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

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TiO₂/g-C₃N₄ composite photocatalysts with various merits, including low-cost, non-toxic, and environment friendliness, have potential application for producing clean energy and removing organic pollutants to deal with the global energy shortage and environmental contamination. Coating a continuous g-C₃N₄ layer on TiO₂ fibers to form a core/shell structure that could improve the separation and transit efficiency of photo-induced carriers in photocatalytic reactions is still a challenge. In this work, porous TiO₂ (P-TiO₂)/g-C₃N₄ fibers were prepared by a hard template-assisted electrospinning method together with the g-C₃N₄ precursor in an immersing and calcination process. The continuous g-C₃N₄ layer was fully packed around the P-TiO₂ fibers tightly to form a TiO₂@g-C₃N₄ core/shell composite with a strong TiO₂/g-C₃N₄ heterojunction, which greatly enhanced the separation efficiency of photo-induced electrons and holes. Moreover, the great length–diameter ratio configuration of the fiber catalyst was favorable for the recycling of the catalyst. The P-TiO₂@g-C₃N₄ core/shell composite exhibited a significantly enhanced photocatalytic performance both in H₂ generation and dye degradation reactions under visible light irradiation, owing to the specific P-TiO₂@g-C₃N₄ core/shell structure and the high-quality TiO₂/g-C₃N₄ heterojunction in the photocatalyst. This work offers a promising strategy to produce photocatalysts with high efficiency in visible light through a rational structure design.

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1 Introduction

With rapid global industrialization and rapid population explosion, the global energy demand is ever growing. Traditional energy sources are non-renewable and thus exhaustible and also have hazardous combustion products, which put human beings under increasing threat from the energy dilemma and environmental contamination.^{1–3} Therefore, it is highly desirable to explore new sources of energy that are sustainable and pollution-free. Among the many candidates, hydrogen energy derived from photocatalytic water decomposition is regarded as the most green and has great potential to substitute conventional fuels in terms of sustainability and cleanliness.^{4–8} Besides, photocatalysts also show outstanding

performance for the degradation of contaminants in water and air.^{9–13}

Among the numerous photocatalysts, TiO₂ has been extensively investigated due to its many outstanding advantages, including non-toxic nature, low-cost, pollution-free, chemical and thermal stability. However, the fast recombination of photo-induced carriers and its limited response to visible light greatly hinder its photocatalysis application. Hence, numerous efforts have been dedicated to the modification of TiO₂ for expanding its light absorption range and for separating the photogenerated holes and electrons rapidly, including surface sensitization, noble metal deposition, element doping, and heterojunction formation.^{14–17} Graphitic carbon nitride (g-C₃N₄), a metalloid and polymeric photocatalyst, has shown great potential application in hydrogen production under visible light since 2009.¹⁸ It has raised wide interested thanks to its excellent characteristics, for instance, chemical stability, cost-effectiveness, visible response, and environmental-friendly nature. The combination of TiO₂ and g-C₃N₄ is a valid way to increase the separation efficiency of photon-induced carriers and expand the light absorption range.^{19,20} Many avenues have been conducted to fabricate different morphologies of g-C₃N₄/TiO₂ nanocomposites. g-C₃N₄/TiO₂ nanosheet composites were fabricated by Keller *et al.* via a sol-gel and thermal

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polycondensation synthesis. The nanocomposites exhibited efficient H₂ production using very low amounts of sacrificial agents under visible light irradiation.²¹ Song *et al.* mixed urea with TiO₂ nanoparticles to fabricate coupled photocatalysts by calcination. The TiO₂/g-C₃N₄ nanocomposite presented better photocatalytic phenol degradation performance.²² TiO₂/g-C₃N₄ nanospheres were fabricated by Wang *et al.* via a melt-infiltration of dicyandiamide into mesoporous TiO₂ spheres followed by calcination. The melt-infiltration process made g-C₃N₄ undergo better fusion into mesoporous TiO₂ and formed a firm interfacial contact, which showed a higher performance for the visible light degradation of organic pollutants.²³ However, all these structures, such as nanosheets, nanoparticles, and nanospheres, are microscopic materials, which makes it difficult to recover and recycle the catalyst in practical application. Notably, fibers with a very large aspect ratio have structural advantages of a microscopic diameter as well as macroscopic length that make them very promising in catalyst recycling.

Among the various methods to fabricate fiber catalysts, electrospinning is a direct and effective approach to produce fibers with various fine structures.^{24–29} Wang and Lei *et al.* synthesized TiO₂/g-C₃N₄ nanocomposites by a simple electrospinning process. Few g-C₃N₄ nanosheets were embedded and interspersed in the TiO₂ nanofibers. The TiO₂/g-C₃N₄ nanofibers showed improved photocatalytic activity for H₂ evolution and rhodamine B (RhB) degradation under simulated solar irradiation.³⁰ Park and Kim *et al.* prepared TiO₂/g-C₃N₄ nanofibers via a two-nozzle electrospinning process combined with a calcination method. The TiO₂/g-C₃N₄ nanofibers showed significantly improved performance for the photocatalytic degradation of RhB and reactive black 5 under solar light irradiation.³¹ However, the g-C₃N₄ content among the composite is typically restricted, which means it is unable to form a large contacted interface with TiO₂ in these methods. Li and Yan *et al.* synthesized a TiO₂/g-C₃N₄ heterojunction nanofibers photocatalyst via electrospinning and an *in situ* evaporation calcination method to control the ratio of g-C₃N₄ and TiO₂ in the composite. The photocatalyst showed high activity in RhB degradation under simulated sunlight.³² Wang *et al.* fabricated TiO₂/g-C₃N₄ nanocomposites by combining electrospun TiO₂ nanofibers and calcinated g-C₃N₄ nanosheets with a hydrothermal reaction. The TiO₂/g-C₃N₄ nanocomposites showed improved photocatalytic degradation performance for RhB solution.³³ However, the massive g-C₃N₄ tended to aggregate on the TiO₂ nanofibers. However, neither the blocks nor the adhesions of g-C₃N₄ were negligible on account of the intrinsic agglomerating properties of g-C₃N₄ on the TiO₂ nanofibers during the calcination, which led to a limited surface area that is detrimental for forming homogeneous heterojunctions between TiO₂ and g-C₃N₄. Heterojunction semiconductors achieved by infiltration approach method showed a greatly enhanced interfacial contact that surpassed that obtained by sol-gel chemistry or standard ball-milling methods.³⁴ Porous materials possess abundant active sites for mass transfer to build heterojunction semiconductors through the high pore volumes and large surface areas. Here, the precursor could

