Electronic Supplementary Information

N-doped TiO_2 Nanotubes Coated with Thin TaO_xN_y Layer for Photoelectrochemical Water Splitting: Dual Bulk and Surface Modification of Photoanode

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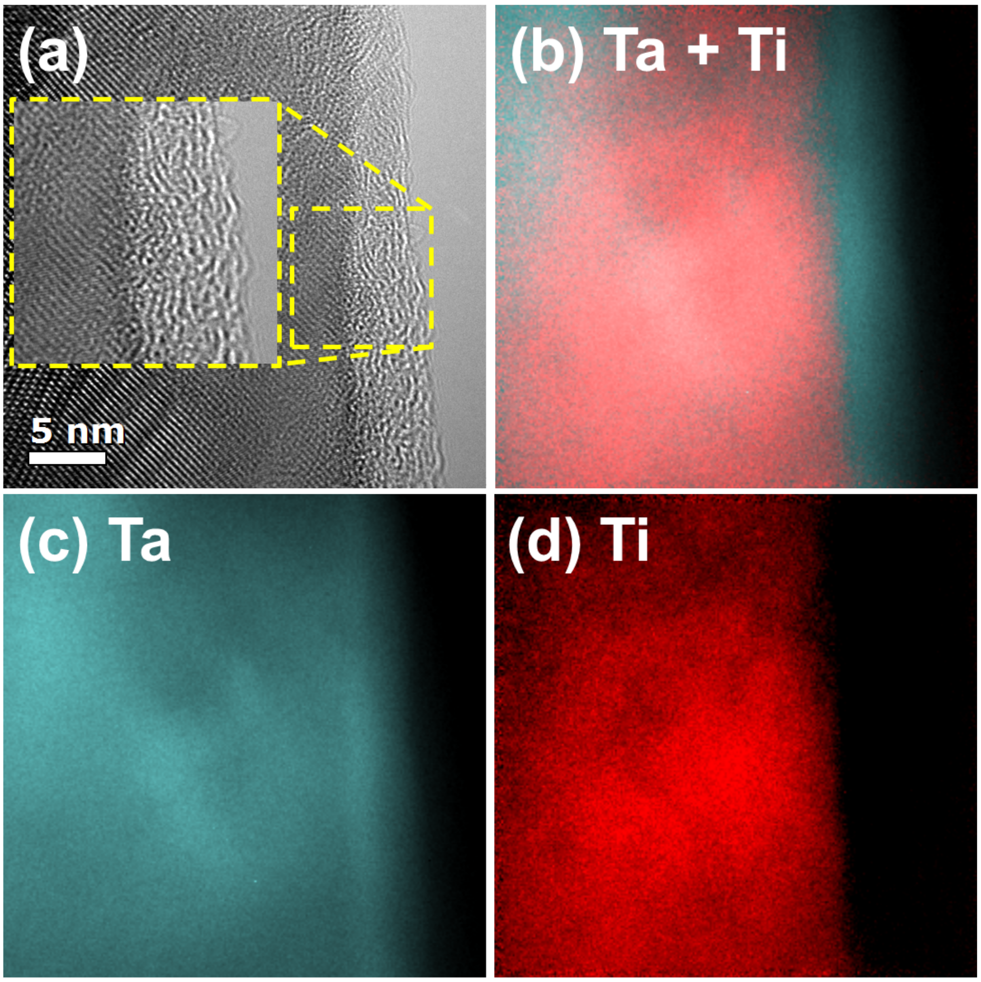


Figure S1. (a) Energy-Filtered TEM (EF-TEM) image and EELS elemental maps of (b) Ta + Ti, (c) Ta, and (d) Ti. The inset shows a magnified EF-TEM image.

