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**TiO₂/g-C₃N₄ heterojunction hollow porous nanofibers as superior visible-light photocatalysts
for H₂ evolution and dye degradation**

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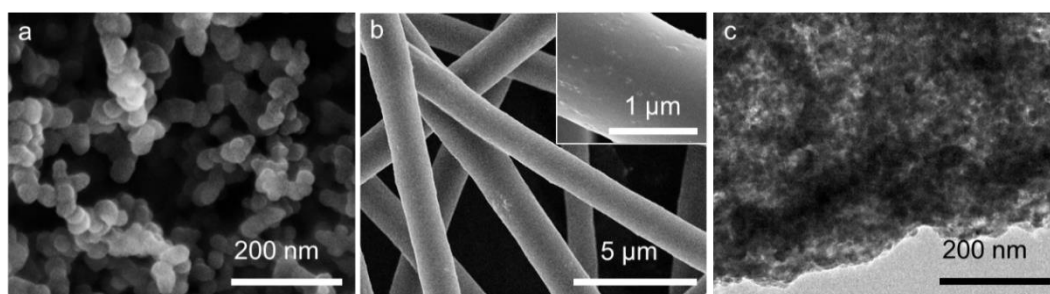


Fig. S1 a) SEM image of C-NPs. b) SEM image of pristine TBOT/C-NPs/PVP nanofibers. The inset is high magnification micrograph. c) TEM image of HP-TiO₂ nanofibers.

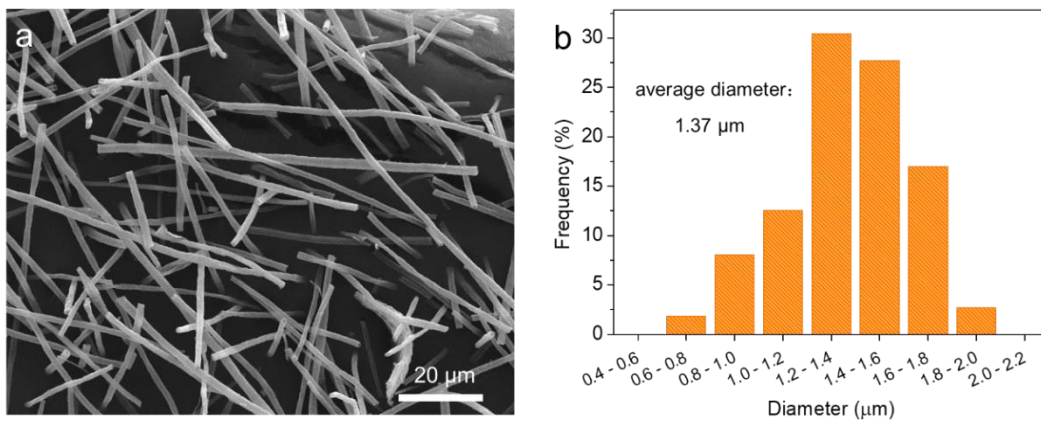


Fig. S2 a) SEM image of HP-TiO₂ nanofibers. b) Diameter distribution of HP-TiO₂ nanofibers. The average diameter is 1.37 μm.

