Supporting Information

Realization of Ultra-Long Columnar Single Crystals in TiO₂ Nanotube Arrays as Fast Electron Transport Channels for High Efficiency Dye-Sensitized Solar Cells

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Figure S1. SEM images of the TiO₂ nanotube arrays obtained from (a) classical EG electrolyte and (b) the newly developed EG/DMSO electrolyte.



Figure S2. Statistical distribution of the grain size of c-TNTAs (purple) and cs-TNTAs (red), evaluated from >10 TEM images from at least 3 batches of samples.



Figure S3. HRTEM image showing the grain boundary of two columnar crystals in cs-

TNTAs, with alternating arrangement of semi-coherent boundary and coherent one.



Figure S4. HRTEM image showing the grain boundary of two small crystals in c-TNTAs, with random arrangement of small particles.



Figure S5. XRD patterns of the c-TNTAs and cs-TNTAs



Figure S6. The current-density variation for titanium anodized at 50V in EG and EG/DMSO (1:1, vol) based electrolyte with 0.4 wt% NH₄F and various water content.

The current transients recorded during the anodizing (at 50 V) show a much smaller current density for TNTAs growth in the EG/DMSO based electrolyte than that in EG based one with identical water content (3 vol%), potentially due to the restrained carbon formation (derived from EG oxidation) in the barrier layer and thus increased the resistance of the barrier film from EG/DMSO electrolyte. The current density increases with the decrease of water content in EG/DMSO based electrolyte, which is similar to that of TNTAs growth in EG based solution.^{\$1,\$2} This is because the lower O^{2-} ions (from H₂O in electrolyte) concentration in electrolyte with less water will result in thinner oxide barrier layer and thus decreased film resistance.^{\$2} A severe anodic etching of Ti substrate and a more vigorous hydrogen evolution at Pt cathode is observed when the water content is less than 1.5 vol%, due to the drastic anodization under large current density.



Figure S7. (a) The X-ray diffraction patterns of the as-prepared TNTAs derived from different anodizing solution. (b) The zoom-in XRD patterns of (a) showing the peaks shift of anatase TiO₂ (112) and Ti₂O₃ (113) planes.

The diffraction peaks of anatase TiO₂ (112) and Ti₂O₃ (113) planes can be clearly observed in the XRD patterns of as-prepared TNTAs derived from both EG and EG/DMSO based electrolyte with 3 vol% H₂O, indicating the partially crystalline nature of the as-formed TNTAs. However, the TiO_x derived from EG/DMSO electrolyte with H₂O less than 1.8 vol% keeps almost amorphous, which is also evidenced by the weak and diffuse Raman response (Fig. S9). Notably, even in the EG/DMSO electrolyte condition, some carbon appears in the TNTAs obtained from anodizing solution with H₂O less than 1.5 vol%, due to the oxidization of EG under violent anodization as revealed above (Fig. S6). The numerous partially crystallized sites and carbon can act as crystal nucleation sites for crystal growth during sintering.



Figure S8. Fourier transform infrared spectra of the as-prepared TNTAs derived from different anodizing solution.

The FTIR spectra reveals that the as-prepared TNTAs derived from EG/DMSO electrolyte with moderate water content (1.8 vol%) contain the lowest amount of oxyhydroxide. This is because higher H₂O content will lead to more OH⁻ in anodizing solution while the drastic electrochemical reaction (mentioned above) in the less H₂O case (≤ 1.5 vol%) will accelerate the H₂O decomposition and results in higher OH⁻ as well.^{s3} The dehydroxylation of the amorphous tube wall during annealing is identified as the initiation of TiO₂ crystallization process.^{s4} Therefore, a larger quantity of oxyhydroxide in the as-formed TNTAs will result in a larger amount of crystal nuclei and thus small grain size of nanotubes after sintering.



Figure S9. (a) The Raman spectra of the as-prepared TNTAs derived from different anodizing solution. (b) The Raman spectrum of the cs-TNTAs after annealing at 500° C for 2 h.