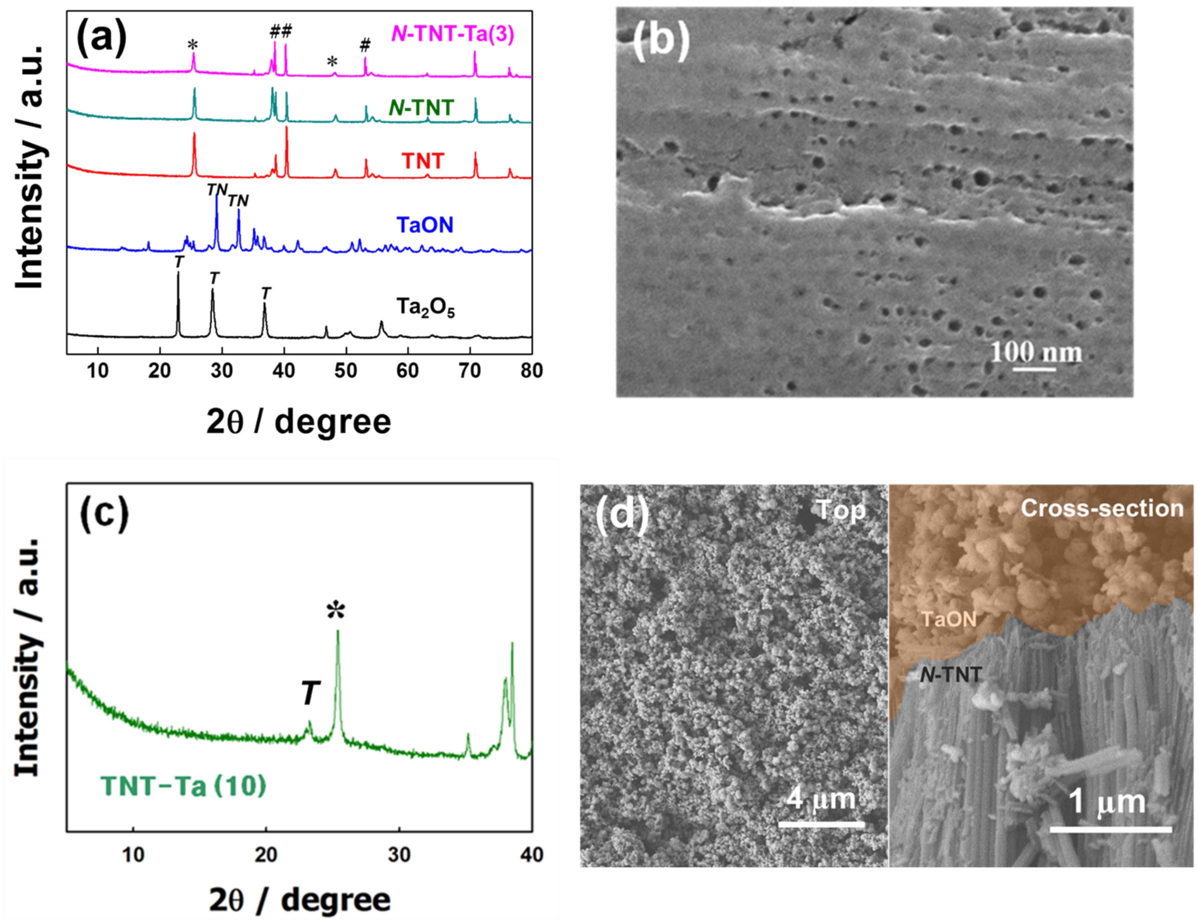
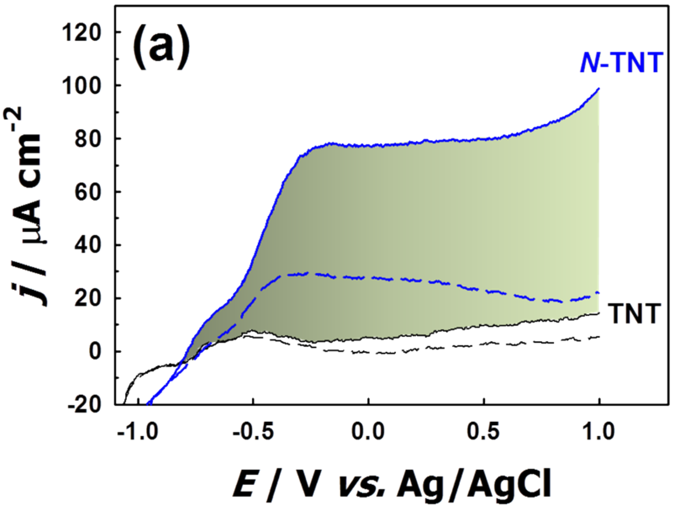


Figure S2. (a) XRD patterns of Ta_2O_5, TaON (nitridation at 850 ^{o}C from Ta_2O_5), TNT, *N*-TNT, and *N*-TNT-Ta(3). (b) SEM image and (c) XRD pattern of TNT-Ta(10). (d) FESEM images of *N*-TNT-Ta(EPD) (the left panel for Top view and the right panel for cross-sectional view). *T*, *TN*, ∗, and # in the XRD figure represent Ta_2O_5, TaON, anatase TiO_2, and Ti foil diffraction peaks, respectively.



