

Supporting Information

***In Situ* Nitrogen-Doped Hollow-TiO₂/g-C₃N₄ Composite Photocatalyst with Efficient Charge Separation boosting Water Reduction under Visible Light**

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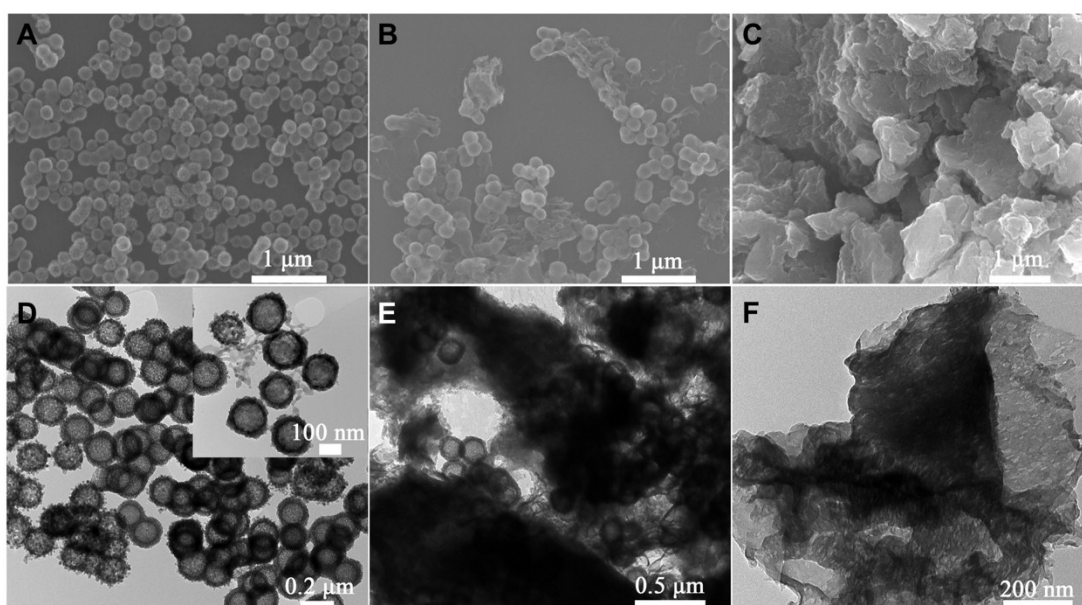


Fig. S1 SEM and TEM images of N-TCN-500 (A and D), N-TCN-1000 (B and E), and pure C₃N₄ (C and F).