facilely penetrate into the porous substrate material and nucleate, and then grow from inside to outside. As a result, substrate materials with a well-developed porosity could promote the growth of a secondary structure on the substrate to form strong contacted heterojunctions and could even enable a high structural stability.^{35,36} In our previous work, hollow porous TiO₂/g-C₃N₄ nanofiber photocatalysts were prepared via a coaxial electrospinning combined with infiltration method.³⁷ The hollow and porous TiO₂/g-C₃N₄ nanofibers showed high photocatalytic performance for H₂ evolution and RhB degradation, ascribed to the intact porous hollow structure and the TiO₂/g-C₃N₄ heterojunctions. However, the g-C₃N₄ layers grown on the TiO₂ nanofiber were cocked, leading to an incomplete contact with the TiO₂ substrate. In addition, the photocatalytic performance of the composite was confined due to the blocking of the hollow structure through the high g-C₃N₄ content. Therefore, a continuous and uniform thin layer structure of g-C₃N₄ on TiO₂ fibers would be more favorable for the construction of intimate contacted TiO₂/g-C₃N₄ heterojunctions, which would be highly beneficial for photocatalysis reactions because of the fast photocarrier separation superiority and large specific surface area.^{38–41}

Herein, we developed a template-assisted electrospinning approach together with a solution infiltration process to coat a continuous g-C₃N₄ layer on to porous TiO₂ (P-TiO₂) fibers to produce a porous TiO₂@g-C₃N₄ core/shell composite. Abundant mesopores in the TiO₂ fibers provided accommodating venues for the precursor of g-C₃N₄ in order that a continuous tightly wrapped g-C₃N₄ shell could be grown on the P-TiO₂ fibers. Moreover, with the high content of g-C₃N₄, the porous TiO₂@g-C₃N₄ composites still maintained the fibers' structure well with no aggregation or adhesion of g-C₃N₄. The intimate heterojunctions between the g-C₃N₄ shell and P-TiO₂ fibers core inhibited the recombination of photo-induced carriers during the photocatalytic process. The H₂ production and dye (RhB) degradation activities were both improved under visible light illumination, ascribed to the synergistic action of the continuous core/shell structure and the high-quality heterojunctions between the g-C₃N₄ layers and TiO₂ fibers.

2 Experimental

2.1 Materials

Polyvinylpyrrolidone (PVP, $M_w = 1\,300\,000$) was provided by Aladdin (Shanghai, China). Titanium butoxide (TBOT), cyanamide (CY), triethanolamine (TEOA), acetylacetone, isopropanol (IPA), *p*-benzoquinone (*p*-BQ), RhB, methylene blue (MB), phenol and absolute ethanol were obtained from Macklin (Shanghai, China). The above reagents were all directly used without further treatment.

2.2 Fabrication of porous TiO₂ (P-TiO₂) fibers

P-TiO₂ fibers were produced via a template-assisted electrospinning technique. Hand-made candle soot carbon nanoparticles (CNPs) were used as the template to create nanopores in the TiO₂ fibers. Generally, 1.2 g CNPs was added to 25.2 mL



ethanol and then ultrasonically processed for 2 h to disperse the CNPs uniformly. Next, 4.8 g PVP was mixed with the above solution with magnetic stirring for 6 h. Afterward, 1.0 g TBOT and 2.4 g acetylacetone were added to the above homogeneous PVP/CS ethanol solution and then stirred for 12 h to obtain the TiO₂ precursor sol. The ejection rate of the spinning fluid was 40 μL min⁻¹. The distance from the syringe needle to collector was 20 cm, and the voltage was 9.0 kV. The as-prepared fibers were calcined at 500 °C for 3 h to prepare the P-TiO₂ fibers. Solid TiO₂ (S-TiO₂) fibers with no nanopores were also fabricated by the same electrospinning condition without CNPs in the TiO₂ precursor sol as a control to explore the role of nanopores in the formation of the TiO₂@g-C₃N₄ core/shell structure.

2.3 Preparation of porous TiO₂@g-C₃N₄ (PTCN) core/shell heterojunction fiber photocatalysts

First, 0.5 mL cyanamide (CY) solution was added to the P-TiO₂ fibers dropwise to make CY solution infiltrate into the P-TiO₂ fibers fully and uniformly. The as-prepared mixture was transferred to a semi-enclosed silica crucible to calcinate at 550 °C for 4 h. PTCN photocatalysts with different CY concentrations were tagged as PTCN-*x* (*x* = 30%, 70%, 90%), where *x* represents the volume fraction of CY aqueous solution. As a control, the S-TiO₂ fibers were also treated by the same process to synthesize solid TiO₂/g-C₃N₄ (STCN). Besides, pure g-C₃N₄ was achieved *via* directly calcinating pristine CY under the same calcination conditions.

