

### Supporting Information

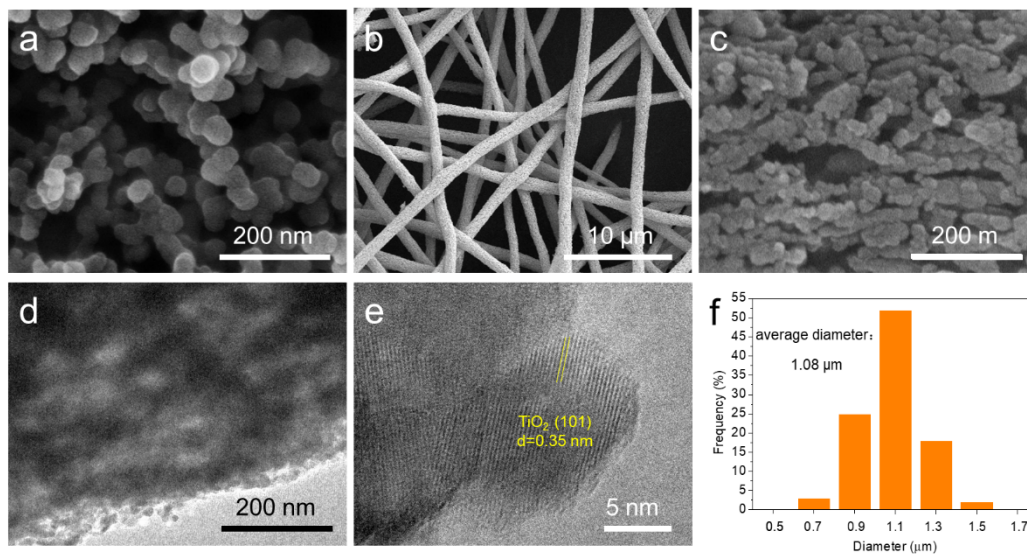
#### **Continuous g-C<sub>3</sub>N<sub>4</sub> layer coated porous TiO<sub>2</sub> fibers with enhanced photocatalytic activity toward H<sub>2</sub> evolution and dye degradation**

