Supplementary Information for

Ultra-stable self-standing Au nanowires/TiO_2 nanoporous membrane system for high-performance photoelectrochemical water splitting cells

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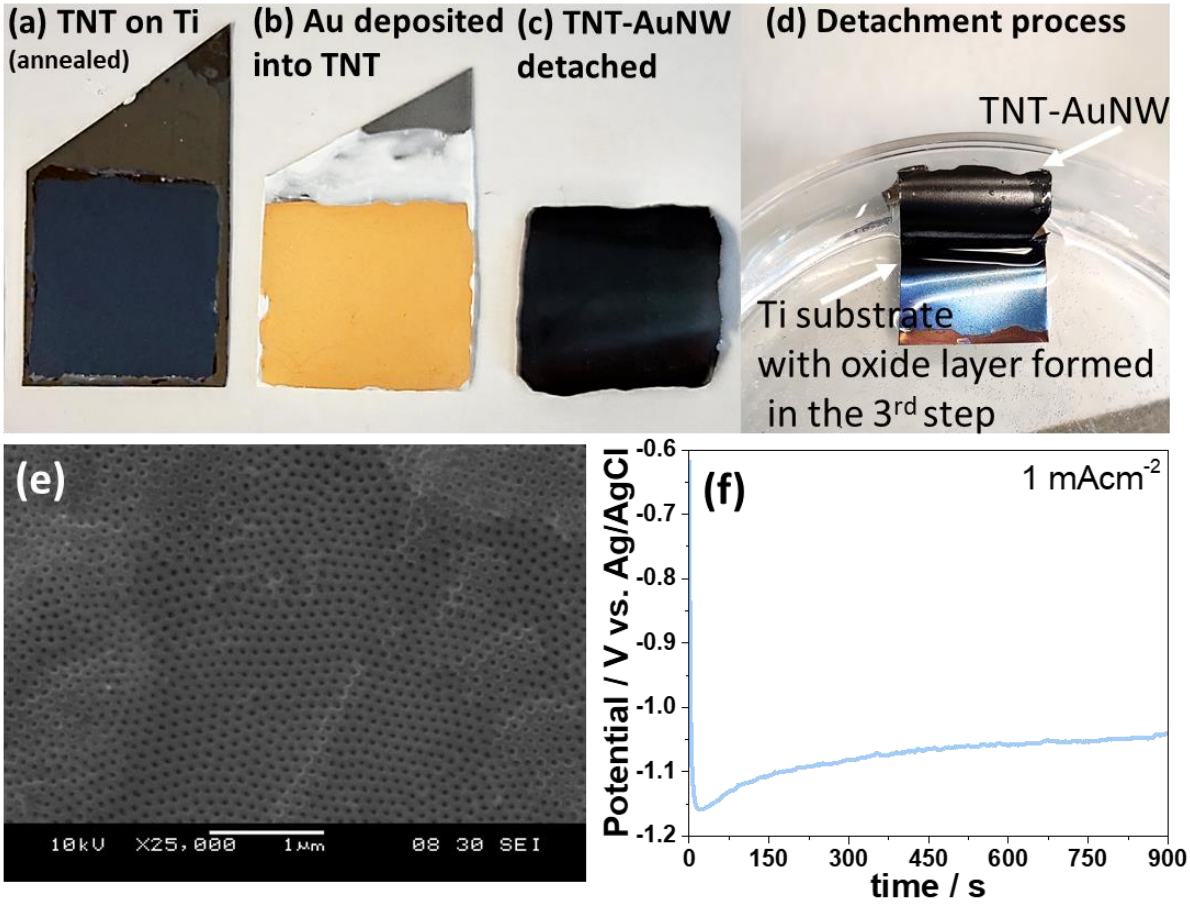

Figure S1. Macrophotographs of the samples prepared at varied synthesis steps: (a) TNT after annealing (b) sample after Au electrodeposited into TNT tubes, (c) self-standing TNT-AuNW photoelectrode (d) TNT-AuNW detachment from Ti substrate. (e) SEM of the thin amorphous porous layer of TiO_2 obtained in the 3rd anodizing step. (f) Potential vs. time curve registered during electrodeposition of Au from cyanide bath into TNT.

