

## Supplementary Information

### Experimental Section

#### 1.1 Fabricating the FS-TNT Array Layers

Vertically oriented, highly ordered TNT array layer was fabricated in the two-electrode electrochemical cell with a 1×4cm Ti substrate (0.5mm, 99.7%) as the work electrode and Pt wire(99.7%) as the counter electrode, where was filled with the ethylene glycol electrolyte containing 0.5wt.% NH<sub>4</sub>F and 3vol.% tri-distilled water at the constant 60V DC potential. Prior to anodization, Ti substrates were orderly degreased in an absolute ethanol, isopropanol and tri-distilled water with ultrasonic treatment. The process was divided into the anodizing pre-treatment, the annealing TNTs, and the detaching TNTs. The Ti substrates pre-anodized at room temperature for 30min, were removed the TNT layer by ultrasonication in tri-distilled water and then the hexagonal patterns were regularly printed on the pre-treatment substrates<sup>1</sup>. The patterned substrates were re-anodized 1, 2, 3, 4h to grow TNT layers followed by annealing at 250-650°C at air for 2h with a heating and cooling rate 2°C/min. The annealed TNT layers grown on the Ti substrates were again implemented the third anodization at 20, 25, 30, 35, 40, 45, 50°C electrolyte and only at 45°C electrolyte the annealed TNT layer (top layer) was successfully detached from the amorphous TiO<sub>2</sub> layer precursor(bottom layer) formed on the Ti substrate in the third reaction, then the detaching layer was again dried at the corresponding annealing temperature after washed in ethanol and tri-distilled water. Moreover, the detaching time promptly decreased from 30min to 10min with the increase of the annealing temperature. According to the anodizing time 1-4h, these detaching TNT layers were marked as FS1-TNTs, FS2-TNTs, FS3-TNTs, FS4-TNTs.

#### 1.2 Assembling the DSSCs

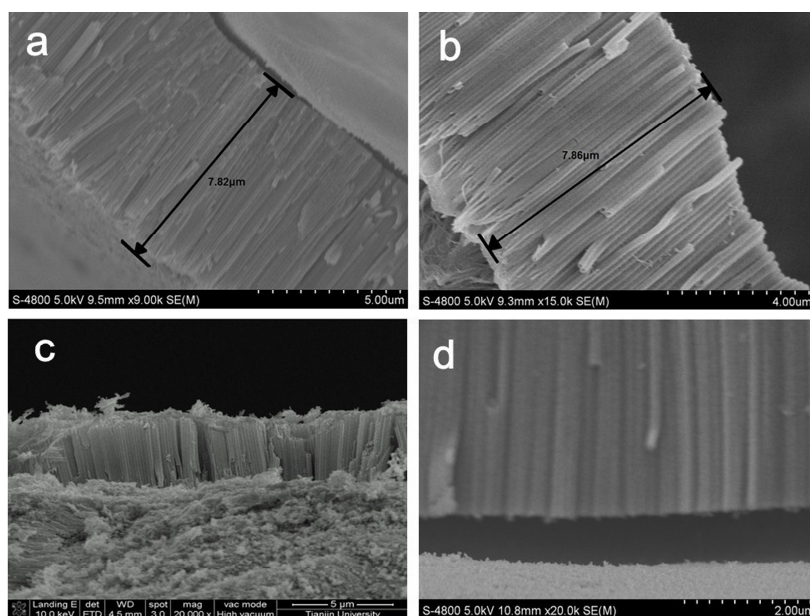
A FTO(thickness for 2.2mm, NSG, Japan) with 2cm×2cm was orderly kept in an ultrasonical ethanol, isopropanol and tri-distilled water for 5min after it was degreased in a detergent solution using a ultrasonic bath for 15min, then it was taken out and dried in the oven at 120°C. The FTO,

pre-treated with 40mM  $\text{TiCl}_4$  solution at  $70^\circ\text{C}$ , was dried and then printed with P25 paste including 6g P25, 16ml absolute ethanol, 0.1ml acetic acid, 0.6g polyethylene glycol(PEG-600, Aldrich), 2g ethocel(Aldrich) by doctor-blading technique, and immediately the fabricating CBU FS2-TNT layer was faced and transferred to P25 paste(as the bonding medium) pre-coated on the FTO<sup>2,3,4</sup> under a slight pressure with a slide glass, followed by annealing from 125 to  $450^\circ\text{C}$ <sup>5</sup>. The CBU FS-P25 film placed on the FTO substrate again treated with 40mM  $\text{TiCl}_4$  solution at  $70^\circ\text{C}$ , was immersed in 30 $\mu\text{M}$  N719(DYESOLD Limited) solution in a mixture of acetonitrile and *tert*-butanol(vol=1:1) for 30-32h to assure complete sensitizer uptake, and the sensitized CBU photoanode(active area  $0.8\times 0.8\text{cm}^2$ ) was further sandwiched with the pre-treated Pt photocathode( $1.2\times 1.8\text{cm}^2$ , Heptachroma, China) in an ultrasonic absolute alcohol for 10min, separated by 60 $\mu\text{m}$  surlyn1702(Solaronix, Switzerland) spacer and the space was filled with the high-performance electrolyte DHS-E23(Heptachroma, China). Compared to the front-illuminated DSSC with the CBU configuration, P25 particle film as the photoanode film was also used to fabricate the counterpart and was further investigated.

### 1.3 Characterization and Measurement

The FS-TNT layer was characterized by FE-SEM(5.0kV, S4800), FE-TEM with EDX(CuK $\alpha$ , 200kV, Tecnai G2 F20) and XRD(Rigaku D/max 2500v/pc, CuK $\alpha$ ), and the bond energy of the FS-TNT, the TNT with Ti substrate was measured by XPS(PHI1600), and the thickness of P25 particle film was measured by surface morphology instrument(DEKTAK6M, VEECO). The *J-V* measurement of DSSCs was implemented via a Keithley 2400 digital source meter controlled by a computer and standard AM1.5 solar simulator(300W, Oriel 91160-1000 SOLAR SIMULATOR 2  $\times$  2 BEAM), calibrated by an Oriel reference solar cell. The monochromatic *IPCE* of DSSCs was performed by using a commercial setup (QTest Station 2000 IPCE Measurement System, CROWNTECH, USA).

## Figure



**Fig. S** The thickness of TNT layer with 2h anodization before(a) and after(b) the detaching the bottom layer on an opaque Ti substrate; The interfacial contact of the FS2-P25 CBU(c) and OTU (d) configuration.

## References

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