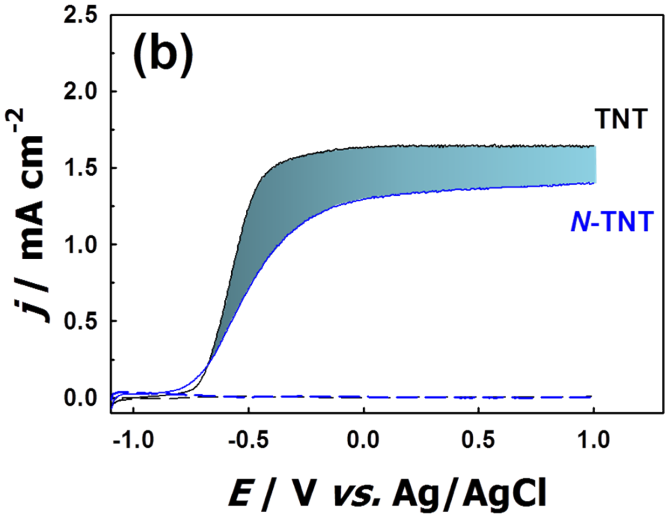


Figure S3. Voltammograms of TNT and *N*-TNT under (a) visible ($\lambda > 420$ nm) and (b) UV ($\lambda > 320$ nm) illumination. Black and blue dashed lines represent voltammograms of TNT and *N*-TNT in the dark, respectively. The area yellow green and sky blue represent the increase (visible) and decrease (UV) of photocurrent after nitridation process (N-doping) compare to TNT, respectively.