2.4 Characterization

The morphologies of the samples were inspected by scanning electron microscopy (SEM) (FEI Quanta FEG 250) with an acceleration voltage of 10 kV and by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) (JEM-F200). The Brunauer–Emmett–Teller (BET) surface areas (*S*_{BET}) of the samples were determined using an ASAP 2420 (Micrometrics Instruments) nitrogen adsorption apparatus. The pore-size distributions were measured by the Barrett–Joyner–Halenda (BJH) model. X-ray diffraction (XRD) patterns were obtained on a Shimadzu XRD-6000, using a Cu Kα source. Fourier transform-infrared (FT-IR) spectra were obtained on a Thermo Scientific Nicolet 6700. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Scientific ESCA Lab 250Xi. UV-Visible diffuse reflectance spectroscopy (DRS) was performed on a Shimadzu UV-3600. Photoluminescence (PL) spectra were obtained on a Cary Eclipse MY14110001. The UV-visible absorption spectra were obtained on an Agilent/Varian Cary 50.

2.5 Photocatalytic hydrogen evolution

The H₂-generation activity of the photocatalysts was characterized by a gas tracing and analysis system (Labsolar-6A, Beijing Perfectlight). Generally, the photocatalyst (50 mg) was dispersed in a mixture of distilled water (85 mL) and TEOA (15 mL) with constant stirring in a transparent quartz reactor. Next, 1 wt% Pt was loaded on to the photocatalyst by a photodeposition process. Previous to irradiation, the dissolved air in the reaction

system was removed by a vacuum pump. Subsequently, a xenon lamp (300 W, λ ≥ 420 nm) (Microsolar 300, Beijing Perfectlight) was equipped to irradiate the photocatalysts suspension. The gaseous product was sampled and analyzed directly by gas chromatography (Techcomp, GC-7900) with an argon gas carrier. The reaction system was kept at 5 °C by recirculating water.

2.6 Photocatalytic degradation

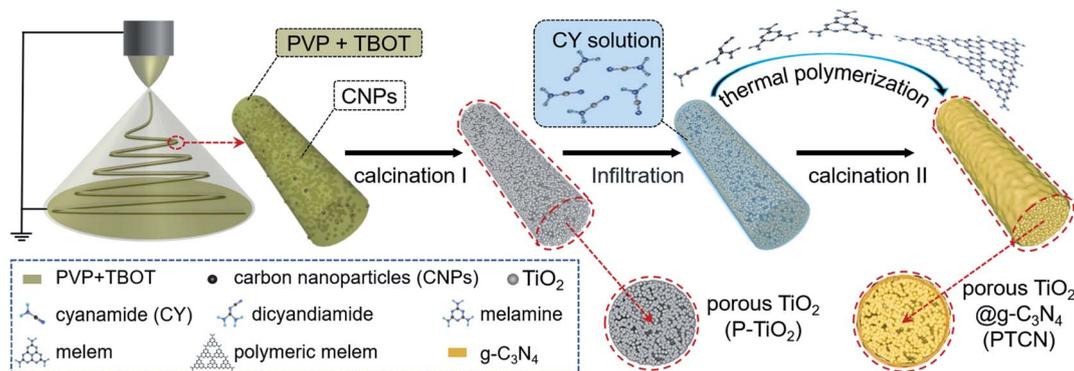
The photodegradations of RhB (10 ppm), MB (10 ppm), and phenol (5 ppm) were employed to characterize the catalytic activity of the photocatalysts under visible light irradiation. Generally, 50 mg catalyst was added to 50 mL RhB (MB and phenol) solution. Before irradiation, the reaction solution was continuously stirred at 25 °C for 60 min in the dark to establish adsorption–desorption equilibrium. Next, 3.5 mL of RhB (MB and phenol) solution was extracted periodically to record the concentration change of RhB by the UV-vis absorbance spectrum at 553 nm (664 nm for MB and 270 nm for phenol). *C*/*C*₀ was calculated, where *C*₀ represents the initial concentration of RhB solution after the adsorption–desorption process, *C* stands for the real-time RhB concentration under visible light. The photocatalyst was recovered and reused in repeat cycles to investigate the stability. Moreover, different scavengers were used to explore the photocatalytic degradation mechanism of the core/shell PTCN composite. Before the reaction, *p*-BQ (0.25 mM), IPA (1 mM), and TEOA (1 mM) were injected in to the RhB solution, respectively, to trap superoxide radicals (·O₂⁻), hydroxyl radicals (·OH), and holes (h⁺) species.

3 Results and discussion

Scheme 1 exhibits a diagrammatic sketch for the preparation of porous TiO₂@g-C₃N₄ (PTCN) fibers with the core/shell structure. The P-TiO₂ fibers were constructed *via* a carbon nanoparticles (CNPs) template-assisted electrospinning approach. The electrospinning fluid was a mixture of home-made candle soot CNPs, PVP, and TBOT. The CNPs with an average diameter of 30 nm served as a template to produce the porous structure (Fig. S1a†). During the first calcination step, the organics and CNPs were removed and thus porous TiO₂ (P-TiO₂) fibers were obtained. After immersing the P-TiO₂ fibers in a certain concentration of cyanamide (CY) solution, followed by second calcination step, PTCN fibers with a core/shell structure were obtained.

Fig. 1a–f display the evolution process from electrospinning the precursor fibers to PTCN core/shell fibers with different g-C₃N₄ contents. The precursor fibers had a relatively smooth appearance with a few CNPs on the surface (Fig. 1a). The calcinated fibers exhibited an incompact and porous surface after removing PVP and CNPs (Fig. 1b and S1b†). The pore size of the P-TiO₂ fibers matched well with the particle size of the CNPs template (Fig. S1c and d†) and the diameter of the P-TiO₂ fiber was approximately 1.08 μm (Fig. S1f†). After the secondary calcination step, the CY underwent a thermal polymerization process and formed a continuous g-C₃N₄ thin layer on the PTCN





Scheme 1 Scheme for the preparation of porous TiO_2 @ $\text{g-C}_3\text{N}_4$ (PTCN) core/shell fibers. Porous TiO_2 (P- TiO_2) fibers were produced via a template-assisted electrospinning technique with subsequent calcination. Then, the P- TiO_2 fibers were immersed in cyanamide (CY) solution followed by a second step of calcination to prepare PTCN with a core/shell structure.