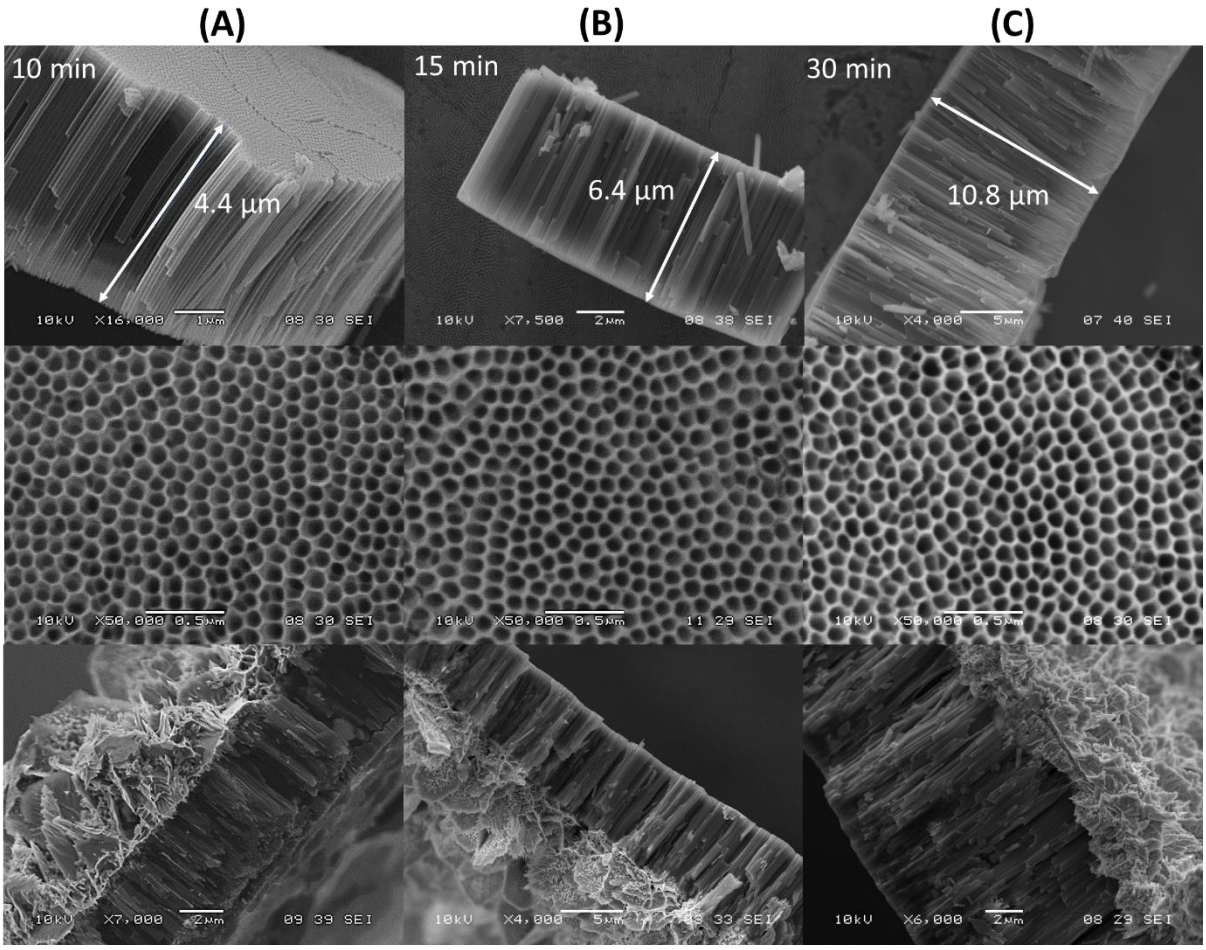

Figure S2. SEM microphotographs of the TNT membranes morphology and resulted TNT-AuNW photoelectrodes, obtained after varied 2nd step anodizing time: column (A) 10 min, (B) 15 min, (C) 30 min.