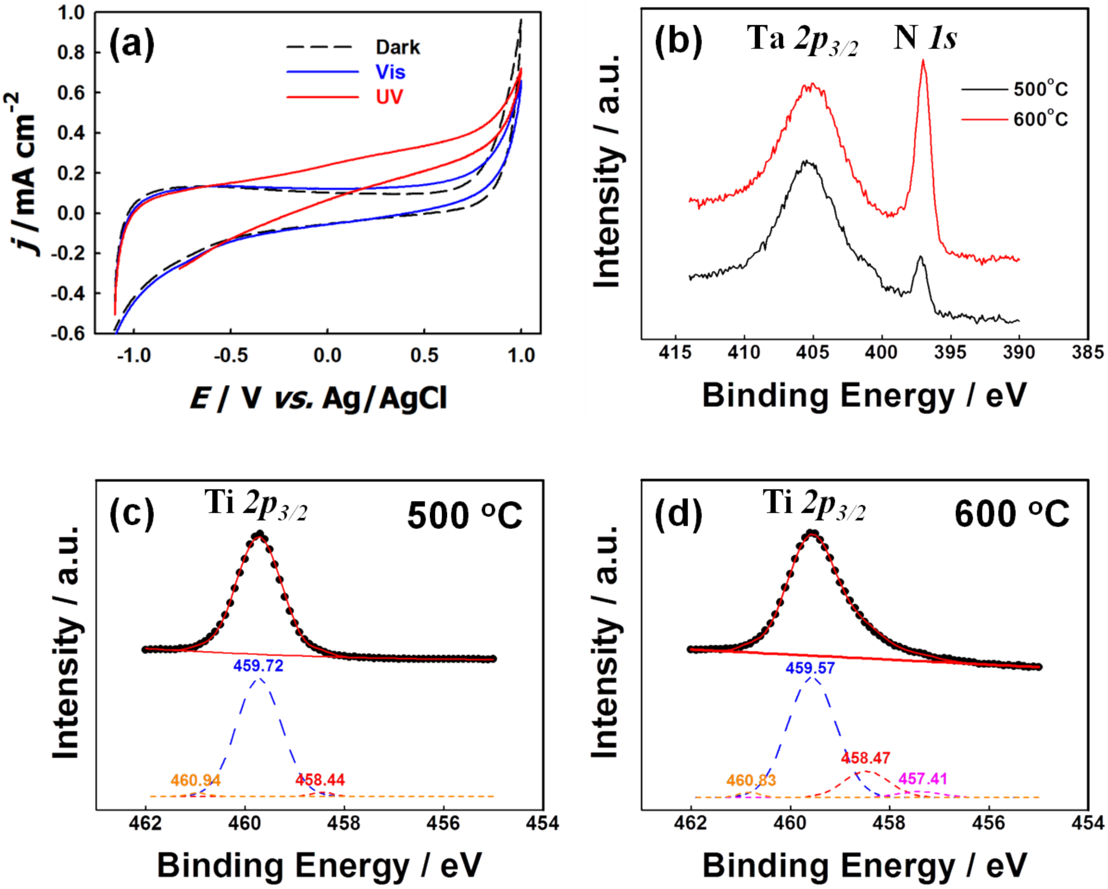


Figure S4. (a) Cyclic voltammetry of *N*-TNT-Ta(3) nitrided at 600°C in the dark, under visible (λ > 420 nm) and UV (λ > 320 nm) illumination. (b) XPS (Ta *2p*$_{3/2}$ and N *1s*) spectra of *N*-TNT-Ta(3) nitrided at 500 °C and 600 °C. Deconvoluted XPS (Ti *2p*$_{3/2}$) spectra of *N*-TNT-Ta(3) nitrided at (c) 500 °C and (d) 600 °C.