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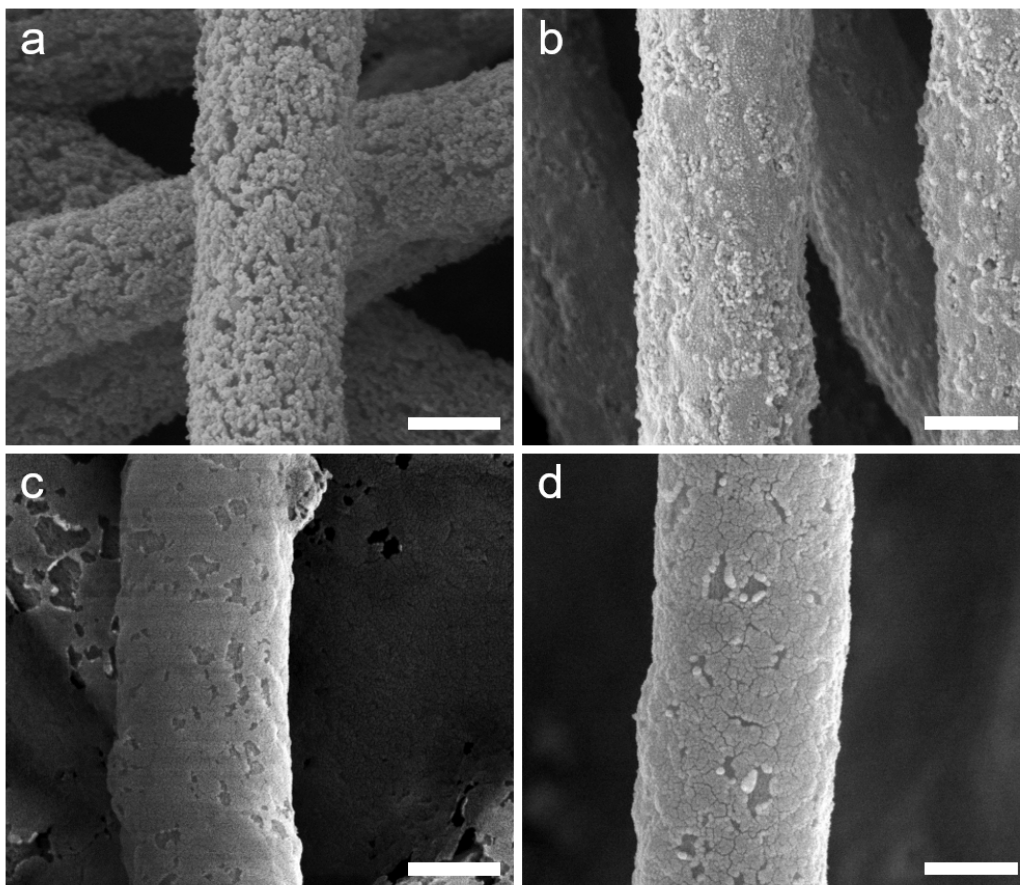
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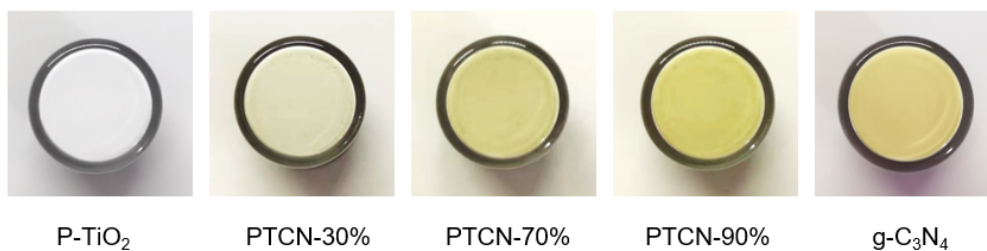
**Fig. S1** a) SEM image of CNPs. b) SEM image and magnified image of P-TiO<sub>2</sub> fibers. d, e) TEM and HRTEM images of P-TiO<sub>2</sub> fibers. f) Diameter distribution of P-TiO<sub>2</sub> fibers. The average diameter is 1.08 μm.



**Fig. S2** SEM images of a) P-TiO<sub>2</sub> fibers, b-d) PTCN-30%, PTCN-70% and PTCN-90% fibers. Scale bars are 1  $\mu$ m.

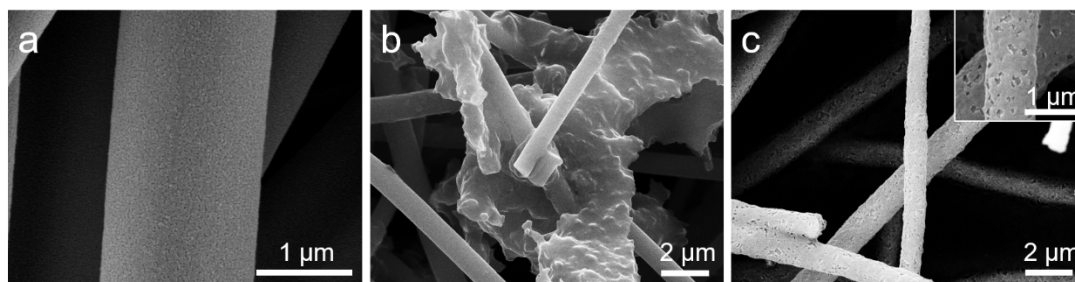
CY solution with different concentration was used to prepare PTCN composite fibers to explore the effect of g-C<sub>3</sub>N<sub>4</sub> content in the heterojunction. The synthesized HPCN fibers are labelled as HPCN-x (x = 30%, 70%, 90%), x is the volume concentration of CY solution. At the same time, P-TiO<sub>2</sub> fibers and g-C<sub>3</sub>N<sub>4</sub> were fabricated by the traditional calcination as the previously mentioned method. Surface SEM image of P-TiO<sub>2</sub> fibers and PTCN fibers are shown in Fig. S3. When the concentration of CY is 30%, the porous structure keeps well in the PTCN fibers. When the concentration of CY is 70%, g-C<sub>3</sub>N<sub>4</sub> almost form a full coverage on the surface of P-TiO<sub>2</sub>. The thin g-C<sub>3</sub>N<sub>4</sub> layer wraps around the P-TiO<sub>2</sub> fiber and exhibit a core-shell structure. The thickness of the shell increases with increasing the CY concentration to 90%. However, cracks emerged in g-C<sub>3</sub>N<sub>4</sub>

