Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Engineered CO_2 conversion performance of nanostructured TiO_2 photocatalysts via electrochemical hydrogenation

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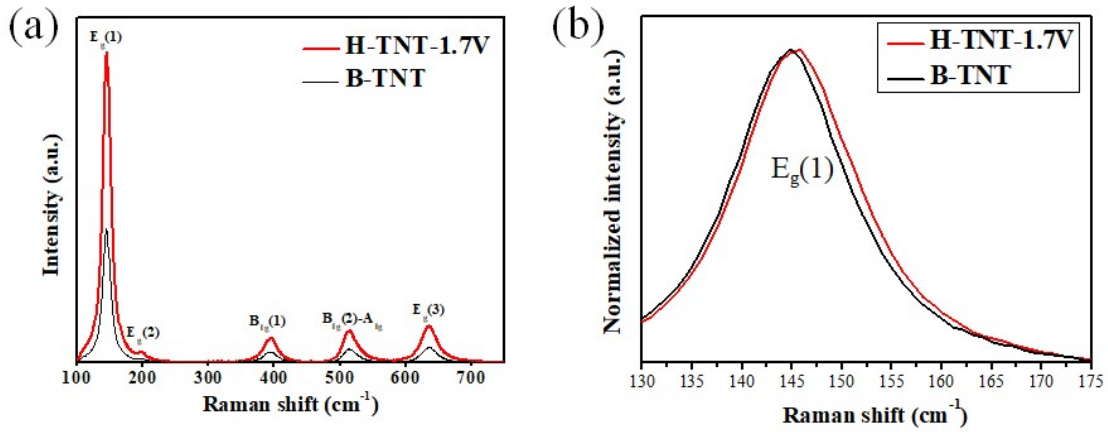

Fig. S1. (a) Raman spectra for TNT-based photocatalysts with and without electrochemical hydrogenation. (b) enlarged view of $E_g(1)$ mode in the Raman spectra.

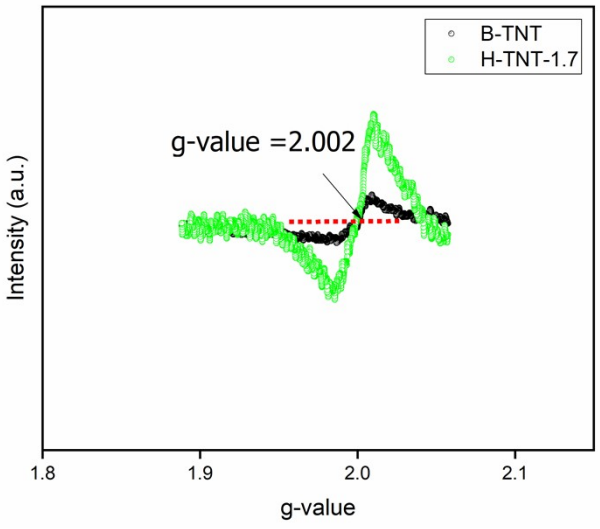

Fig. S2. EPR measurements for B-TNT and H-TNT-1.7 catalysts.

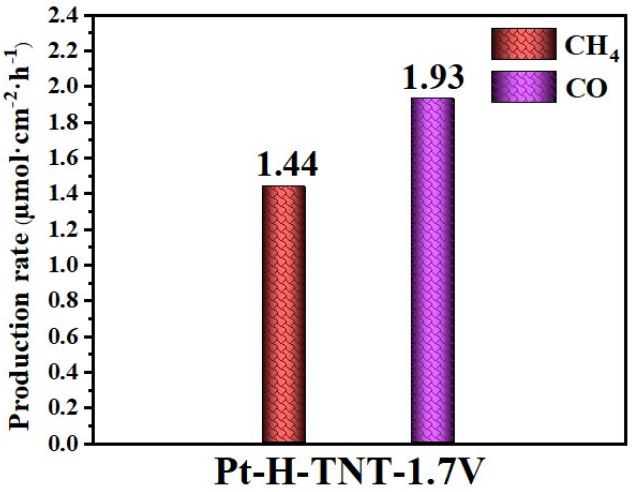

Fig. S3. Production rate by Pt-decorated H-TNT photocatalysts.

Decoration of hydrogenated TiO_2 nanotubes by Pt nanoparticles: the precursor was first mixed with 10 vol% of TEOA with 18 ml DI water stirred overnight, then added 0.2 vol% of H_2PtCl_6 sonicated and purged with Ar gas for 2 min. H-TNTx was immersed into the precursor and illuminated for 2 h under AM1.5 illumination. Then, the samples were heated up in the oven at 90 ℃ for 24 h.