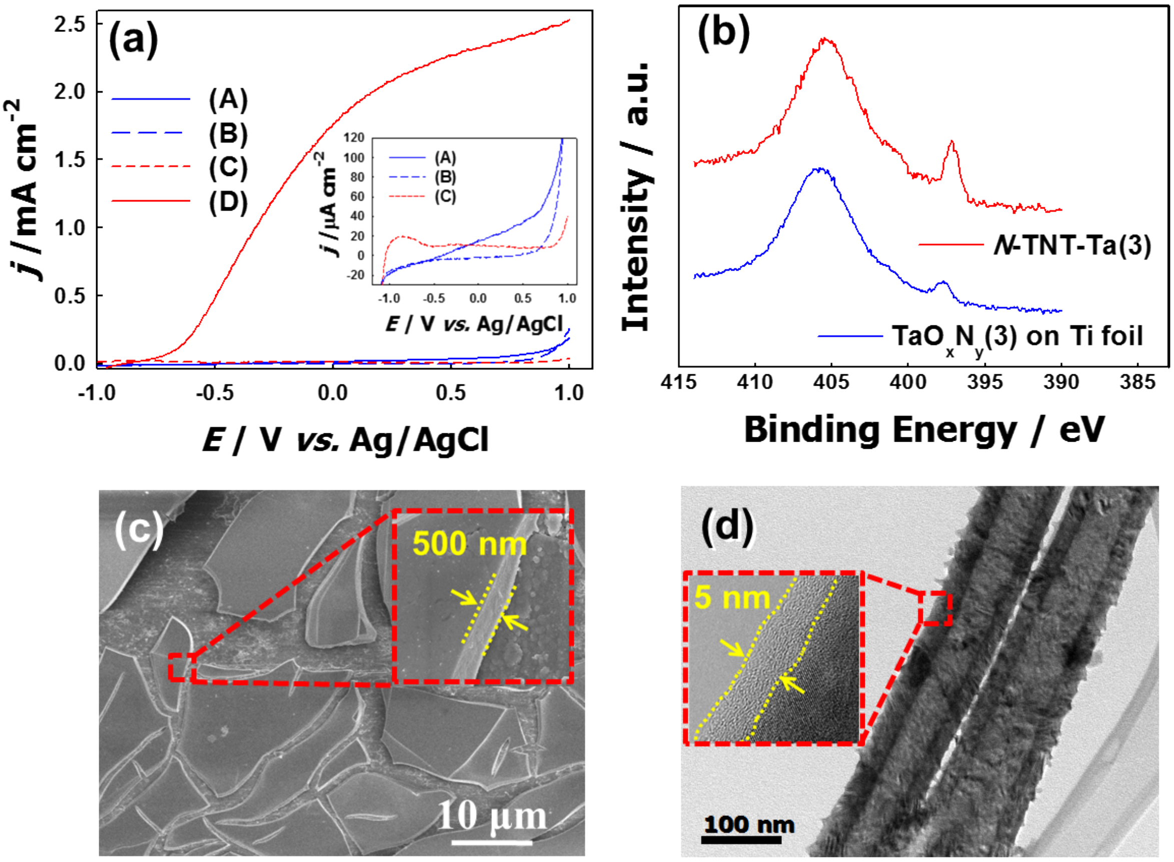


Figure S5. (a) Voltammograms of (A, B) TaO$_x$N$_y$(3) on Ti foil and (C, D) *N*-TNT-Ta(3) under dark (dotted line) and UV illumination (λ > 320 nm, solid line). (b) XPS (Ta *2p*$_{3/2}$ and N *1s*) spectra of *N*-TNT-Ta(3) and TaO$_x$N$_y$ (3) film grown over Ti foil. (c) SEM image of TaO$_x$N$_y$ (3) on Ti foil. (d) TEM image of TaO$_x$N$_y$(3) coated *N*-TNTs detached from the *N*-TNT-Ta(3) film. The insets in (c) and (d) represent their magnified images.