layer due to the agglomeration of g-C<sub>3</sub>N<sub>4</sub>. Porous structure disappeared on the surface when the CY concentration is more than 70%. It is ascribed to plenty of g-C<sub>3</sub>N<sub>4</sub> wrap around TiO<sub>2</sub> grains forming a core-shell structure and blocking the pores.

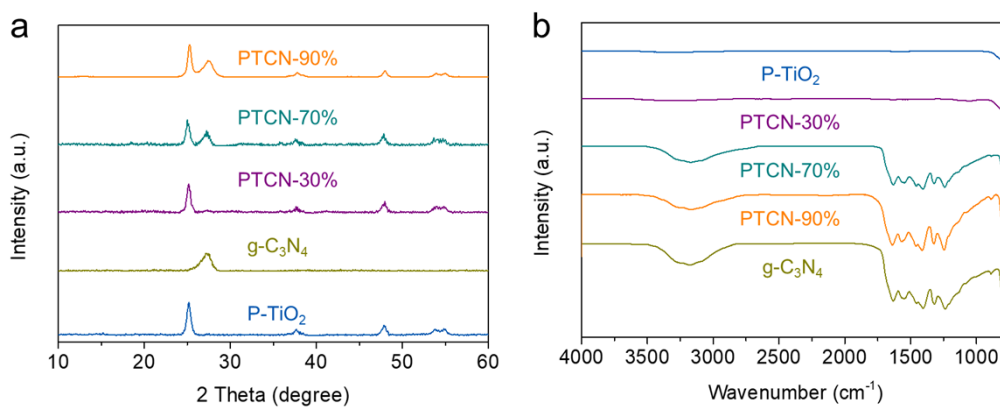


**Fig. S3** Optical images of P-TiO<sub>2</sub>, PTCN-30%, PTCN-70%, PTCN-90% and pristine g-C<sub>3</sub>N<sub>4</sub>.

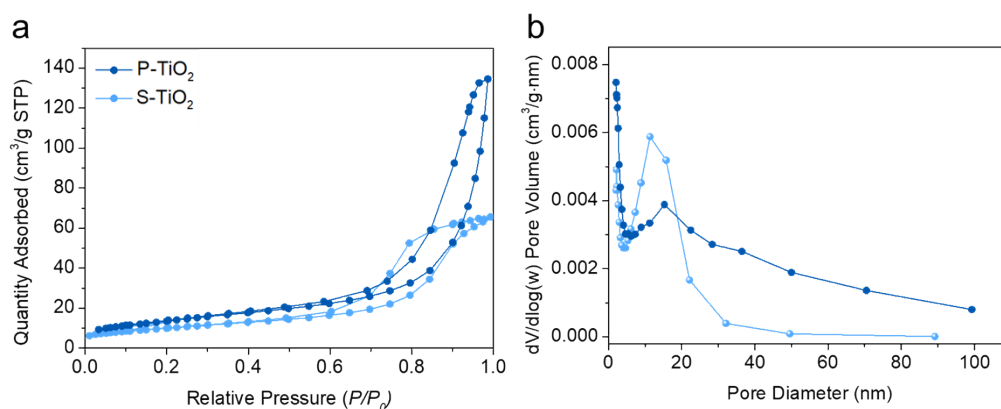
G-C<sub>3</sub>N<sub>4</sub> exhibits conventional faint yellow and P-TiO<sub>2</sub> fibers presents pure white. PTCN composite fibers show different shades of yellow. The color ranges from light to dark correspond to the amount of g-C<sub>3</sub>N<sub>4</sub> is changed from small quantity to large quantity in PTCN composite.