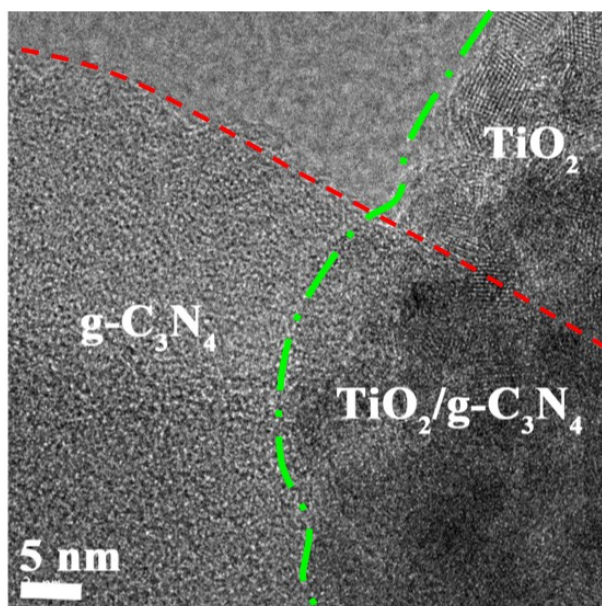


Fig. S2 HRTEM image of N-TCN-700

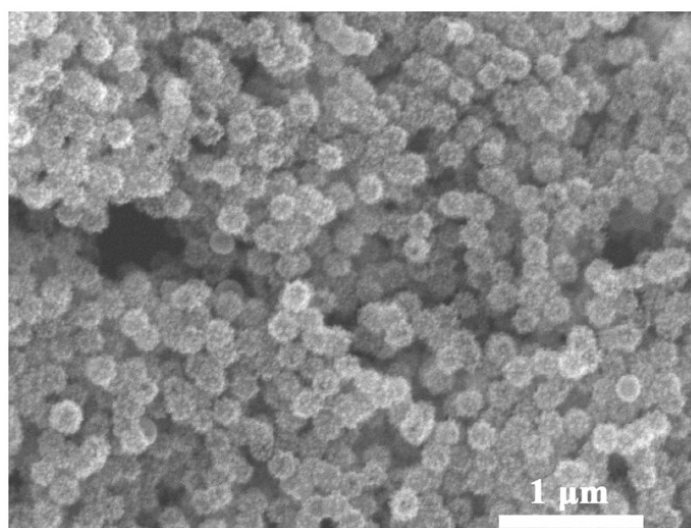


Fig. S3 SEM image of TiO₂ after calcination under 550 °C for 2h.

Table S1 TGA, BET surface area, BJH pore size and volume of various photocatalysts.

Photocatalysts	g-C ₃ N ₄ (wt%)	Surface area	Pore size	Pore volume
	(TG)	(m ² g ⁻¹)	(nm)	(cm ³ g ⁻¹)
TiO ₂	0	239	2.18	0.3910

N-TCN-200	0	66.5	2.08	0.2043
N-TCN-500	42.9	63.3	2.08	0.1227
N-TCN-700	69.8	39.9	2.08	0.0576
N-TCN-1000	87.8	19.2	1.75	0.0453
g-C₃N₄	100	4.32	1.34	0.0147

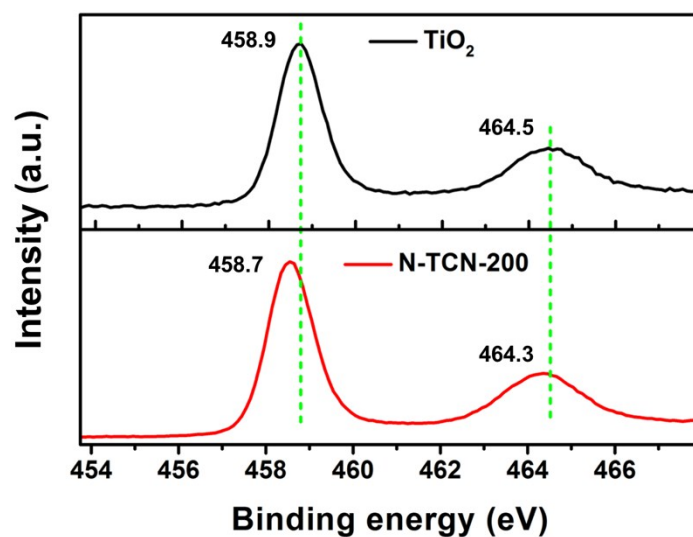


Fig. S4 XPS spectra of Ti 2p of pure TiO_2 and N-TCN-200.