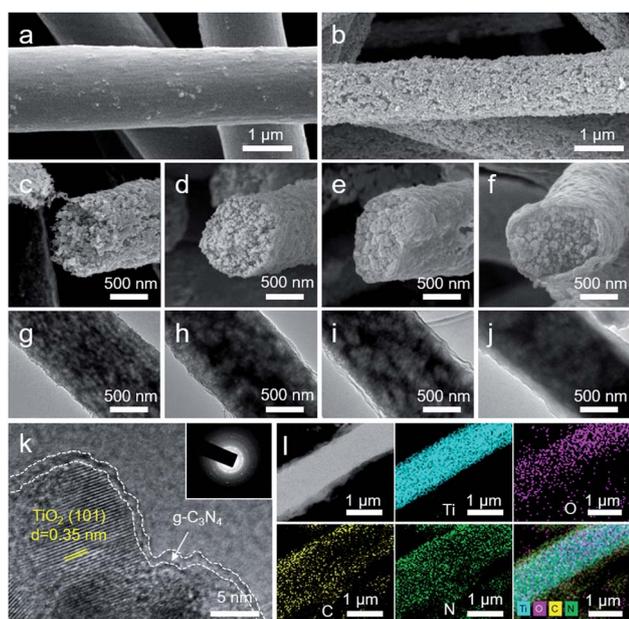


Fig. 1 SEM images of (a) pristine electrospinning fibers and (b) P- TiO_2 fibers. (c–f) Cross section images of P- TiO_2 , PTCN-30%, PTCN-70%, and PTCN-90%. (g–j) TEM images of P- TiO_2 , PTCN-30%, PTCN-70%, and PTCN-90%. The $\text{g-C}_3\text{N}_4$ shell of PTCN became more contiguous and thicker apparently with the increase in CY concentration. (k) HRTEM image of PTCN-90% (the inset exhibits the SAED pattern of PTCN-90%, indicating the polycrystalline configuration). (l) HAADF-STEM image and EDX mapping images of elemental Ti, O, C, N and a layer image of a single PTCN-90% fiber. Mesopores homogeneously distributed in the PTCN-90% core/shell fiber. The distribution of four elements in the fiber further confirmed the formation of the TiO_2 @ $\text{g-C}_3\text{N}_4$ core/shell structure.

fibers. The cross-section SEM and TEM images revealed the detailed structures of the P- TiO_2 and PTCN fibers. The P- TiO_2 fibers were composed of small nanoparticles (Fig. 1c and g). Layered $\text{g-C}_3\text{N}_4$ could be observed from all the PTCN samples (PTCN-30%, 70%, and 90%). When the concentration of CY solution was 30%, a very thin layer about 36 nm thick was detected around the outside of the P- TiO_2 fibers (Fig. 1d and h).

As the CY concentration increased to 70%, the outer shell of the fiber became distinct with a thickness of about 50 nm (Fig. 1e and i). When the CY concentration was up to 90%, a dense and continuous shell of approximately 85 nm thickness was wrapped around the P- TiO_2 fiber tightly (Fig. 1f and j). The surface SEM image also showed the $\text{g-C}_3\text{N}_4$ shell covers around the P- TiO_2 fiber became thicker and denser as the CY concentration increased (Fig. S2†). The digital photos of all samples presented a gradual color change from white to yellow with the increase in CY concentration (Fig. S3†). Fig. 1k shows the high-resolution TEM (HRTEM) image of the PTCN-90% composite. The boundary of a TiO_2 crystalline grain with a lattice fringe of 0.35 nm was coherent with the anatase $\text{TiO}_2(101)$ lattice plane (Fig. 1k and S1e†).³² A thin $\text{g-C}_3\text{N}_4$ layer could be observed around the TiO_2 grain, which was the $\text{g-C}_3\text{N}_4$ phase.⁴² In the inset of Fig. 1k, the selected area electron diffraction pattern (SAED) of HPCN-90% revealed the polycrystalline configuration of the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ heterojunction. The HAADF-STEM image and EDX elemental mapping images of PTCN-90% are shown in Fig. 1l. The broader distribution range of C and N agreed well with the TiO_2 @ $\text{g-C}_3\text{N}_4$ core/shell structure, while the overlapping distribution range of Ti, O, C, and N indicated that an intimate $\text{TiO}_2/\text{g-C}_3\text{N}_4$ heterojunction was also constructed in the P- TiO_2 fiber together with the continuous $\text{g-C}_3\text{N}_4$ coating.

As contrast, solid TiO_2 (S- TiO_2) fiber@ $\text{g-C}_3\text{N}_4$ (STCN) nanostructures were also prepared to investigate the effect of the nanopores in TiO_2 fiber for the growth of the $\text{g-C}_3\text{N}_4$ coating. S- TiO_2 fibers were fabricated by almost the same electrospinning method but without the CNPs template. After the first calcination step, only tiny holes could be observed on the surface of the S- TiO_2 fibers (Fig. S4a†). After immersing the S- TiO_2 fibers in a certain concentration of CY solution and followed by a second calcination step, the STCN composite was obtained. However, plenty of separate $\text{g-C}_3\text{N}_4$ nanosheets could be observed by the side of the S- TiO_2 fiber in the STCN composite (Fig. S4b†). Although a small amount of $\text{g-C}_3\text{N}_4$ was coated on the S- TiO_2 fibers, a continuous $\text{g-C}_3\text{N}_4$ layer was not formed like in PTCN (Fig. S4c†). This significant difference was because $\text{g-C}_3\text{N}_4$ is easy to agglomerate on S- TiO_2 fibers during calcination at high



temperature, while the porous structure of P-TiO₂ makes CY solution easily infiltrate into the internal structure of the TiO₂ fibers and hence forms a continuous g-C₃N₄ shell layer around the P-TiO₂ fibers core. Apparently, the porous structure of P-TiO₂ fibers is not only crucial for the intimate contact between TiO₂ fibers and g-C₃N₄, but also significant for the continuous g-C₃N₄ coating on the TiO₂ fibers.

