Supporting Information

Continuous g-C₃N₄ layer coated porous TiO₂ fibers with enhanced photocatalytic activity toward H₂ evolution and dye degradation

Jing Liu,¹ Jinxiao Zheng,¹ Guichu Yue,¹ Huaike Li,¹ Zhaoyue Liu,¹ Yong Zhao,¹ Nü Wang*¹, Chenghua Sun*¹ and Zhimin Cui*¹

a. Key Laboratory of Bioinspired Smart Interfacial Science and Technology of Ministry of Education, Beijing Key Laboratory of Bioinspired Energy Materials and Devices, School of Chemistry, Beijing Advanced Innovation Center for Biomedical Engineering, Beihang University, Beijing, 100191 (P. R. China). E-mail: wangn@buaa.edu.cn; cuizhm@buaa.edu.cn

b. Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100029 (P. R. China).

c. Inner Mongolia Key Laboratory of Industrial Catalysis, Chemical Engineering College. Inner Mongolia University of Technology, Hohhot, 010051 (P. R. China).
Fig. S1  a) SEM image of CNPs. b) SEM image and magnified image of P-TiO$_2$ fibers. d, e) TEM and HRTEM images of P-TiO$_2$ fibers. f) Diameter distribution of P-TiO$_2$ fibers. The average diameter is 1.08 µm.
Fig. S2 SEM images of a) P-TiO$_2$ fibers, b-d) PTCN-30%, PTCN-70% and PTCN-90% fibers. Scale bars are 1 µm.

CY solution with different concentration was used to prepare PTCN composite fibers to explore the effect of g-C$_3$N$_4$ 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$_2$ fibers and g-C$_3$N$_4$ were fabricated by the traditional calcination as the previously mentioned method. Surface SEM image of P-TiO$_2$ 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$_3$N$_4$ almost form a full coverage on the surface of P-TiO$_2$. The thin g-C$_3$N$_4$ layer wraps around the P-TiO$_2$ 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$_3$N$_4$
layer due to the agglomeration of g-C₃N₄. Porous structure disappeared on the surface when the CY concentration is more than 70%. It is ascribed to plenty of g-C₃N₄ wrap around TiO₂ grains forming a core-shell structure and blocking the pores.

![Optical images of P-TiO₂, PTCN-30%, PTCN-70%, PTCN-90% and pristine g-C₃N₄.](image)

**Fig. S3** Optical images of P-TiO₂, PTCN-30%, PTCN-70%, PTCN-90% and pristine g-C₃N₄.

G-C₃N₄ exhibits conventional faint yellow and P-TiO₂ 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-C₃N₄ is changed from small quantity to large quantity in PTCN composite.
**Fig. S4** SEM images of a) S-TiO$_2$ fibers, b) S-TiO$_2$/C$_3$N$_4$-90% fibers, c) PTCN-90% fibers. Inset shows amplified image of PTCN-90% fibers.

**Fig. S5** XRD patterns and FTIR images of P-TiO$_2$, g-C$_3$N$_4$, PTCN-30%, PTCN-70% and PTCN-90%.
**Fig. S6** N$_2$ adsorption-desorption isotherms and corresponding pore size distributions of P-TiO$_2$, and S-TiO$_2$.

![Graph](image)

**Fig. S7** N$_2$ adsorption-desorption isotherms and corresponding pore size distributions of PTCN-30%, PTCN-70% and PTCN-90%.

![Graph](image)

**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$_3$N$_4$ and P-TiO$_2$. 

![Graph](image)
**Fig. S9** a) XRD pattern and b) SEM image of PTCN-90% after four times H$_2$ evolution experiments.

**Fig. S10** The adsorption peak changes of RhB solution in a) P-TiO$_2$, b) g-C$_3$N$_4$, 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$_2$ g-C$_3$N$_4$ and PTCN with different g-C$_3$N$_4$ content (PTCN-30%, PTCN-70% and PTCN-90%) in visible light irradiation. b) Phenol photocatalytic degradation performance for P-TiO$_2$, g-C$_3$N$_4$, 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$_2$, indicating that phenol could not act as photoactivator with TiO$_2$. 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$_2$ and g-C$_3$N$_4$.