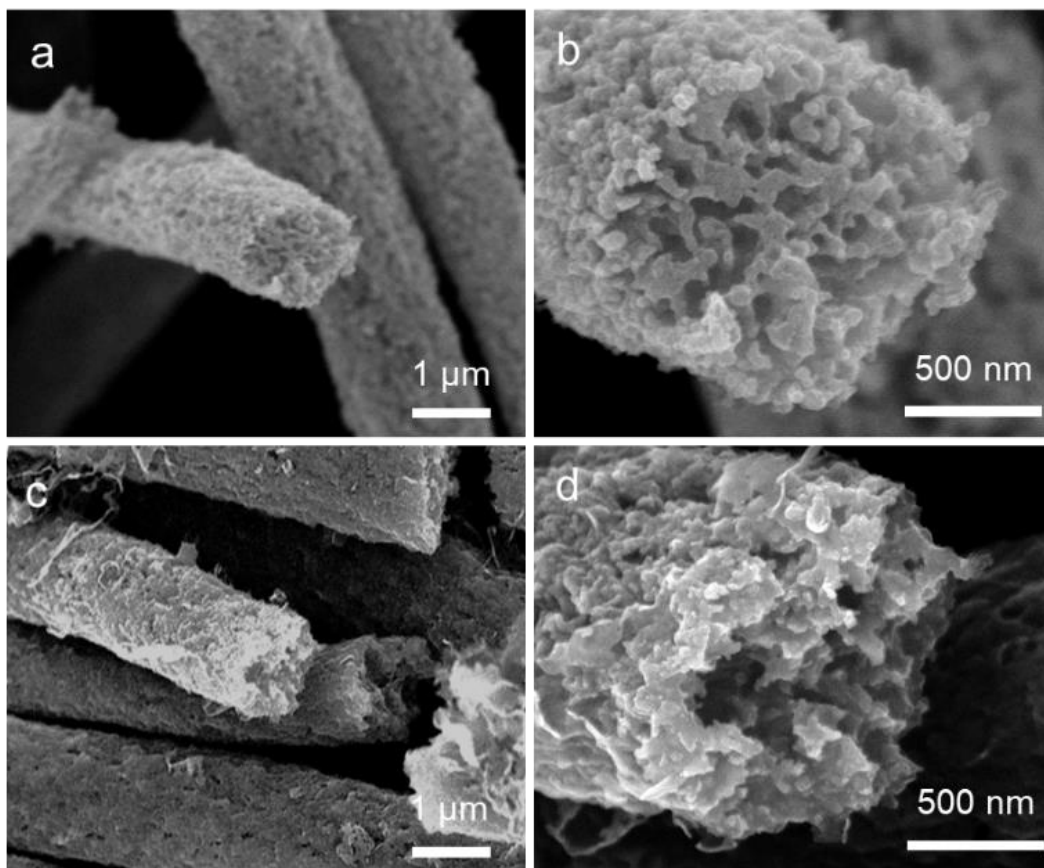


Fig. S3 SEM images of a) P-TiO₂ nanofibers and c) P-TiO₂/C₃N₄-50% composite nanofibers. b, d)

The magnified SEM images of image a and b.

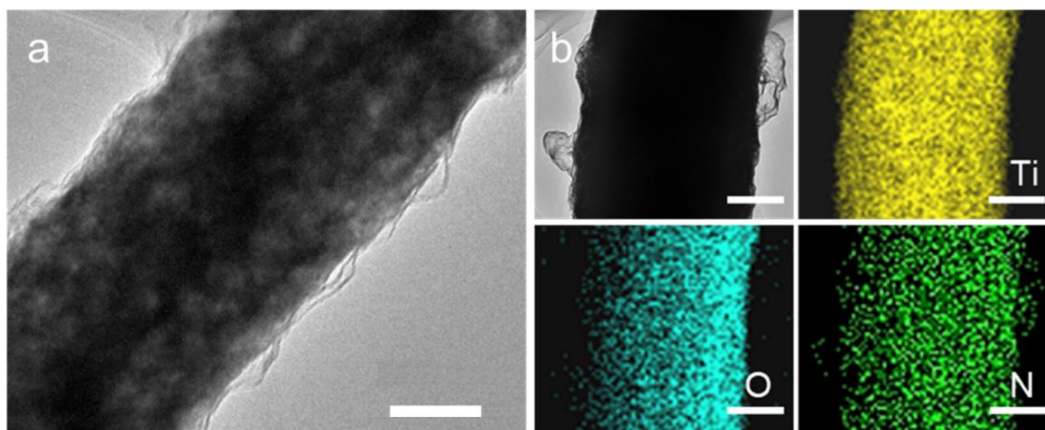


Fig. S4 a) HR-TEM image of P-TiO₂/C₃N₄-50% nanofibers. b) EDS element mapping images for P- TiO₂/C₃N₄-50% nanofibers, indicating the existence of Ti, O, N. Scale bars are 500 nm.