X-ray diffraction (XRD) patterns were measured to investigate the crystal phases of TiO₂, g-C₃N₄, and PTCN-90% (Fig. 2a). The diffraction peaks at 25.1°, 37.7°, and 47.9° corresponded to the (101), (004), and (221) lattice planes of anatase TiO₂ (JCPDS no. 21-1272). The characteristic peak of g-C₃N₄ was located at 27.5°, corresponding to the (002) diffraction plane.²³ The peak intensity of g-C₃N₄ in the PTCN became stronger with the increase in CY concentration from 30% to 90%, indicating a more crystalline g-C₃N₄ was grown in the P-TiO₂ fibers (Fig. S5a†). The FT-IR spectra of the TiO₂, g-C₃N₄, and PTCN-90% heterojunction photocatalysts are presented in Fig. 2b. In the range of 700–900 cm⁻¹, TiO₂ exhibited a wide band because of the Ti–O–Ti stretching vibration. Pure g-C₃N₄ displayed three feature adsorption regions located at 3000–3500, 1200–1700, and 810 cm⁻¹, respectively. The broad adsorption region around 3000–3500 cm⁻¹ was indexed to the N–H typical stretching vibration. The strong feature peaks between 1200 to 1700 cm⁻¹ were attributed to the C–N heterocycles stretching vibration. Moreover, the sharp absorption peak at 810 cm⁻¹ was

related to the specific triazine units breathing mode.⁴³ In the FT-IR spectra of PTCN-90%, we could easily find the characteristic peaks for TiO₂ and g-C₃N₄ in the relevant positions, which indicated that g-C₃N₄ was formed in PTCN fiber. With the concentration of CY increasing from 30% to 90%, the peak intensity of g-C₃N₄ became stronger in the PTCN heterojunction photocatalysts (Fig. S5b†). N₂ adsorption–desorption isotherms were obtained and showed that all the samples presented type IV isotherms (Fig. 2c and S7a†). S-TiO₂ exhibited an H2 hysteresis loop, illustrating that the S-TiO₂ fiber possessed uniform intergranular pores (Fig. S6a†). P-TiO₂ and PTCN-90% showed H2 and H3 hysteresis loops, indicating the existence of ink-bottle pores and slit-shaped pores, resulting from interconnected pore channels and plate-like particles aggregation. Only a type H3 hysteresis loop was observed in g-C₃N₄, owing to its layered structure.^{44,45} P-TiO₂ had a larger *S*_{BET} of 53.71 m² g⁻¹, which was 1.48 times that of S-TiO₂ (36.25 m² g⁻¹) owing to the introduction of mesopores in the electrospun TiO₂ fibers. Compared to P-TiO₂, the *S*_{BET} of the PTCN-90% sample (22.85 m² g⁻¹) clearly dropped, ascribed to the coating of the g-C₃N₄ layer on the P-TiO₂ nanopores. The coated g-C₃N₄ layer blocks part of the nanopores and nanocavities of PTCN-90%. By comparison, pure g-C₃N₄ presented the lowest *S*_{BET} of 13.20 m² g⁻¹ (Table S1†). A main pore-size distribution around 10–15 nm was detected in S-TiO₂, ascribed to the thermal decomposition of organic substances in the process of the calcination. P-TiO₂ exhibited a larger pore diameter and wider pore distribution than S-TiO₂, owing to the abundant pore structure in the fibers (Fig. S6b†). As shown in Fig. 2d and S7b,† PTCN-90% showed a much lower pore volume than P-TiO₂, PTCN-30%, and PTCN-90%, on account of filling up the plentiful g-C₃N₄ nanosheets into the nanopores of P-TiO₂. The pore-size distribution results coincided with the *S*_{BET} and morphology characterization results.

X-ray photoelectron spectroscopy (XPS) was performed to further explore the compositions and surface chemical status of the obtained photocatalysts. C, N, Ti, and O elements were all detected in the spectra of PTCN-90%, which was consistent with the EDX results (Fig. S8a†). Fig. 2e displays the N 1s high-resolution spectrum of PTCN-90% with g-C₃N₄ for comparison. N 1s peaks at 398.4, 398.9, and 400.9 eV were ascribed to the sp²-hybridized nitrogen of triazine rings (C=N–C), tertiary nitrogen ((C)₃–N), and nitrogen in the amino functional groups (C–N–H), respectively. The isolated peak at 403.3 eV was attributed to the charging effect or a positive charge localization in the heterocycles.³⁰ The binding energy of N–(C)₃ (398.9 eV) showed a slight negative shift of 0.2 eV by contrast with g-C₃N₄ (399.1 eV), confirming the strong interfacial interaction between the TiO₂ fiber and g-C₃N₄ layer rather than a simple physical mixing.⁴⁴ The C 1s spectral peaks in PTCN-90% at 284.8 and 288.0 eV represented the sp²-hybridized carbon (N–C=N) groups and graphitic carbon (C–C), respectively (Fig. S8b†). A negative shift of 0.1 eV compared with pure g-C₃N₄ was observed, attributed to the interaction effect of O–Ti–O–C–N bonds between g-C₃N₄ and TiO₂.²¹ The O 1s peaks at 530.2 and 531.6 eV in HPCN-90% were associated with Ti–O and Ti–OH (Fig. 2e). Fig. S8c† displays the Ti 2p high-resolution