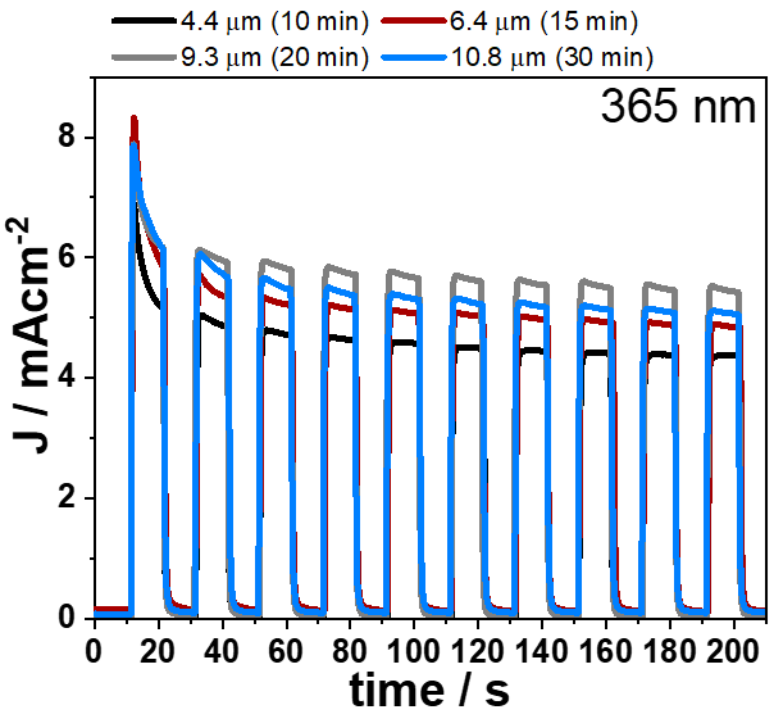

Figure S3. Transient photocurrent responses of TNT-AuNW photoanodes of different TNT layer thicknesses between 4.4 and 10.8 μm (10-30 minutes of anodizing), measured under 365 nm LED illumination and at 1.25 V vs. RHE in a 0.1 M Na_2SO_4 solution.

The PEC performance is closely related to the thickness of photoelectrocatalysts. For open circuit conditions, this is a result of a trade-off between photoelectrocatalyst photon absorption and charge carriers diffusion length.[1] On the one hand, the light absorber must be thick enough to absorb all or almost all the incident photons that reach the material surface (Bouguer's law). On the other hand, each material shows a specific diffusion length, which is the average length a carrier moves between generation and recombination. Under an applied forward bias separation of the photogenerated charges is facilitated. The electrons are forced to travel into the counter electrode (reduction process) and holes into the photoanode (oxidation). Still, after exceeding the optimal thickness of the material, the PEC performance drops due to the increase of the charges recombination (the longer the distance excitons must travel the higher the probability they will recombine before reaching the electrode surface).[2]

