# Supporting Information

# Black $TiO_2$ Nanotube Arrays for High-Efficiency Photoelectrochemical Water-Splitting

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## Experimental Details

### Preparation of TNTs and B-TNTs

The highly ordered TNTs were prepared on Ti foil (99.5% purity, 250 μm in thickness, Alfa Aesar) via a two-step electrochemical anodization process with copper plate as the cathode. The electrolyte consisted of 0.4 wt% $NH_4F$ dissolved in a mixture of glycol and de-ionized water (97:3 in volume ratio). The Ti foil was first anodized at 100 V supplied by a DC power supply (INTERLOCK IPD-20001SLU, China) for 25 min. The pre-formed TNTs layer was peeled off via ultrasonication to produce bowl-like footprints on the Ti foil. The second step of anodization was carried out in the same electrolyte at 100 V for another 5 min to obtain high-quality TNTs. After dried in air, the as-prepared TNTs were first annealed at 500 °C for 4 h in air, and further Al reduced at 500 °C for 4 h. When conducting Al reduction process, TNTs samples and aluminum powder were placed separately in a two-zone tube furnace and then evacuated to a base pressure below 8 Pa. Subsequently, TNTs samples and aluminum powder were heated to 500 °C and 850 °C, respectively.

### Characterization of TNTs Samples

To investigate the microstructure and composition of the samples, UV-Vis-NIR spectrometer

(Hitachi U4100), field emission scanning electron microscopy (FE-SEM, Hitachi S-4800), transmission electron microscopy (TEM, JEOL JEM-2100F) with an energy dispersive spectrometer (Oxford), X-ray diffraction (XRD, Bruker D8 Advance), X-ray photoelectron spectroscopy (XPS, PHI 5000C ESCA System) with Mg Ka X-ray (hv=1253.6 eV) at 14 kV and Raman spectroscopy (Thermal Dispersive Spectrometer) with 532 nm laser excitation were employed.

To characterize the photoelectrochemical performance of the samples, a conventional three-electrode system was utilized to conduct electrochemical measurements with an electrochemical workstation (CHI660B, CH Instruments). The TNTs attached on Ti substrates were used directly as the working electrode, with a Pt wire and an Ag/AgCl (KCl saturated) electrode as counter and reference electrodes respectively in 1 M NaOH aqueous solution (pH = 13.6). A set of linear sweeps and transient photocurrent responses were recorded in dark and under illumination. A 150W Xe lamp was used as the light source to simulate the sunlight irradiation. The light intensity was measured by a calibrated Si photodiode. Mott-Schottky plots were derived from impedance-potential tests conducted at a frequency of 1 kHz in dark. The IPCE was measured using a 300 W Xe lamp and a monochromator (Oriel Cornerstone 130 1/8 m). The visible light was obtained by excluding the UV part of the simulated sunlight with a 420 nm cutoff glass light filter.