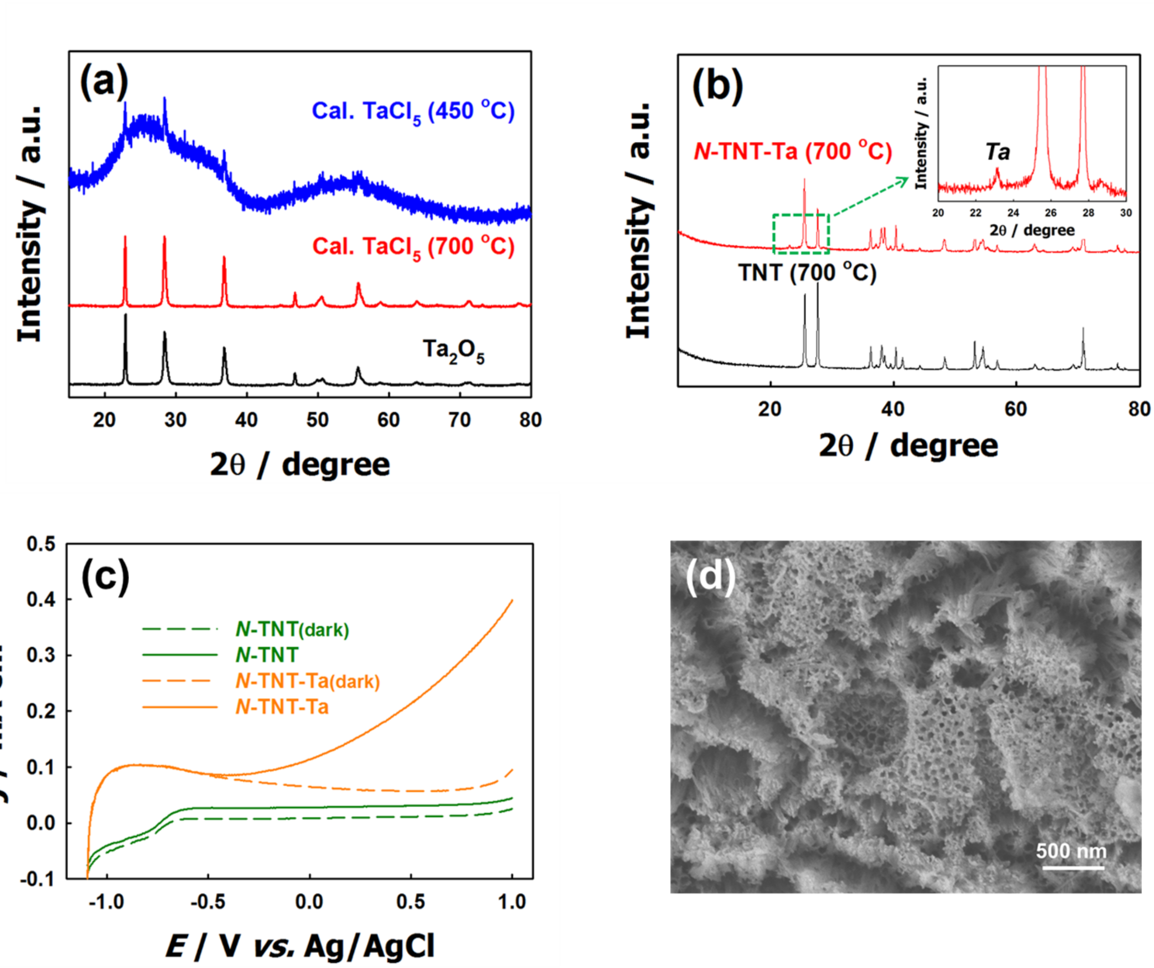


Figure S6. (a) XRD spectra of commercial Ta_2O_5 (Aldrich), amorphous Ta_2O_5 calcined at 450°C (blue line), and crystalline Ta_2O_5 calcined at 700 °C (red line) from $TaCl_5$. (b) XRD spectra of TNT and *N*-TNT-Ta(3), both calcined at 700 °C. Inset shows magnified XRD spectrum of *N*-TNT-Ta(3). The "Ta" label in the inset represents TaO_xN_y diffraction peak. (c) Voltammetry of *N*-TNT and *N*-TNT-Ta(3) electrodes were annealed at 700 °C in the dark and under visible light illumination ($\lambda > 420$ nm). (d) FESEM image of TNT annealed at 700 °C.

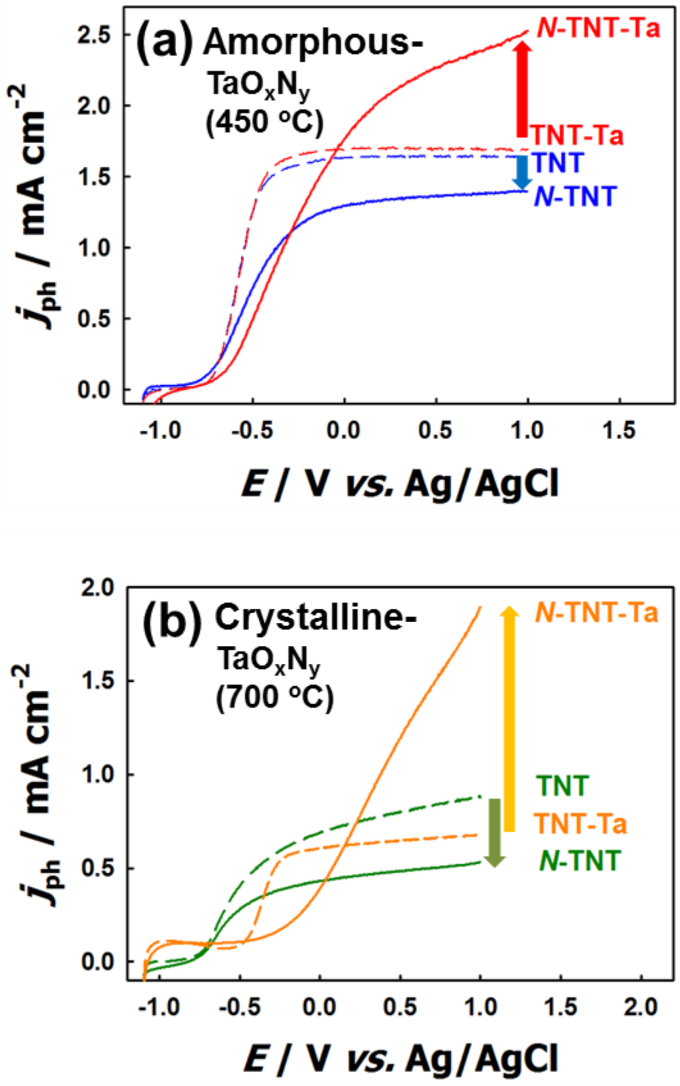


Figure S7. Voltammograms of (a) low temperature (450 °C) and (b) high temperature (700 °C) annealed TNT, *N*-TNT, TNT-Ta(3), and *N*-TNT-Ta(3) under UV ($\lambda > 320$ nm) illumination.