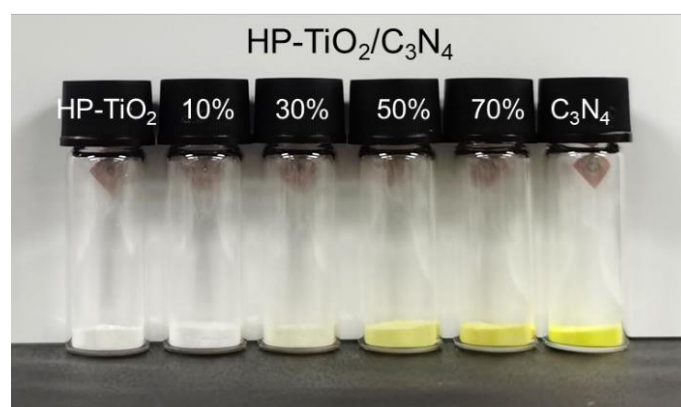


Fig. S5 Optical images of HP-TiO₂, HP-TiO₂/C₃N₄ nanofibers decorated with different content of g-C₃N₄ (10%, 30%, 50% and 70%) and pristine g-C₃N₄.

In order to investigate the effect of g-C₃N₄ content in the heterojunction catalysts. Different concentration of CY solution was used to synthesis HP-TiO₂/C₃N₄ nanofibers. The as prepared HP-TiO₂/C₃N₄ nanofibers are labelled as HP-TiO₂/C₃N₄-x (x=10%, 30%, 50%, 70%), where x indicates the volume concentration of CY aqueous solution. Meanwhile, bare HP-TiO₂ nanofibers and g-C₃N₄ were also fabricated by the same processes as above. Pristine g-C₃N₄ presents typical faint yellow. HP-TiO₂ nanofibers show purely white, while composite nanofibers reveal diverse yellows from light to dark, resulting from different content of g-C₃N₄ coated on the TiO₂ substrate. As the

concentration of CY aqueous solution increases, the color of composite photocatalyst gets darker (Figure S5). Pure S-TiO₂ nanofibers without adding C nanoparticles in the precursor, exhibit relative smooth surface (Fig. S6a). Bare HP-TiO₂ nanofibers exhibit hollow and porous structure (Fig. S6b). Morphologies of HP-TiO₂/C₃N_{4-x} nanofibers are shown in Fig. S6c-e. It is obvious that in the low concentration of 30% CY, g-C₃N₄ roots into the mesoporous nanofibers and form a uniform layer attached to the nanofiber tightly. With the concentration of CY solution increasing to 50%, g-C₃N₄ nanosheets aggregate on the surface of nanofibers and form a thin layer around the TiO₂ nanofiber substrate and form some bubbles on parts of the nanofibers. When the concentration adds to 70%, the nanosheets aggregate closely both on the outer and inner spaces of HP-TiO₂ nanofibers. It is obviously that clusters of g-C₃N₄ nanosheets block the hollow space of HP-TiO₂ nanofibers. As a contrast, S-TiO₂/C₃N₄-50% was observed that the g-C₃N₄ nanosheets gather independently from S-TiO₂ nanofibers with only small part contacting to the substrate (Fig. S6f). It confirms that the g-C₃N₄ nanosheets are in situ grown on both outside and inside of HP-TiO₂ nanofibers due to the hollow porous structure of substrate.