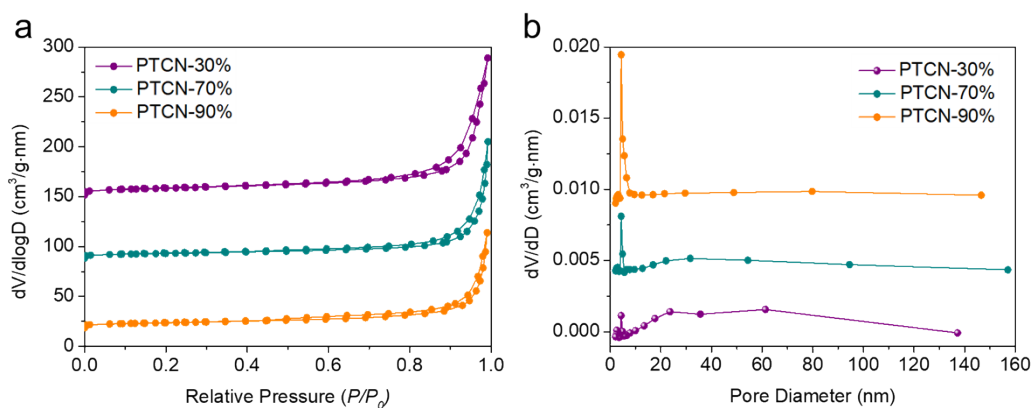
**Fig. S4** SEM images of a) S-TiO<sub>2</sub> fibers, b) S-TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>-90% fibers, c) PTCN-90% fibers. Inset shows amplified image of PTCN-90% fibers.



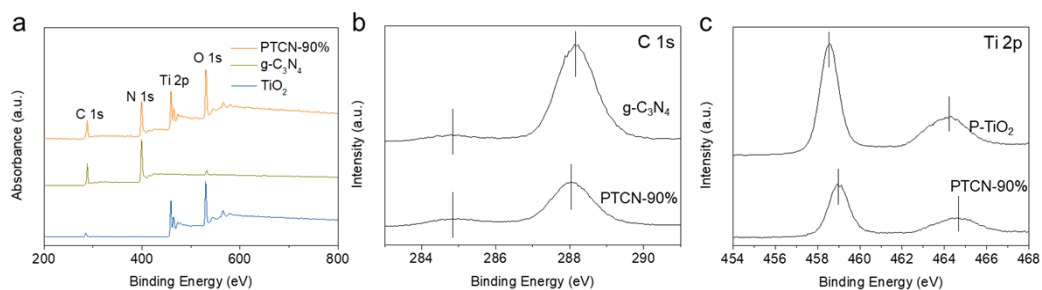
**Fig. S5** XRD patterns and FTIR images of P-TiO<sub>2</sub>, g-C<sub>3</sub>N<sub>4</sub>, PTCN-30%, PTCN-70% and PTCN-90%.