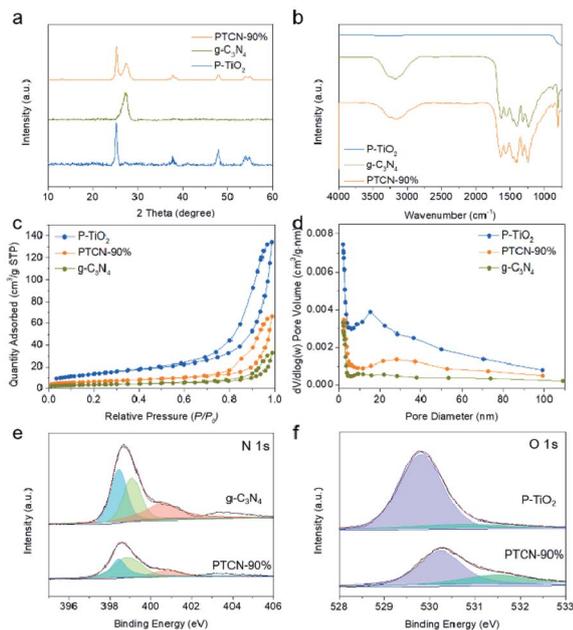


Fig. 2 (a and b) XRD patterns and FT-IR spectra for P-TiO₂, g-C₃N₄, and PTCN-90%. The characteristic peaks of TiO₂ and g-C₃N₄ were both found in PTCN-90%, indicating g-C₃N₄ was successfully coupled on the TiO₂ fibers. (c and d) The N₂ adsorption–desorption isotherms and corresponding pore-size distributions of P-TiO₂, PTCN-90%, and g-C₃N₄. Both *S*_{BET} and pore volume of PTCN-90% decrease apparently compared with P-TiO₂, due to the filling of g-C₃N₄ in to the nanopores of the P-TiO₂ fibers. (e and f) High-resolution XPS spectra of N 1s and O 1s of PTCN-90%, g-C₃N₄, and P-TiO₂.



spectrum. The two peaks at 459.0 and 464.7 eV corresponded to Ti 2p_{3/2} and Ti 2p_{1/2} and originated from the spin orbit interaction, indicating that the Ti ions were tetravalent.⁴⁶ Apparently positive shifts in the binding energies in Ti 2p and O 1s were observed, confirming the intimate contact of the g-C₃N₄ layer and P-TiO₂ fiber in HPCN-90%. The high-quality TiO₂/g-C₃N₄ heterojunction is crucial to accelerate the separation and transport of photo-induced electrons and holes.^{46,47}

Photocatalytic H₂ production performance measurements of all the samples were conducted under a xenon lamp (300 W, λ ≥ 420 nm). A 1 wt% platinum (Pt) loading on the photocatalysts was performed by a photodeposition method to serve as a cocatalyst. As shown in Fig. 3a and b, P-TiO₂ had almost no photocatalytic activity for H₂ production under visible light irradiation, due to its limited photoresponse to visible light. Pure g-C₃N₄ showed a lower H₂ evolution rate on account of the fast recombination of photo-induced carriers.⁴⁸ All the PTCN samples showed a higher H₂ production rate when compared with that of P-TiO₂ and g-C₃N₄ under visible light. The H₂-production efficiency gradually improved with the increase in CY concentration. To further investigate the influence of the photocatalyst structure on H₂ evolution, the photocatalytic H₂-generation performances of g-C₃N₄, P-TiO₂, STCN-90%, and PTCN-90% were assessed and are depicted in Fig. 3c. STCN-90% and PTCN-90% showed evidently higher H₂ performances compared to g-C₃N₄ and TiO₂. The photocatalytic H₂-evolution rate of STCN-90% was 310 μmol g⁻¹ h⁻¹, which was 4.4 times as much as that of g-C₃N₄ (70 μmol g⁻¹ h⁻¹). This demonstrated that the combination of TiO₂ and g-C₃N₄ favored improving the photocatalytic H₂-evolution rate. PTCN-90% presented the highest rate of 436 μmol g⁻¹ h⁻¹, which was 6.2 times higher than that of pure g-C₃N₄. The H₂-evolution rate of PTCN-90% was improved by 40.6% when compared with STCN-90%,

indicating that the intimate core/shell heterojunction with a continuous g-C₃N₄ layer played an important role in the photocatalytic H₂-evolution performance. The reductions of the H₂-production efficiency and structures were not significantly impacted after four cycles tests, demonstrating the great recyclability of PTCN-90% (Fig. 3d and S9†). The g-C₃N₄ layer still adhered to the TiO₂ fibers firmly, which confirmed the high stability of the PTCN-90% photocatalyst. When comparing the different TiO₂/g-C₃N₄ composite photocatalysts with other structures, such as nanowires, nanospheres, and nanosheets, the PTCN photocatalyst still exhibited an excellent H₂-evolution performance (Table S2†).