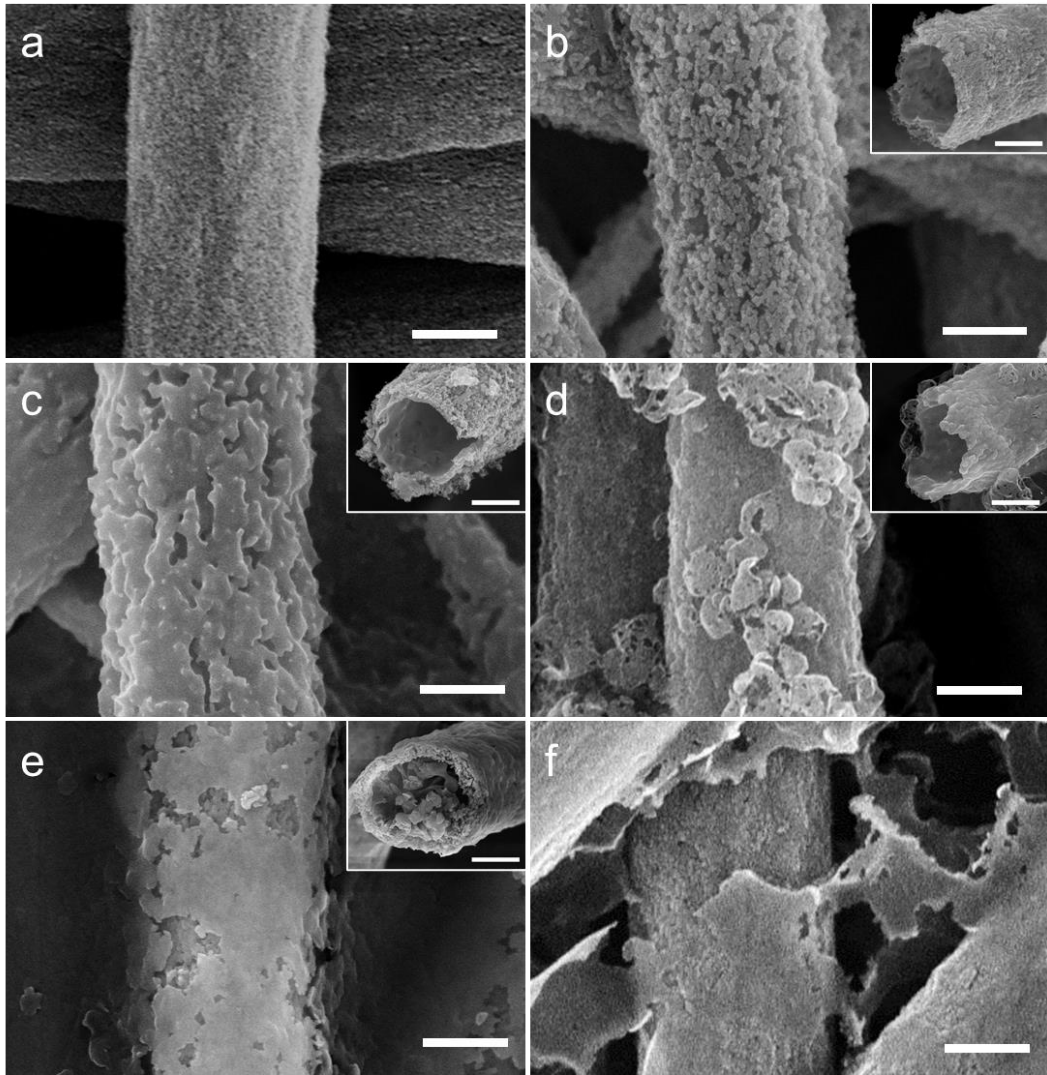


Fig. S6 SEM images of a) S-TiO₂ nanofibers, b) HP-TiO₂ nanofibers, c-e) HP-TiO₂/C₃N₄-30%, HP-TiO₂/C₃N₄-50% and HP-TiO₂/C₃N₄-70%, f) S-TiO₂/C₃N₄-50% nanofibers. Insets show cross section images of HP-TiO₂, HP-TiO₂/C₃N₄-30%~70% and S-TiO₂/C₃N₄-50% nanofibers. Scale bars are 500 nm.