The band structures of TiO$_2$ and g-C$_3$N$_4$ in the nanocomposite are calculated by the DRS results and the following formulas:

\[ E_{CB} = \chi - E^C - 0.5E_g # (1) \]

\[ E_{VB} = E_{CB} + E_g # O_2 (2) \]

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$_2$ and g-C$_3$N$_4$ 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$_2$ are calculated to be -0.23 eV and 2.85 eV, respectively. Correspondingly, \(E_{CB}\) and \(E_{VB}\) values of g-C$_3$N$_4$ are -1.08 eV and 1.52 eV, respectively.

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

| Samples     | BET Surface Area (cm$^2$·g$^{-1}$) | Pore Volume (cm$^2$·g$^{-1}$) |
|-------------|-----------------------------------|-------------------------------|
| S-TiO$_2$   | 36.25                             | 0.10                          |
| P-TiO$_2$   | 53.71                             | 0.21                          |
| PTCN-90%    | 22.85                             | 0.10                          |
| g-C$_3$N$_4$| 13.20                             | 0.05                          |
Tab. S2 Visible light performance of TiO$_2$/g-C$_3$N$_4$ photocatalyst with different structures

| Photocatalyst          | Size     | Cocatalyst | Light Condition     | H$_2$ Production (µmol·g$^{-1}$·h$^{-1}$) | Ref. |
|------------------------|----------|------------|---------------------|------------------------------------------|------|
| TiO$_2$/g-C$_3$N$_4$ nanowire | 150 nm   | 1 wt% Pt   | 300W Xe lamp (λ>420 nm) | 63.7 | [1] |
| TiO$_2$/g-C$_3$N$_4$ nanosphere | 150 nm   | 1 wt% Pt   | 300W Xe lamp (λ>400 nm) | 64.0 | [2] |
| TiO$_2$/g-C$_3$N$_4$ nanoparticle | 250 nm   | 1 wt% Pt   | 300W Xe lamp (λ>420 nm) | 80.4 | [3] |
| TiO$_2$/g-C$_3$N$_4$ nanoparticle | 18 nm    | 0.5 wt% Pt | 300W Xe lamp (λ>420 nm) | 219.9 | [4] |
| TiO$_2$/g-C$_3$N$_4$ nanosheet | unknown | 350W Xe lamp (λ>420 nm) | 210.0 | [5] |
| TiO$_2$/g-C$_3$N$_4$ microsphere | 10 µm    | 0.5 wt% Pt | 300W Xe lamp (λ>420 nm) | 250.0 | [6] |
| TiO$_2$/g-C$_3$N$_4$ hollow nanosphere | 250 nm   | unknown | 300W Xe lamp (AM 1.5) | 195.0 | [7] |
| TiO$_2$/g-C$_3$N$_4$ hollow nanosphere | 100 nm   | unknown | 350W Xe lamp (λ>420 nm) | 296.4 | [8] |
| TiO$_2$/g-C$_3$N$_4$ nanofiber | 330 nm   | 1 wt% Pt   | 300W Xe lamp (400-780 nm) | 251.7 | [9] |
| C@TiO$_2$−x/g-C$_3$N$_4$ nanosheet | unknown | 350W Xe lamp (λ>420 nm) | 417.2 | [10] |
| TiO$_2$/g-C$_3$N$_4$ porous nanofiber | 1.41 µm  | 1 wt% Pt   | 300W Xe lamp (λ>420 nm) | 436.3 | our work |

In comparison with other TiO$_2$/g-C$_3$N$_4$ photocatalysts, PTCN-90% exhibits high performance, with about 6.8 times higher than the nanowire and nanosphere structure, $^{1,2}$ 5.5 times the nanoparticle structure, $^{3}$ and 3.2 times the nanosheet structure. $^{5}$ When compared with STCN-90% (prepared in the same method by ourselves), PTCN-90% improves H$_2$ evolution performance by 40.6%.
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