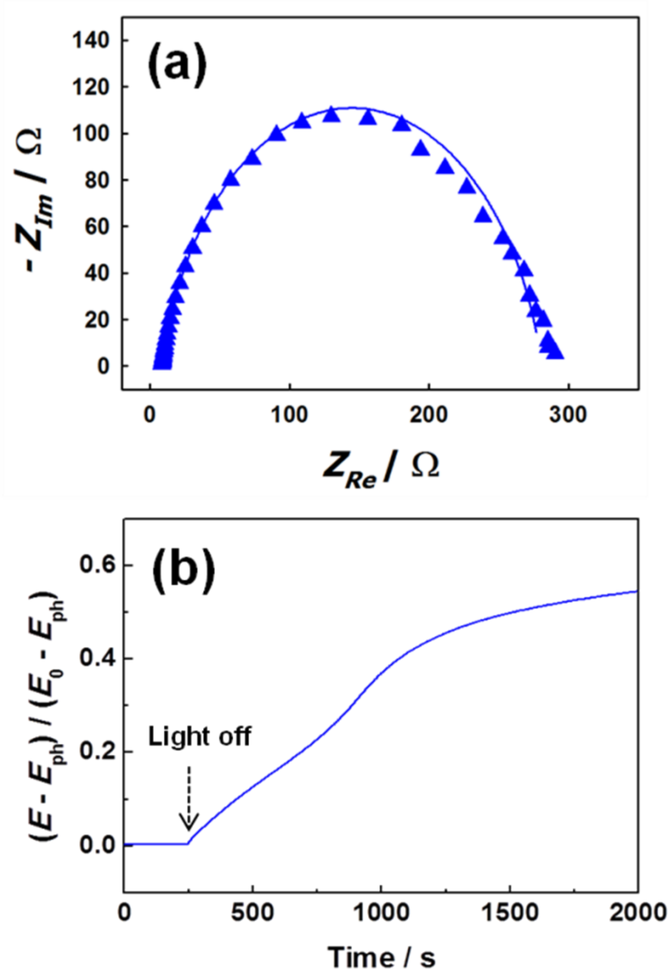


Figure S8. (a) Nyquist plot of TNT obtained at an applied potential of 0 V vs. Ag/AgCl and under UV light (λ > 320 nm) irradiation. Impedance data was fitted to a conventional Randles circuit (solid blue line). (b) Normalized open-circuit potential (OCP) decay curve of TNT after turning off the UV light (λ > 320 nm) irradiation.

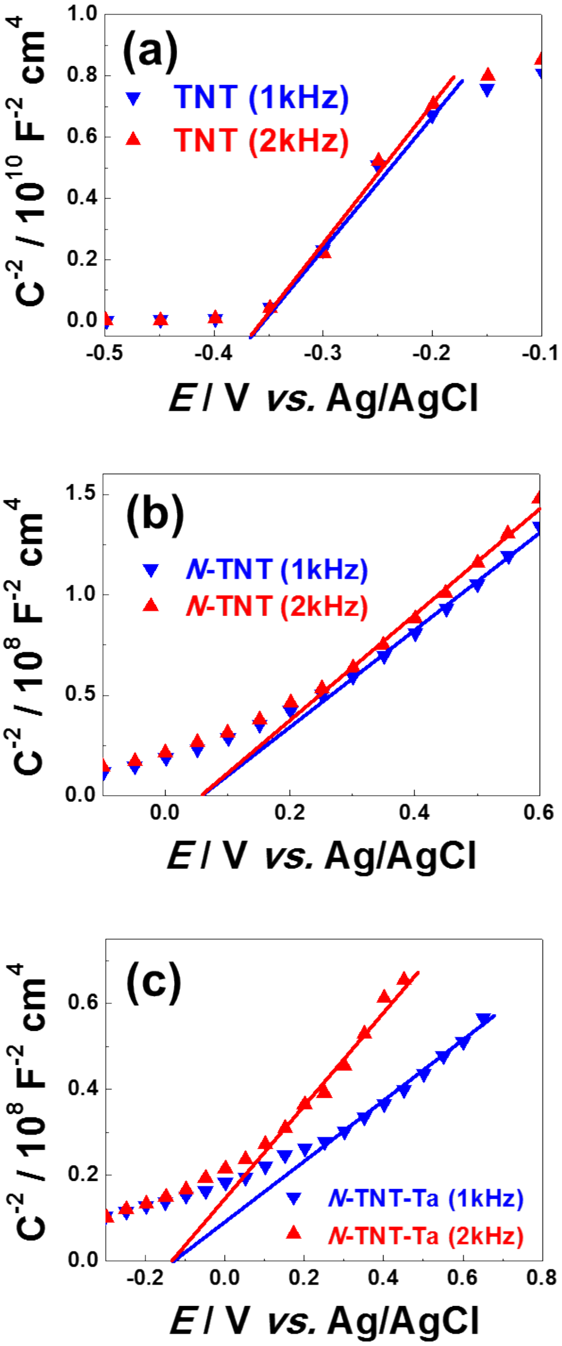


Figure S9. Mott-Schottky plots of (a) TNT, (b) *N*-TNT, and (c) *N*-TNT-Ta(3) were measured at fixed frequencies of 1 and 2 kHz in the dark with a potential amplitude of 10 mV.