The photocatalytic RhB degradation activities of all the samples were characterized under visible light irradiation with a wavelength longer than 420 nm. The photodegradation of RhB was negligible in the absence of the photocatalyst. All the PTCN photocatalysts exhibited higher activity for RhB degradation than P-TiO₂ and g-C₃N₄. Especially, PTCN-90% showed the best RhB photodegradation performance, with the complete degradation of RhB in 30 min (Fig. 4a). The photocatalytic degradation reaction conformed to pseudo-first-order kinetics described as $-\ln(C/C_0) = kt$, where k stands for the pseudo-first-order rate constant, which corresponds to the fitting line slope,

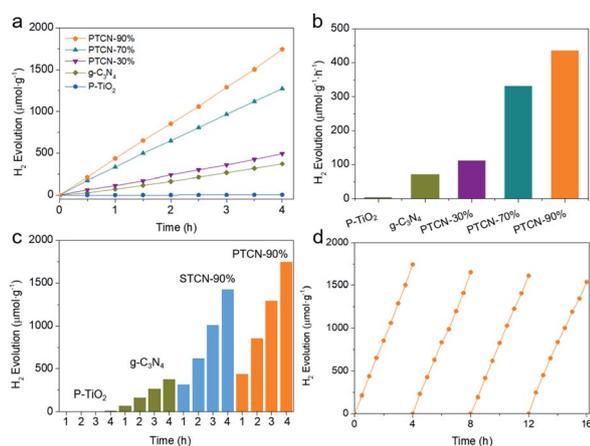


Fig. 3 (a and b) Time courses of H₂ generation and average generation rate of P-TiO₂, g-C₃N₄, PTCN-30%, PTCN-70%, and PTCN-90% under visible-light irradiation. With the increase in CY concentration, the photocatalytic hydrogen generation efficiency of PTCN was improved. (c) Time courses of H₂ generation of P-TiO₂, g-C₃N₄, STCN-90%, and PTCN-90%. The intimate core/shell in PTCN-90% was beneficial to enhancing the H₂-generation efficiency. (d) Cyclic runs for the photocatalytic H₂ evolution of PTCN-90%.

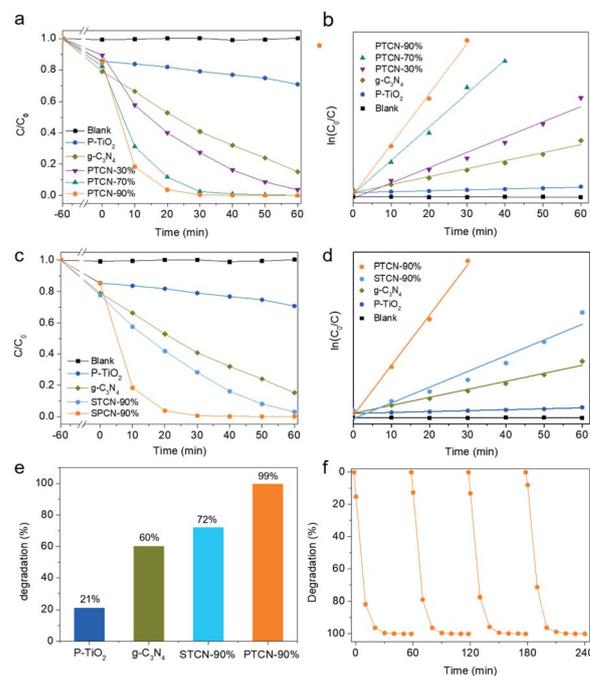


Fig. 4 (a and b) Photocatalytic RhB degradation performance and degradation kinetic curves of P-TiO₂, g-C₃N₄, PTCN-30%, PTCN-70%, and PTCN-90% under visible light irradiation. The RhB degradation rate was improved by raising the content of g-C₃N₄. PTCN-90% possessed the highest RhB degradation rate. (c and d) RhB photocatalytic degradation performance and degradation kinetic curves for P-TiO₂, g-C₃N₄, STCN-90%, and PTCN-90%. (e) RhB photocatalytic degradation efficiency of P-TiO₂, g-C₃N₄, STCN-90%, and PTCN-90% in 30 min. PTCN-90% had a much higher RhB degradation rate than STCN-90% due to the continuous core/shell structure advantage in PTCN. (f) Cyclic runs for RhB degradation over PTCN-90%.



and C_0 and C represent the solution concentrations at time 0 and t , respectively. The kinetic curves of all the samples for photocatalytic RhB degradation are demonstrated in Fig. 4b. PTCN-90% had the highest k value of 0.1674 min^{-1} , which was 54 times that of TiO_2 (0.0030 min^{-1}) and 6.3 times that of $\text{g-C}_3\text{N}_4$ (0.0267 min^{-1}). In order to verify the effect of the intimate core/shell structure in PTCN, the photocatalytic RhB photodegradation performance and degradation kinetic curves for P-TiO₂, $\text{g-C}_3\text{N}_4$, STCN-90%, and PTCN-90% were also assessed (Fig. 4c and d). The degradation rate of PTCN-90% was significantly higher than for STCN-90% (0.0524 min^{-1}) due to the specific core/shell structure and strong heterojunction between TiO_2 and $\text{g-C}_3\text{N}_4$. In 30 min, RhB was degraded almost completely by PTCN-90%; however, it could only be degraded 72% by STCN-90% (Fig. 4e). The corresponding changes in the UV-vis absorption spectra and optical images of RhB solution are exhibited in Fig. S10.† The absorption peak of the PTCN-90% sample dropped rapidly with prolonging the irradiation time and disappeared completely after 30 min. The inset shows the color change of RhB solution. The stability analysis of PTCN-90% for RhB degradation was also conducted by the recycling experiment (Fig. 4f). The performance of RhB degradation did not change obviously within four cycles, demonstrating the stability of the PTCN heterojunction photocatalyst. The core/shell PTCN-90% photocatalyst also exhibited good degradation performance for MB, in addition to RhB (Fig. S11†), where 10 ppm MB solution was completely degraded within 50 min by PTCN-90% under visible light irradiation. In consideration of the decolorization of dyes caused by a self-sensitization mechanism,^{49,50} phenol, which has no photosensitization, was selected as the substrate to further investigate the photocatalytic performance of the core/shell PTCN-90% photocatalyst (Fig. S12†). The core/shell PTCN-90% photocatalyst also exhibited good degradation performance for phenol, which was completely degraded within 3.5 h under visible light irradiation. This proved that the core/shell PTCN photocatalyst has wide application prospects in the field of photocatalysis for organic pollutant degradation.