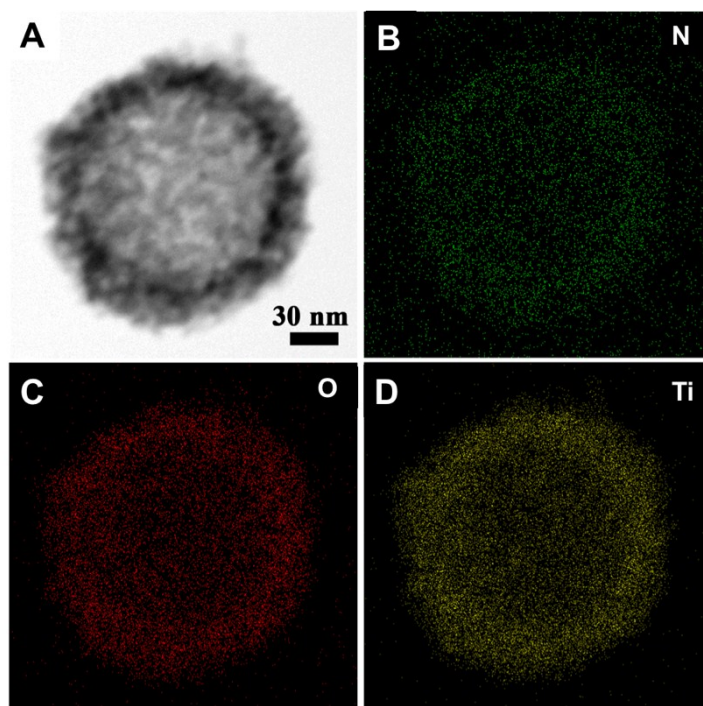


Fig. S5 TEM image (A) and elemental mappings of N (B), O (C), and Ti (D) of N-TCN-

200.

Table S2 Values of C/N and O/Ti ratios in the all photocatalysts.

Sample	TiO ₂	N-TCN- 200	N-TCN- 500	N-TCN- 700	N-TCN- 1000	g-C ₃ N ₄
C/N ratio	-	-	0.69	0.67	0.66	0.66
O/Ti ratio	1.91	2.19	2.12	1.91	2.29	-

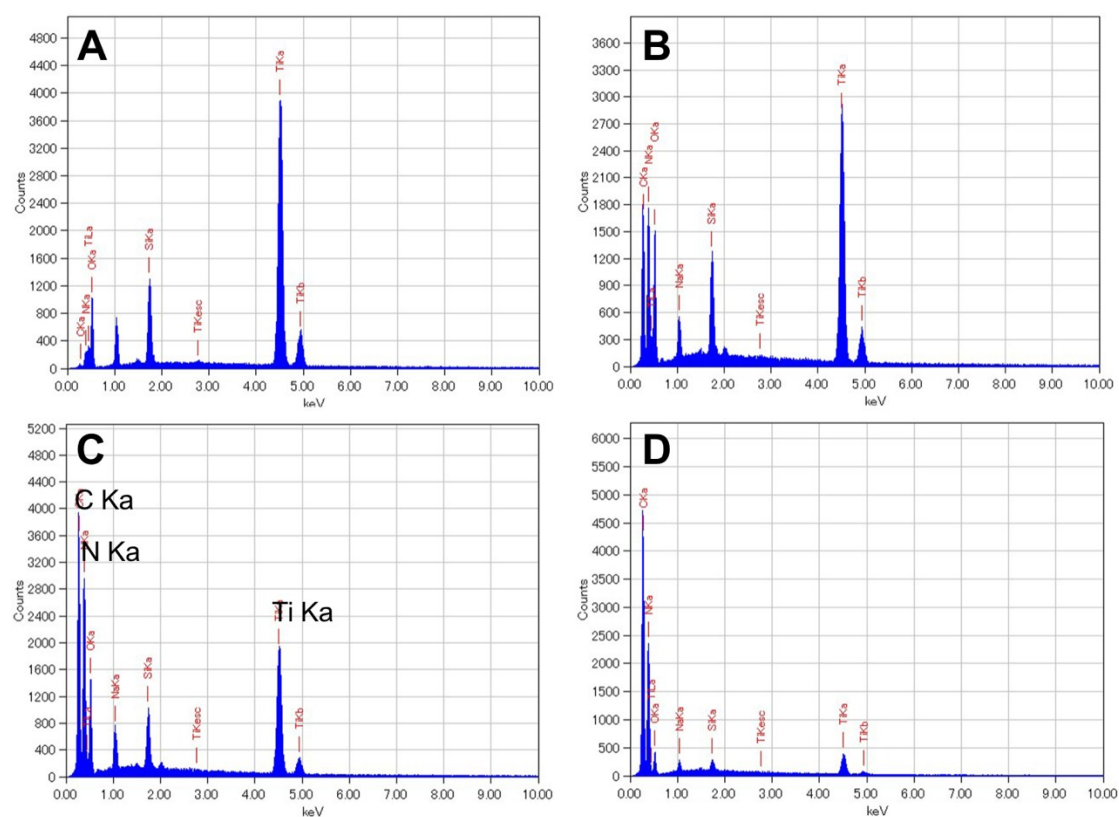


Fig. S6 EDS spectra of N-TCN-200 (A), N-TCN-500 (B), N-TCN-700 (C) and N-TCN-1000 (D). The calculated C/N atomic ratio are 0.69, 0.62 and 0.60 corresponding to N-TCN-500, N-TCN-700 and N-TCN-1000, respectively.