Figure S10. TEM images of TNTAs prepared at 50 V applied potential for 120 min in the 0.4 wt% NH₄F based anodizing electrolyte with different solvent and various H₂O content (a) EG-3.0 vol%, (b) EG/DMSO-3.0 vol%, (c) EG/DMSO-1.8 vol%, (d) EG/DMSO-1.5 vol%, (e) EG/DMSO-0.5 vol%. The insets show statistical distribution of grain size of the corresponding TNTAs, evaluated from >10 TEM images.



Figure S11. Schematic representation showing the effect of TiO₂ nuclei, titanium oxyhydroxide, carbon and residue stress on the formation of small grain based- and large-columnar-crystals based TNTAs.



Figure S12. SEM images showing top surface morphology of cs-TNTAs electrode subjected to a "TiO₂-filling" without the evacuation process, showing the TiO₂-blocked orifices (inset) and residual TiO₂-cakes on the top surface.



Figure S13. SEM images showing the top surface morphologies of (a) pristine cs-TNTAs and (b) the hybrid structure after the vacuum-assisted F68-free TiO_2 sol filling, suggesting that only a compact layer was formed along the nanotube walls to "add" the thickness of the walls.



Figure S14. X-ray diffraction (XRD) patterns of the cs-TNTAs hybrid structures after 0, 1, 2, and 3 times of filling, respectively.



Figure S15. UV-Vis absorption spectra of the dye solution desorbed from the TNTAs electrodes anodized in the classical ethylene glycol (EG) based electrolyte (c-TNTAs) and EG/DMSO based electrolyte (cs-TNTAs).

Table S1. Photovoltaic parameters of the nanoparticle/c-TNTAs hybrid structure based hierarchical DSSCs, measured under 100 mW cm⁻² under front-illumination.

Devices	Dye-loading [mol cm ⁻²]	J _{sc} [mA m ⁻²]	V _{oc} [V]	FF	PCE [%]	$R_{ m w}$ [Ω]	$R_{ m k}$ $[\Omega]$	η _{cc} [%]
c-TNTAs-0	1.01×10 ⁻⁷	10.84	0.73	0.61	4.83	2.59	21.2	88
c-TNTAs-1	1.89×10 ⁻⁷	12.72	0.74	0.63	5.98	2.79	18.6	85
c-TNTAs-2	2.31×10 ⁻⁷	13.47	0.71	0.61	5.75	2.96	14.8	80
c-TNTAs-3	2.62×10 ⁻⁷	13.97	0.66	0.55	5.07	3.04	13.2	77

Hall-effect measurement:

For the Hall-effect measurement, the thickness of freestanding c-TNTAs and cs-TNTAs films were subtracted to about 800 nm by mechanical grinding and then ion beam milling. TiO₂ network with thickness about 800 nm was prepared by spin-coating the F68 contained TiO₂-sol onto a glass, followed by a thermal annealing at 450°C for 30 min.

Four electrodes were constructed according to the following scheme for Halleffect measurements with contacts produced by indium soldering to reduce contact resistances.



Table S2. Summary of Hall-effect results of c-TNTAs, cs-TNTAs and TiO₂ network films

Matariala	II-11	Resistivity	Carrier	Mobility	
Materials	Hall constant	$[\Omega \text{ cm}]$	concentration [cm ⁻³]	$[cm^2 v^{-1} s^{-1}]$	
c-TNTAs	2.32	3.74	2.69×10 ¹⁸	0.62	
cs-TNTAs	0.52	0.17	1.20×10 ¹⁹	3.14	
TiO ₂ network	2.67	6.21	2.34×10 ¹⁸	0.43	



Figure S16. Comparison of the I-V curves of the c-TNTAs and cs-TNTAs film, showing the conductivity of the films.



Figure S17. Equivalent circuits represented by a transmission line model for fitting the EIS results



Figure S18. The dye-loading amount of TiO₂/cs-TNTAs hybrids and NPs-based electrodes as a function of film thickness of photoanodes.



Figure S19. *I-V* characteristic curve of TiO₂ nanoparticle based DSSCs with optimized photoanode, measured under 100 mW cm⁻² illumination.

Reference

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