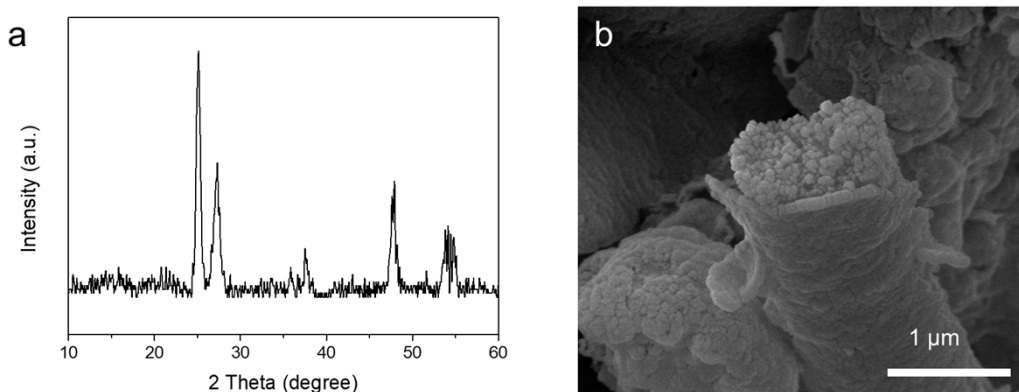
**Fig. S6** N<sub>2</sub> adsorption-desorption isotherms and corresponding pore size distributions of P-TiO<sub>2</sub>, and S-TiO<sub>2</sub>.



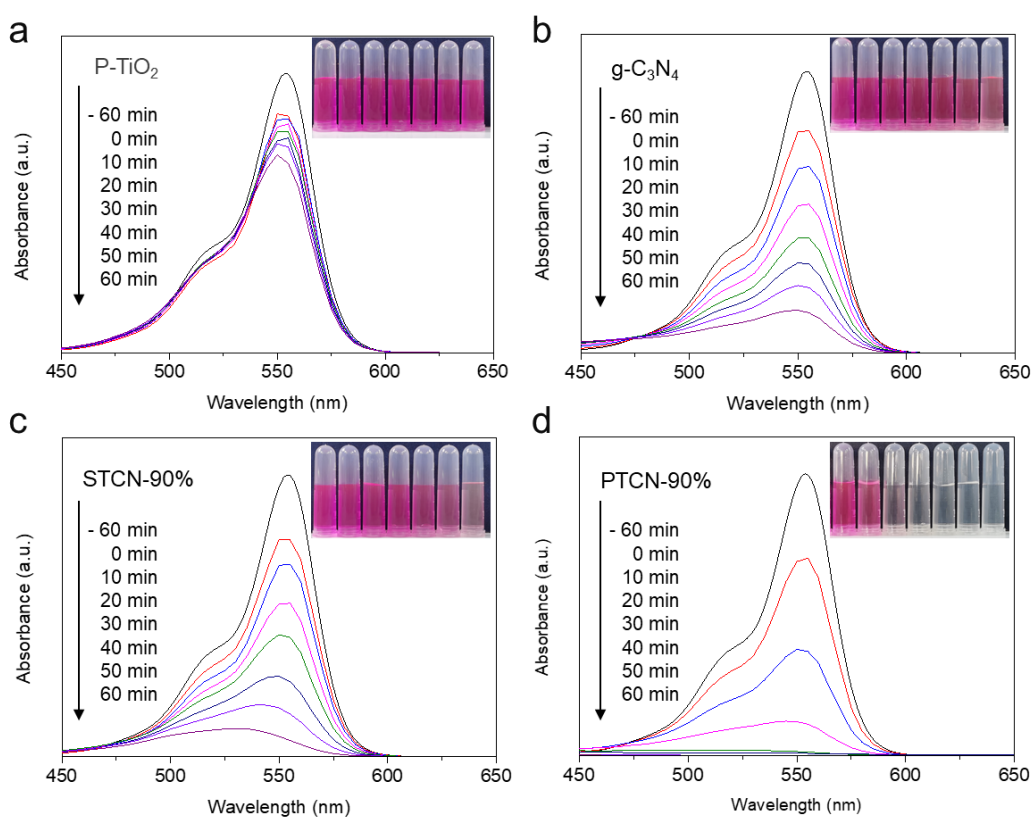
**Fig. S7** N<sub>2</sub> adsorption-desorption isotherms and corresponding pore size distributions of PTCN-30%, PTCN-70% and PTCN-90%.