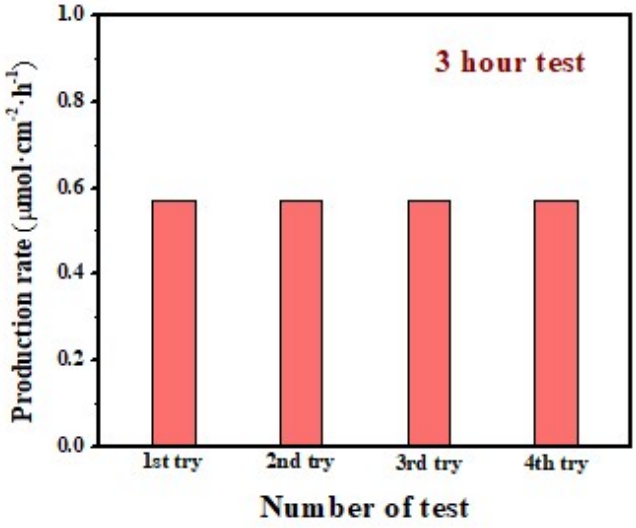

Fig. S4. Cyclic stability test for H-TNT-1.7V.

Fig. S5. Photographs of B-TNT and H-TNT-x catalysts.

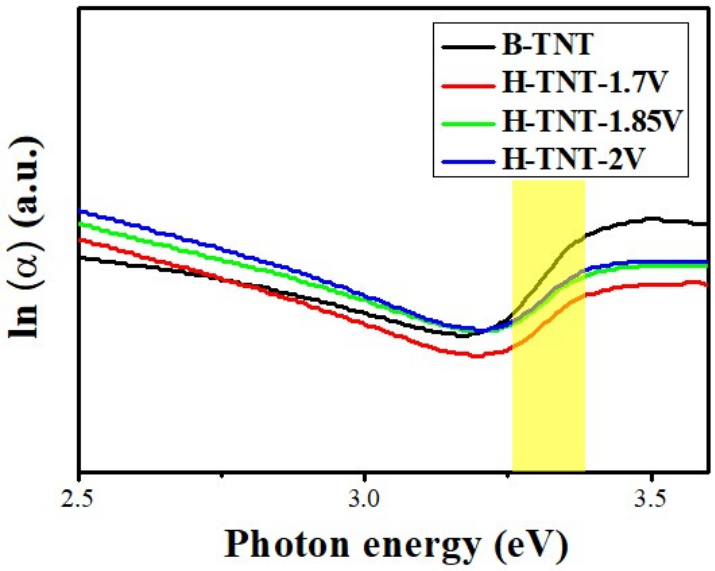

Fig. S6. ln (α) Vs Photon energy plot for various TNT-based photocatalysts. The yellow-shaded area is the fitted area for the Urbach energy calculation.

Unit conversion for the CH_4 production rate

To convert the production rate of the samples from the surface area to the total weight, the tube volume, and the density are being considered for conversion. The tube diameters and lengths were observed through SEM to evaluate the average tube volumes on the surface. Three tubes were selected for the image, and each tube has various outer circle (OC) and inner circle (IC) diameters, respectively shown in Table S1. The average tube area was then calculated. The ratio of the tube area to the square area evaluates how much area of the tube contains in the sample. The average area $_{tube/square}$ = 0.6427 means that in 2.25 cm^2 of the sample, there is 1.446 cm^2 of tube area from the surface.

	Tube 1	Tube 2	Tube 3
OC (nm)	121.4	115.9	108.5
IC (nm)	49.66	49.66	47.82
Tube area (nm^2)	3068 π	2742 π	2371 π
Square area (nm^2)	$(121.4)^2$	$(115.9)^2$	$(108.5)^2$
Ratio $_{Tube/square}$	0.654	0.641	0.633
Average ratio	0.6427		

Table S1. The parameters for 3 random tubes.

The total volume of the sample is the multiplication of the average tube area (1.446 cm^2) and the tube length, while the average tube length is 7.62 um. The total volume is $1.1 \cdot 10^{-3}$ cm^3. To convert the tube volume to weight. The anatase TiO_2 density has been considered, and the total volume is divided by the density.

$1.1 \cdot 10^{-3}\ cm^3 \times 3.89\ g/cm^3 = 4.28 \cdot 10^{-3}\ g$

The final result indicates that the 2.25 cm^2 sample contains 4.28 mg of TNT.

Last, the production rates converted from the surface area to weight are shown in Table S2.

Unit	**B-**	**H-TNT-**	**H-TNT-**	**H-TNT-**	**Pt-H-TNT-1.7V**

	TNT	**1.7V**	**1.85V**	**2V**		
μmol · cm^{-2} · h^{-1}	0.14	0.57	0.35	0.09	1.44 for CH_4	1.93 for CO
μmol · g^{-1} · h^{-1}	73.6	299.6	184	47.3	757 for CH_4	1014.6 for CO

Table S2. The production rate chart.

Catalysts	**R_s (Ω)**	**R_{ct} (Ω)**
B-TNT	34.11	1.36 x 10^5
H-TNT-1.7V	31.86	5518
H-TNT-1.85V	33.75	4798
H-TNT-2V	34.69	4433

Table S3. The simulated EIS results.