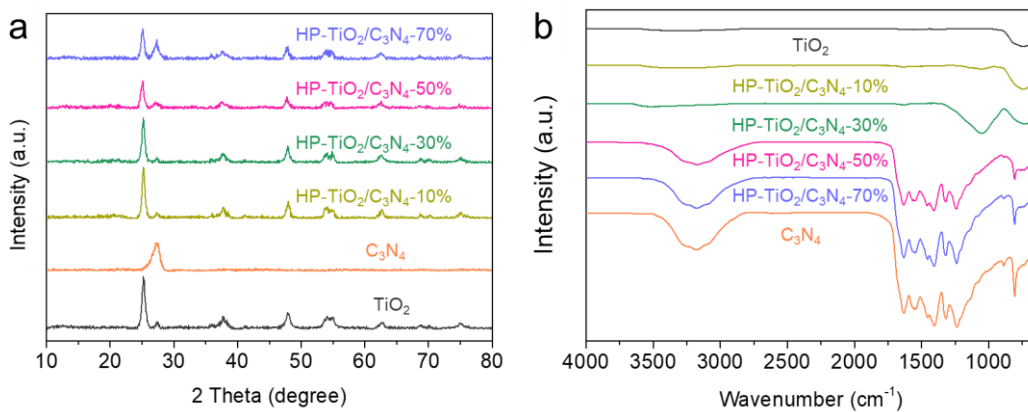


Fig. S7 a, b) XRD patterns and FTIR images of TiO₂, HP-TiO₂/C₃N₄-10%~70% and g-C₃N₄.

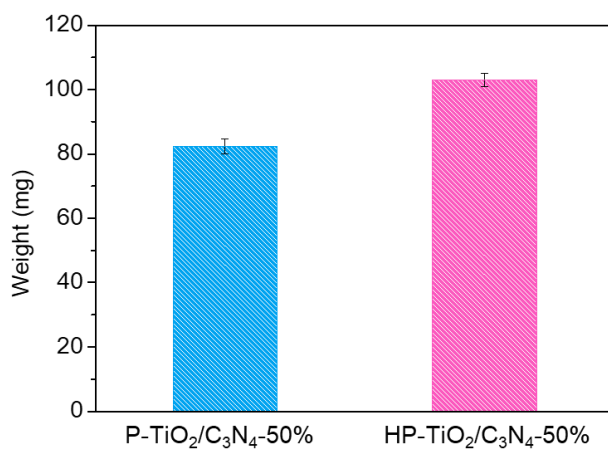


Fig. S8 The average weight of P-TiO₂/C₃N₄-50% and HP-TiO₂/C₃N₄-50% derived by immersing 50 mg P-TiO₂ and HP-TiO₂ in 50% CY solution followed by calcination.

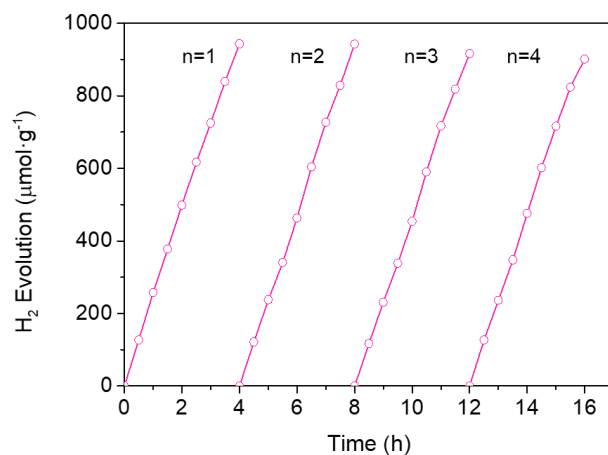


Fig. S9. Cyclic runs for the photocatalytic H₂ production over HPTCN- 50%.

