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.% NH₄F 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. 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 TiO₂ 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 over at 120°C. The FTO,
pre-treated with 40mM TiCl$_4$ solution at 70°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$^{2,3,4}$ under a slight pressure with a slide glass, followed by annealing from 125 to 450°C$^5$. The
CBU FS-P25 film placed on the FTO substrate again treated with 40mM TiCl$_4$ solution at 70°C,
was immersed in 30μM 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 0.8×0.8cm$^2$) was further sandwiched with the pre-treated Pt
photocathode(1.2×1.8cm$^2$, Heptachroma, China) in an ultrasonic absolute alcohol for 10min,
separated by 60μm 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(CuKa,
200kV, Tecnai G2 F20) and XRD(Rigaku D/max 2500v/pc, CuKa), 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
×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

![Figure](image)

**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