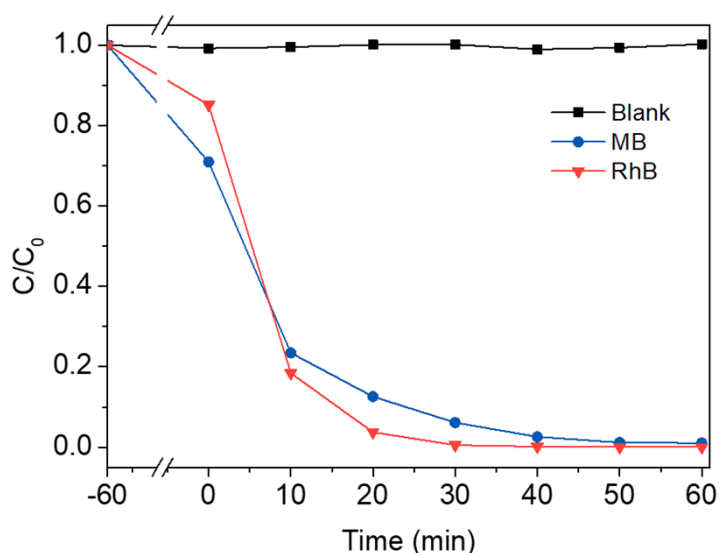
**Fig. S8** a) XPS survey spectra of PTCN, indicating the existence of C, N, Ti and O elements. b, c) High resolution XPS spectra of C 1s and Ti 2p of PTCN-90%, g-C<sub>3</sub>N<sub>4</sub> and P-TiO<sub>2</sub>.



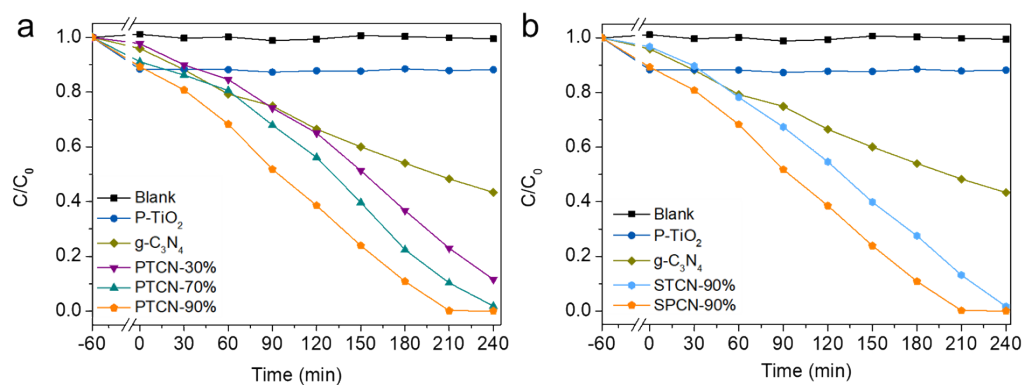
**Fig. S9** a) XRD pattern and b) SEM image of PTCN-90% after four times H<sub>2</sub> evolution experiments.



**Fig. S10** The adsorption peak changes of RhB solution in a) P-TiO<sub>2</sub>, b) g-C<sub>3</sub>N<sub>4</sub>, c) STCN-90% and d) PTCN-90% with increasing of irradiation time under visible light ( $\lambda \geq 420$  nm).



**Fig. S11** Photocatalytic curves of PTCN-90% for photodegradation of RhB and MB solution in visible light.



**Fig. S12** Photocatalytic phenol degradation performance of P-TiO<sub>2</sub> g-C<sub>3</sub>N<sub>4</sub> and PTCN with different g-C<sub>3</sub>N<sub>4</sub> content (PTCN-30%, PTCN-70% and PTCN-90%) in visible light irradiation. b) Phenol photocatalytic degradation performance for P-TiO<sub>2</sub>, g-C<sub>3</sub>N<sub>4</sub>, PTCN-90% and STCN-90% in visible light irradiation.