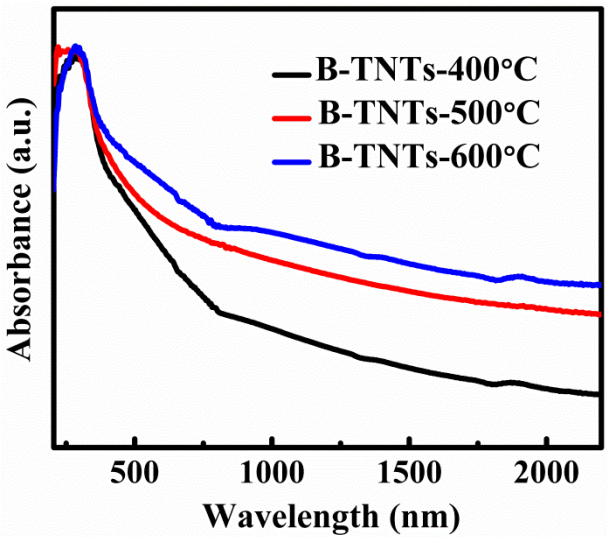


**Figure. S1.** Absorption spectra of B-TNTs generated by Al reduction at different temperature.

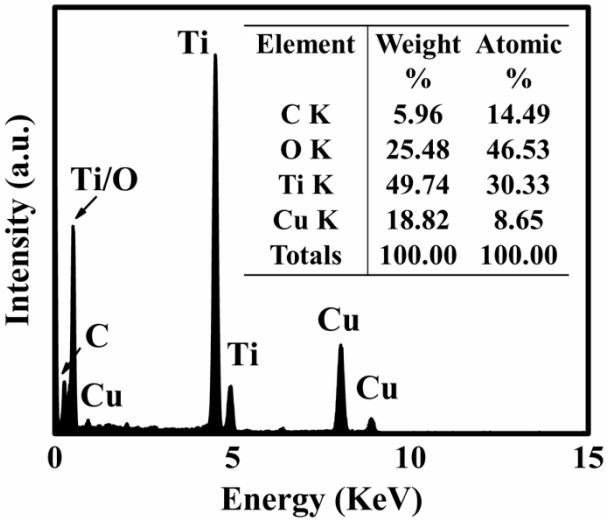


**Figure. S2.** EDS scanned spectrum of B-TNTs.

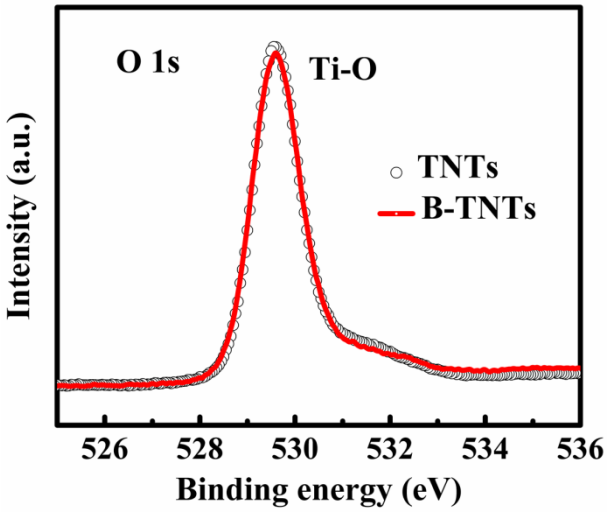


**Figure S3.** O 1*s* XPS spectra of TNTs and B-TNTs.

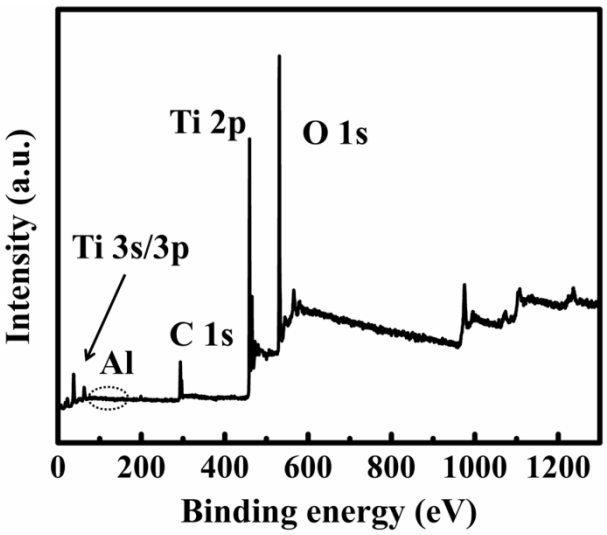


**Figure S4.** XPS survey spectrum of B-TNTs.

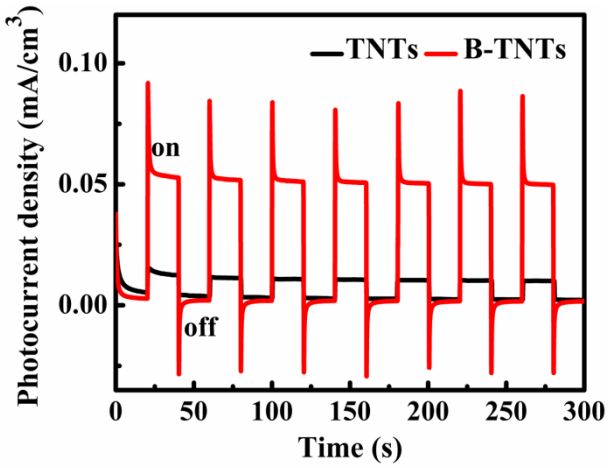


**Figure S5.** Transient photocurrent response to visible light of TNTs and B-TNTs at 0.23 $V_{Ag/AgCl}$.

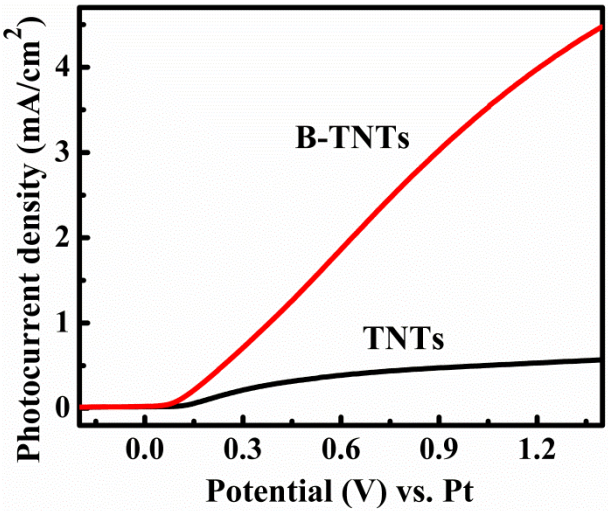

**Figure S6.** 2-electrode *J-V* curves of TNTs and B-TNTs.