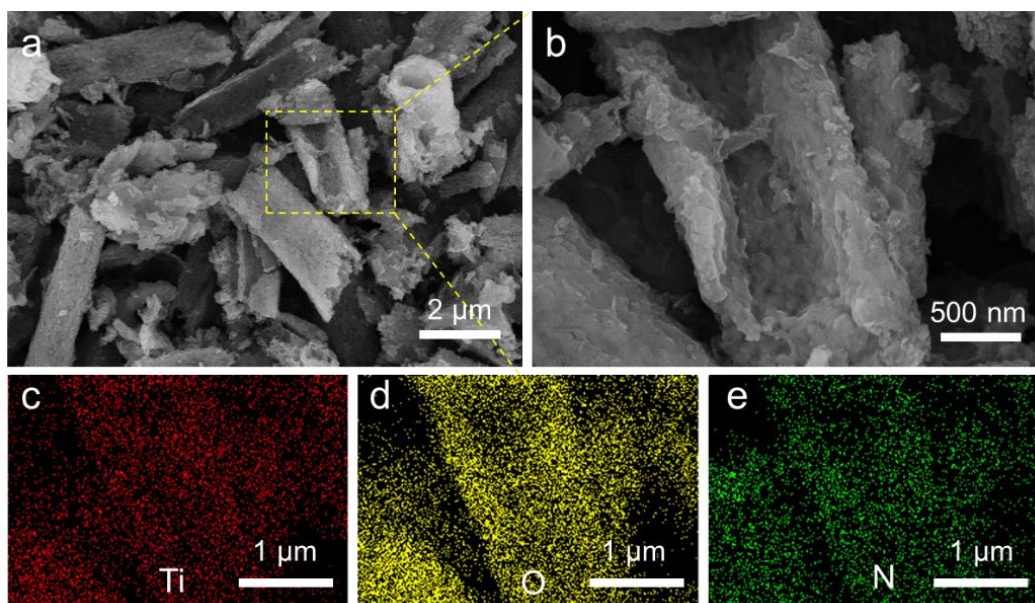


Fig. S10 The morphology and elemental mapping images of HP-TiO₂/C₃N₄-50% after four cycling tests. a, b) SEM images of HP-TiO₂/C₃N₄-50% nanofibers. c-d) Elemental mapping images for HP-TiO₂/C₃N₄-50% nanofibers indicating the existence of Ti, O, N.

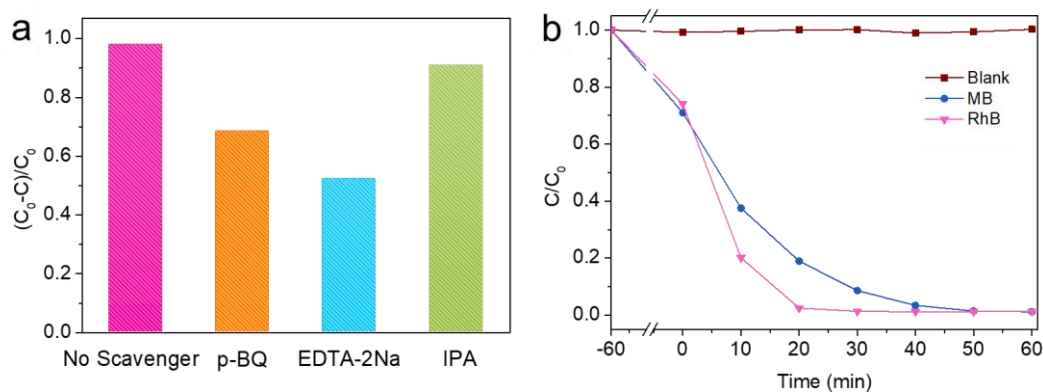


Fig. S11 a) Reactive species trapping during RhB photodegradation over HP-TiO₂/C₃N₄-50% under visible irradiation for 20 min. b) Photocatalytic curves of HP-TiO₂/C₃N₄-50% for degradation of RhB and MB solution under visible light.