After stirring in dark for 60 min to build adsorption-desorption equilibrium, the concentration of phenol almost unchanged with the exist of bare P-TiO<sub>2</sub>, indicating that phenol could not act as photoactivator with TiO<sub>2</sub>. PTCN-90% still exhibits the highest photodegradation performance for phenol when compared with PTCN-30% and PTCN-70%. The phenol solution was completely



degraded by PTCN-90% in 3.5 h. When compared with STCN-90%, PTCN-90% also shows better photodegradation activity, due to the core/shell structure and strong heterojunction between TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>.

The band structures of TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> in the nanocomposite are calculated by the DRS results and the following formulas:

$$E_{CB} = \chi - E^C - 0.5E_g \quad (1)$$

$$E_{VB} = E_{CB} + E_g \quad (2)$$

where  $E_{CB}$  and  $E_{VB}$  stand for the conduction and valence band potential.  $\chi$  represents the electronegativity obtained by the geometrical mean of every element. The  $\chi$  values for TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> are 5.81 and 4.72 eV, respectively.  $E^C$  is the free electron energy on the hydrogen scale, which is 4.5 eV. Therefore,  $E_{CB}$  and  $E_{VB}$  values of TiO<sub>2</sub> are calculated to be -0.23 eV and 2.85 eV, respectively. Correspondingly,  $E_{CB}$  and  $E_{VB}$  values of g-C<sub>3</sub>N<sub>4</sub> are -1.08 eV and 1.52 eV, respectively.

**Tab. S1** S<sub>BET</sub> and pore volume of samples

Samples	BET Surface Area (cm <sup>2</sup> ·g <sup>-1</sup> )	Pore Volume (cm <sup>3</sup> ·g <sup>-1</sup> )
S-TiO <sub>2</sub>	36.25	0.10
P-TiO <sub>2</sub>	53.71	0.21
PTCN-90%	22.85	0.10
g-C <sub>3</sub> N <sub>4</sub>	13.20	0.05

**Tab. S2** Visible light performance of TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> photocatalyst with different structures

Photocatalyst	Size	Cocatalyst	Light Condition	H <sub>2</sub> Production ( $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ )	Ref.
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub> nanowire	150 nm	1 wt% Pt	300W Xe lamp ( $\lambda>420$ nm)	63.7	[1]
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub> nanosphere	150 nm	1 wt% Pt	300W Xe lamp ( $\lambda>400$ nm)	64.0	[2]
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub> nanoparticle	250 nm	1 wt% Pt	300W Xe lamp ( $\lambda>420$ nm)	80.4	[3]
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub> nanoparticle	18 nm	0.5 wt% Pt	300W Xe lamp ( $\lambda>420$ nm)	219.9	[4]
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub> nanosheet	-	unknown	350W Xe lamp ( $\lambda>420$ nm)	210.0	[5]
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub> microsphere	10 $\mu\text{m}$	0.5 wt% Pt	300W Xe lamp ( $\lambda>420$ nm)	250.0	[6]
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub> hollow nanosphere	250 nm	unknown	300W Xe lamp (AM 1.5)	195.0	[7]
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub> hollow nanosphere	100 nm	unknown	350W Xe lamp ( $\lambda>420$ nm)	296.4	[8]
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub> nanofiber	330 nm	1 wt% Pt	300W Xe lamp (400~780 nm)	251.7	[9]
C@TiO <sub>2-x</sub> /g-C <sub>3</sub> N <sub>4</sub> nanosheet	-	3 wt% Pt	350W Xe lamp ( $\lambda>420$ nm)	417.2	[10]
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub> porous nanofiber	1.41 $\mu\text{m}$	1 wt% Pt	300W Xe lamp ( $\lambda>420$ nm)	436.3	our work

In comparison with other TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub> photocatalyst, PTCN-90% exhibits high performance, with about 6.8 times higher than the nanowire and nanosphere structure,<sup>1,2</sup> 5.5 times the nanoparticle structure,<sup>3</sup> and 3.2 times the nanosheet structure.<sup>5</sup> When compared with STCN-90% (prepared in the same method by ourselves), PTCN-90% improves H<sub>2</sub> evolution performance by 40.6%.

## References

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