Table S1. XPS Peak Positions (compositions) and Ta/Ti Ratio in TNT, *N*-TNT, and *N*-TNT-Ta hybrids prepared at 450ºC.

Sample	Peak position (eV)				Ta / Ti Ratio
	Ta *4f*	Ti $2p_{3/2}$	O *1s*	N *1s*	
TNT	-	458.7	530.0	-	-
N-TNT	-	458.7	530.0	396.7 (0.7%)	-
N-TNT-Ta (1)	25.9 (5.0%)	458.8	530.1	396.0 (0.6%)	0.22
N-TNT-Ta (2)	25.9 (9.2%)	458.7	530.1	396.3 (1.2%)	0.51
N-TNT-Ta (3)	25.8 (11.4%)	458.8	530.1	396.2 (1.5%)	0.77
N-TNT-Ta (4)	25.8 (14.3%)	458.8	530.2	396.3 (2.0%)	1.11

Table S2. Photocurrent (j_{ph}) generation and corresponding enhancement factors (EFs) obtained from voltammetry.

	450 °C		700 °C	
	visible	*UV*	*visible*	*UV*
Sample	EF[b] (j_{ph} /μA cm^{-2})[a]	EF[b] (j_{ph} /mA cm^{-2})[a]	EF[b] (j_{ph} /μA cm^{-2})[a]	EF[b] (j_{ph} /mA cm^{-2})[a]
TNT	-	1.2 (1.64)	-	1.6 (0.87)
N-TNT	1 (90)	1 (1.39)	1 (41)	1 (0.53)
N-TNT-Ta(3)	3.6 (325)	1.8 (2.45)	8.5 (350)	3.3 (1.75)

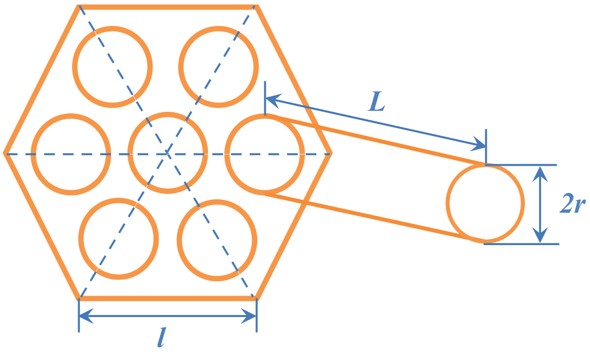
[a] j_{ph} was obtained at a bias of +0.9 V (vs. Ag/AgCl) from Figs. 5a, S6c, and S7.
[b] EF (enhancement factor) was obtained from j_{ph} with respect to the *N*-TNT.

Estimation of the Real Surface Area of Titanium Dioxide Nanotubes Photoanodes

In order to estimate the charge donor density (N_d, cm^{-3}) of the electrode from Mott-Schottky (MS) plots, we need its real surface area (A_r). To estimate it, we shall consider that:

1. The nanotubes are arranged on the surface as a two-dimensional (2D) honeycomb-like hexagonal unit cell that infinitely repeats itself over the whole electrode geometric (projected) surface.
2. The real-to-geometric surface area ratio (A_r / A_g) can be estimated from the same area ratio corresponding to the unit cell.

The main geometric features of such 2D unit cell are the next:



where l is the side length of the unit cell, r is the pore radius and L is the pore depth. The geometric surface area (A_g) of this unit cell equals that of a hexagon:

$$A_g = \frac{3\sqrt{3}}{2} l^2$$

On the other hand, the real surface area (A_r) has the contribution from the hexagon and the lateral walls of the 7 pores (A_p) contained within the 2D unit cell:

$$A_r = A_g + 7A_p = \frac{3\sqrt{3}}{2} l^2 + 14\pi r L$$

Thus, the real-to-geometric surface area ratio (i.e. roughness factor) will be given by:

$$\frac{A_r}{A_g} = 1 + \frac{7A_p}{A_g} = \boxed{1 + \frac{28\pi\sqrt{3}}{9}\left(\frac{rL}{l^2}\right)}$$

From SEM images, the parameters r, L and l can be estimated. Taking r = 37.5 nm, L = 4500 nm and l = 250 nm, the roughness factor will be:

$$\frac{A_r}{A_g} = 46.7$$

For the geometric area of 1 cm^2, the real surface area will be 46.7 cm^2.