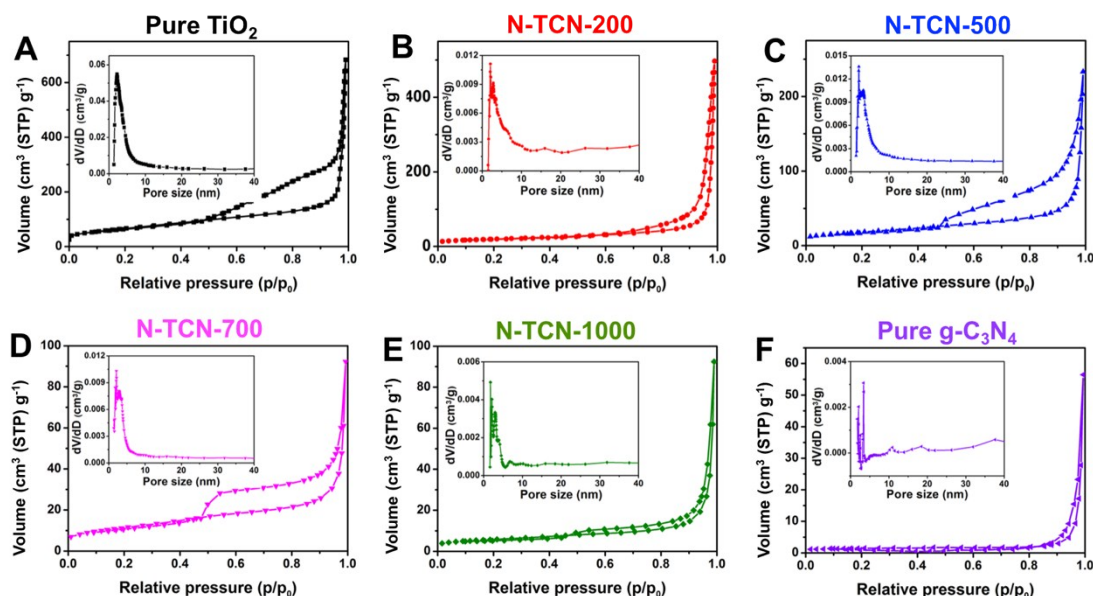


Fig. S7 N₂ adsorption-desorption isotherms and pore size distribution curves (inset) of pure TiO₂ (A), N-TCN-200 (B), N-TCN-500 (C), N-TCN-700 (D), N-TCN-1000 (E), and pure g-C₃N₄ (F).

The isotherms were of typical type IV pattern with distinct H₃ hysteresis loops in the range of 0.4-1.0 P/P_0 , indicating the presence of slit-like pores according to the IUPAC classification. Surface areas of N-TCN-x measured by multi-point Brunauer-Emmett-Teller (BET) method from the adsorption branch were all lower than that of TiO₂ hollow nanospheres. Their corresponding pore size distribution profiles determined using the Barrett-Joyner-Halenda (BJH) method from the desorption branch of isotherms are shown in the inset in Figure S5, which indicate the mesoporous nature of synthesized TiO₂ hollow nanospheres and N-TCN-x.

Table S3 The comparison of photocatalytic performance for N-TCN-700 and previous g-C₃N₄-based photocatalysts in recent years.