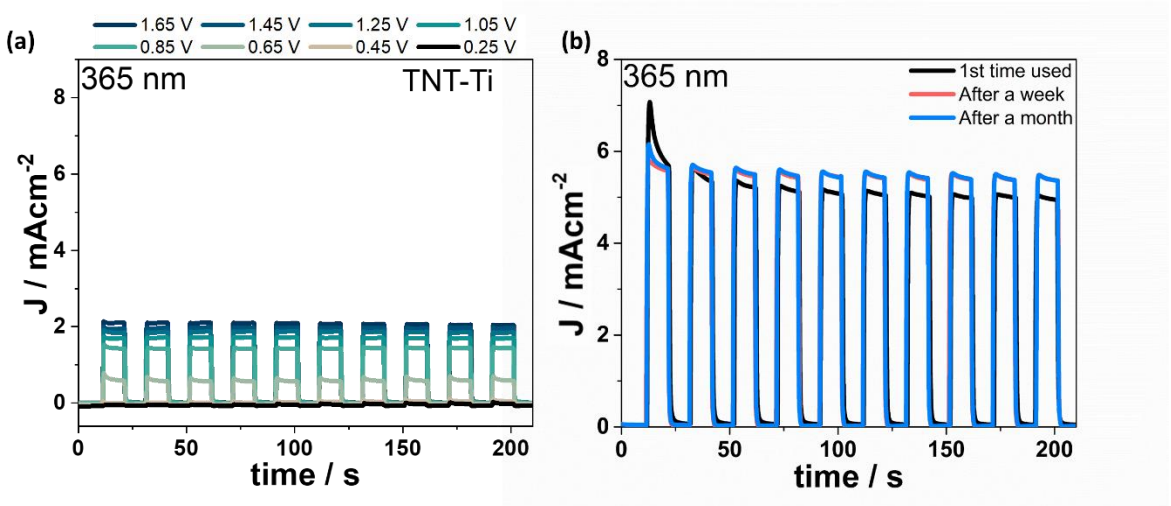

Figure S4. Transient photocurrent responses of TNT-Ti photoanode measured under 365 nm LED illumination and varied constant potentials in a range from 0.25 to 1.65 V vs. RHE in a 0.1 M Na_2SO_4 solution. (b) Long-term stability test of the TNT-AuNW electrode.

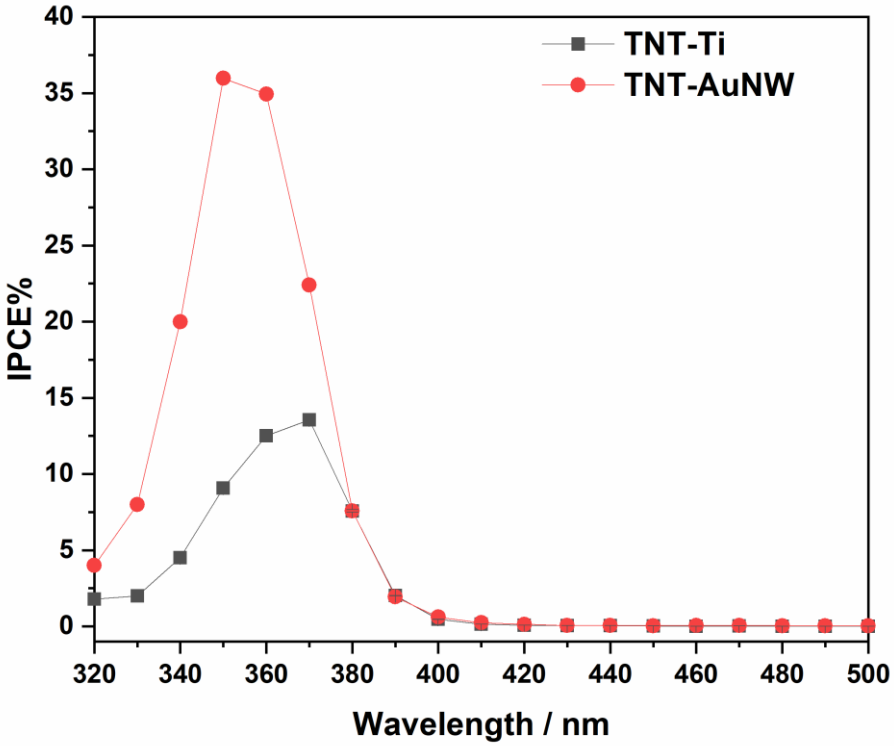

Figure S5. IPCE spectra calculated from TNT-Ti and TNT-AuNW at 1.25 V vs. RHE.

