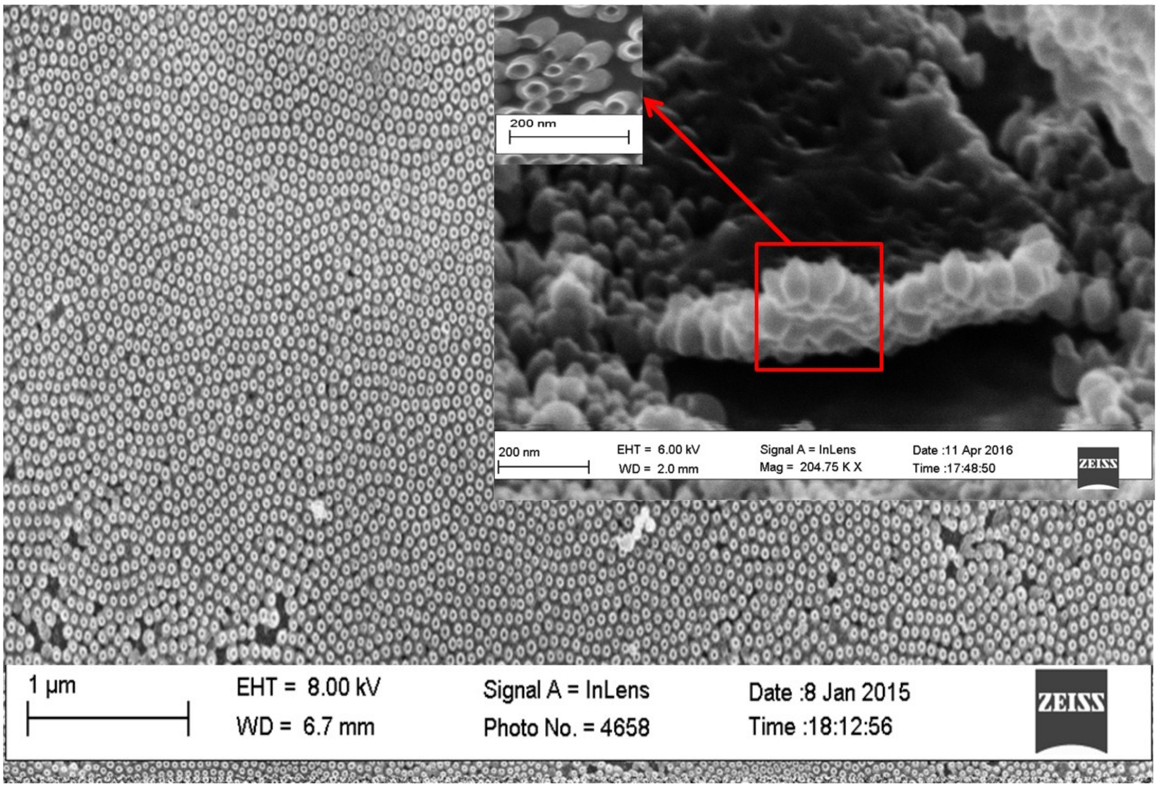

Figure S4. A large scale SEM image and the corresponding cross-sectional view of an as-prepared tubes sample

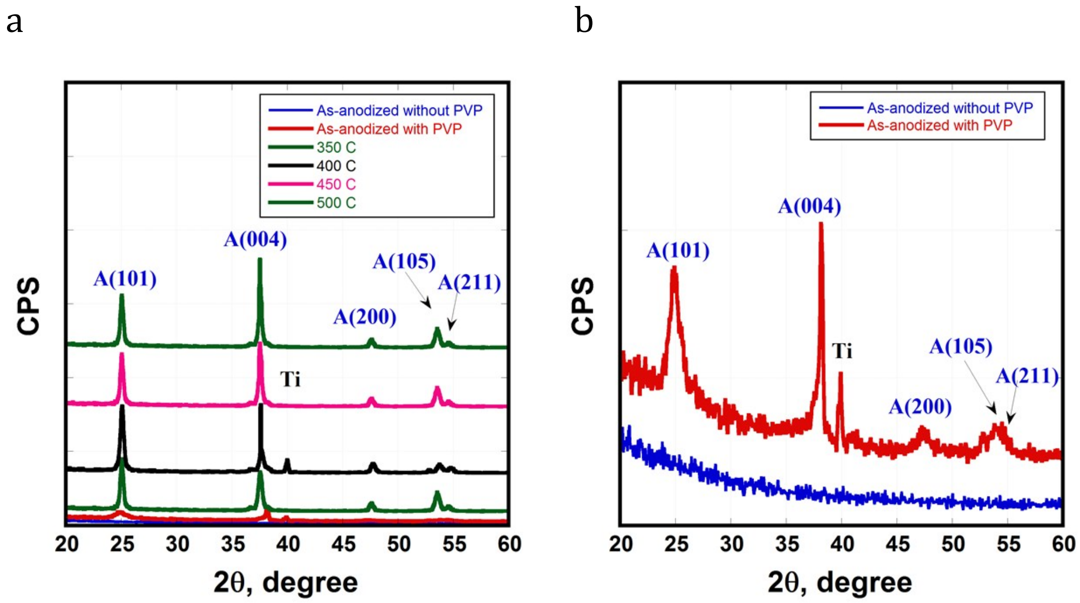

Figure S5. XRD patterns of the sub-100 nm TiO_2 tubes: (a) before and after annealing (i) as-prepared in PVP-rich electrolyte, (ii) as-prepared in PVP-free electrolyte, (iii) annealed at 200°C, (iv) annealed at 350°C, (v) annealed at 400°C, (vi) annealed at 450°C, and (vii) annealed at 500°C. (b) Magnified GAXRD patterns of an as-anodized sample obtained from PVP-rich and PVP-free electrolytes.