Photocatalyst	Light source	AQE	Ref.
g-C ₃ N ₄ nanosheets	420 nm	4.03%	S1
g-C ₃ N ₄ nanosheets	420 nm	3.75%	S2
g-C ₃ N ₄ Seaweed	420 nm	7.8%	S3
Porous g-C ₃ N ₄	420 nm	1.62%	S4
P-doped g-C ₃ N ₄	420 nm	3.56%	S5

monolayer g-C ₃ N ₄	420 nm	5.1%	S6
MoS ₂ /mpg-C ₃ N ₄	420 nm	2.1%	S7
ompg-C ₃ N ₄	455 nm	6.77%	S8
WO ₃ /g-C ₃ N ₄	420 nm	3.9%	S9
N-TCN-700	420 nm	1.2%	Our work

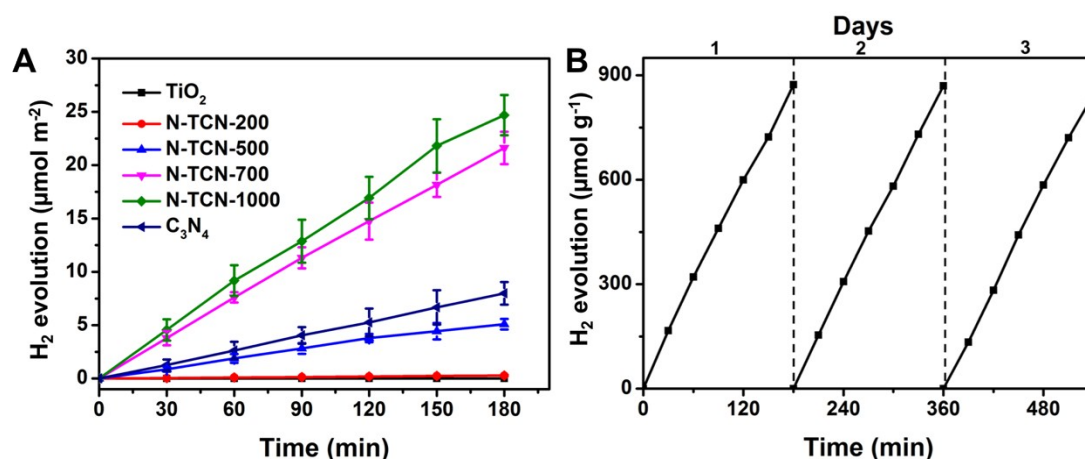


Fig. S8 Plots of H₂ evolution volume normalized by the surface areas of various photocatalysts vs. irradiation time (A). Stability test of N-TCN-700 photocatalyst (B).

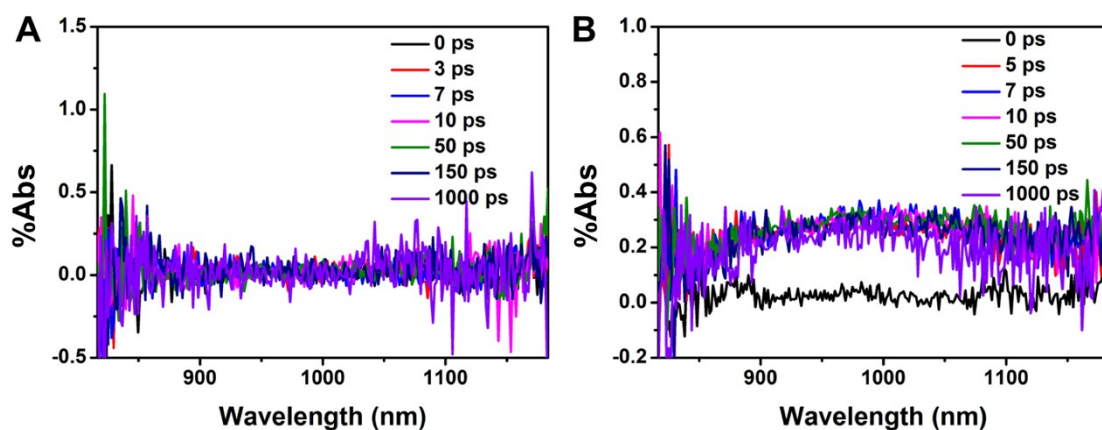


Fig. S9 Time-resolved diffuse reflectance spectra observed after 420-nm laser pulse irradiation for pure TiO₂ (A) and N-TCN-200 (B).

Notes and references

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