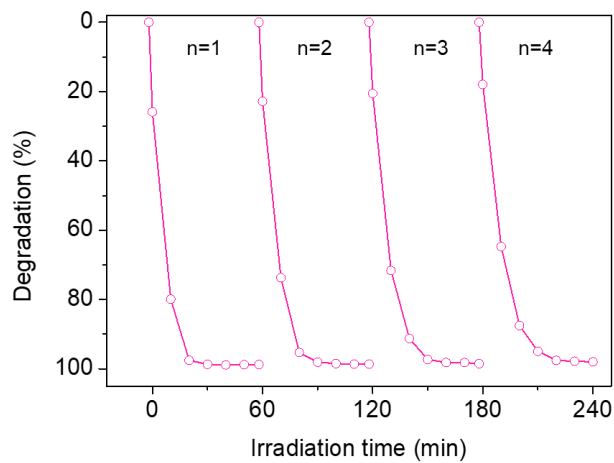


Fig. S12. Cyclic runs for the photocatalytic RhB degradation over HPTCN- 50%.

Tab. S1 S_{BET} and pore volume of samples

Samples	BET Surface Area ($\text{cm}^3 \cdot \text{g}^{-1}$)	Pore Volume ($\text{cm}^3 \cdot \text{g}^{-1}$)
S-TiO ₂	38.02	0.10
HP-TiO ₂	50.18	0.20
HP-TiO ₂ /C ₃ N ₄ -50%	22.36	0.09
g-C ₃ N ₄	13.20	0.05

Tab. S2 Visible light performance of TiO₂/g-C₃N₄ photocatalyst with different structures

Photocatalyst	Cocatalyst	Size	Light Condition	H ₂ Production ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	Ref.
TiO ₂ /g-C ₃ N ₄ nanowire	1 wt% Pt	~150 nm	300W Xe lamp ($\lambda>420$ nm)	63.7	[1]
TiO ₂ /g-C ₃ N ₄ nanosphere	1 wt% Pt	~150 nm	300W Xe lamp ($\lambda>400$ nm)	64.0	[2]
TiO ₂ /g-C ₃ N ₄ nanoparticle	1 wt% Pt	~250 nm	300W Xe lamp ($\lambda>420$ nm)	80.4	[3]
TiO ₂ /g-C ₃ N ₄ nanosheet	unknown	-	350W Xe lamp ($\lambda>420$ nm)	210.0	[4]
TiO ₂ /g-C ₃ N ₄ microsphere	0.5 wt% Pt	~10 μm	300W Xe lamp ($\lambda>420$ nm)	250.0	[5]
TiO ₂ /g-C ₃ N ₄ hollow nanosphere	unknown	~250 nm	300W Xe lamp (AM 1.5)	195.0	[6]
TiO ₂ /g-C ₃ N ₄ nanofiber	1 wt% Pt	~1.41 μm	300W Xe lamp ($\lambda>420$ nm)	189.8	our work
TiO ₂ /g-C ₃ N ₄ hollow nanofiber	1 wt% Pt	~1.37 μm	300W Xe lamp ($\lambda>420$ nm)	257.8	our work

In comparison with other TiO₂/C₃N₄ photocatalyst, hollow porous TiO₂/C₃N₄ nanofiber structure exhibits high performance, with about 4 times higher than the nanowire and nanosphere structure, 3.2 times the nanoparticle structure and 1.2 times the nanosheet structure. When compared with solid nanofiber (prepared in the same method by ourselves) and hollow nanosphere, HP-TiO₂/C₃N₄ improves H₂ evolution performance by a further 35.8% and 31.8%.

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