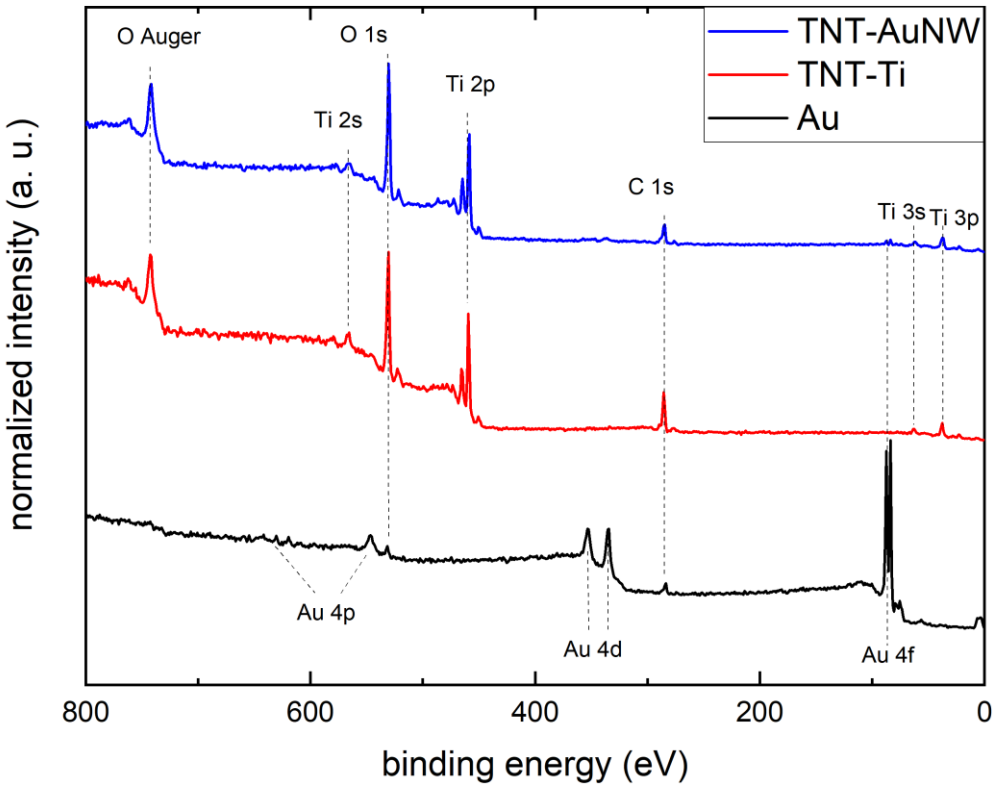

Figure S6. XPS survey spectra of Au, TNT-Ti and TNT-AuNW.

Table S1. EIS parameters calculated using the equivalent circuits in Figure 5b,e for TNT-AuNW and TNT-Ti structures.

Photoanode	Condition	R_s [Ω]	R_{ct} [Ω]	Q_{dl} [mF]	R_{SC} [Ω]	Q_{SC} [mF]	Z_W [$\Omega \cdot s^{-1/2}$]
TNT-Ti	dark	63.9	54 923	0.473	291.8	0.05	-
	light	63.6	9 883	5.336	-	-	-
TNT-AuNW	dark	63.3	6 462	1.279	-	-	628.8
	light	60.7	2 078	26.93	-	-	27.4

References:

1 G. Cha, P. Schmuki and M. Altomare, *Electrochimica Acta*, 2017, **258**, 302–310.

2 R. P. Lynch, A. Ghicov and P. Schmuki, *Journal of The Electrochemical Society*, 2010, **157**, G76.