To further explore the photodegradation mechanism of RhB, active material trapping experiments were conducted (Fig. 5a). Superoxide radicals (O_2^-), photoexcited holes (h^+), and hydroxyl radicals (OH) generated in the photocatalytic system could be shielded by *p*-BQ, TEOA, and IPA, respectively.¹² The RhB degradation decline of PTCN-90% was not significant with the presence of IPA. However, the degradation effect dramatically decreased when TEOA was added. This demonstrated that h^+ was the dominant active species in the photodegradation reaction of RhB. Moreover, the O_2^- derived from dissolved O_2 also acted as a partial player in the photocatalytic system. Photoluminescence (PL) emission spectroscopy is the most intuitive detection method to determine the separation efficiency of photo-induced carriers. The PL spectra for P-TiO₂, $\text{g-C}_3\text{N}_4$, and PCN-90% were evaluated with an excitation wavelength of 320 nm (Fig. 5b).⁵¹ It was revealed that $\text{g-C}_3\text{N}_4$ had a strong peak at 470 nm related to the band-band PL phenomenon.⁵² The bandgap energy was almost equal to the emission light energy of $\text{g-C}_3\text{N}_4$.⁵³ The emission peak of the

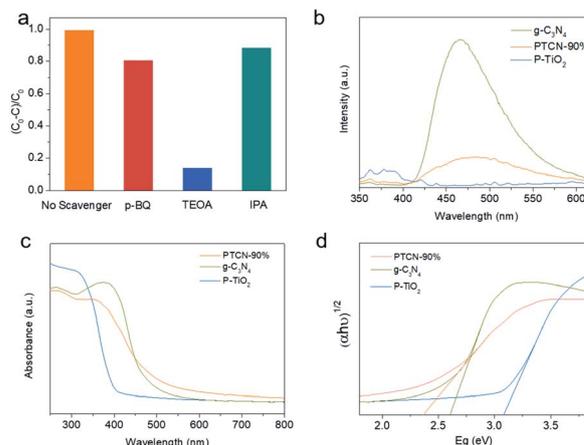
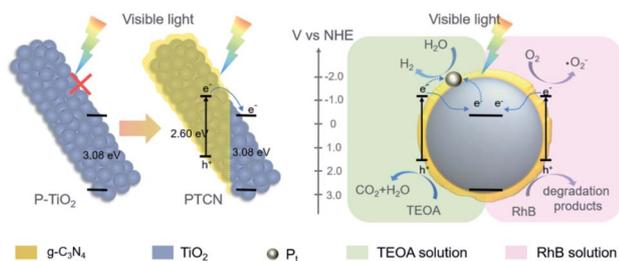


Fig. 5 (a) Active species trapping during RhB photodegradation over PTCN-90% under visible light irradiation for 30 min. (b) PL spectra of PTCN-90%, $\text{g-C}_3\text{N}_4$, and P-TiO₂. The strong heterojunction between $\text{g-C}_3\text{N}_4$ and TiO_2 accelerated the separation and transportation rate of photo-induced carriers. (c) DRS spectra and (d) corresponding band gap energy of PTCN-90%, $\text{g-C}_3\text{N}_4$, and P-TiO₂. A significant red-shift of absorption was observed in PTCN-90%, suggesting the close mutual effect between the $\text{g-C}_3\text{N}_4$ layer and P-TiO₂ fibers.

PTCN-90% heterojunction photocatalyst was weaker than for $\text{g-C}_3\text{N}_4$, which proved that PTCN-90% had a higher photo-induced carriers separation rate by virtue of the heterojunction between $\text{g-C}_3\text{N}_4$ and P-TiO₂. These results explain well its enhanced photocatalytic performance in photocatalytic H_2 generation and dye degradation.⁵⁴ Next, UV-visible diffuse reflectance spectroscopy (DRS) was performed to understand the optical absorption property of the photocatalysts. The DRS absorption edge of pure TiO_2 was 398 nm, implying that pure TiO_2 only has a response in the UV region; while $\text{g-C}_3\text{N}_4$ presented a wider absorption in the visible and UV region with the absorption edge of 450 nm. PTCN-90% showed an obvious absorption extension to the visible region compared to that of pure TiO_2 (Fig. 5c).¹³ The absorption extension of PTCN was ascribed to the strong heterojunction between $\text{g-C}_3\text{N}_4$ and P-TiO₂ in the composites. A close-contacted core-shell structure and heterojunction in PTCN catalysts are favorable for separating the photogenerated electrons rapidly, which is highly conducive to accelerating photocatalytic reactions. The band gap energy of photocatalysts could be calculated by $E_g = 1240/\lambda_g$, where E_g is the bandgap energy and λ_g is the edge of optical absorption.⁵⁵ The calculated band gap energy of TiO_2 , $\text{g-C}_3\text{N}_4$ and PTCN-90% were 3.08, 2.60, and 2.37 eV, respectively (Fig. 5d). The PTCN-90% core/shell photocatalyst presented the narrowest band gap compared with P-TiO₂ and $\text{g-C}_3\text{N}_4$, indicating its higher responsive to visible light.

A reasonable mechanism is proposed to illustrate the improved performance of the PTCN core/shell photocatalyst (Scheme 2). The E_{CB} and E_{VB} values of TiO_2 were calculated to be -0.23 and 2.85 eV. Correspondingly, the E_{CB} and E_{VB} values of $\text{g-C}_3\text{N}_4$ were -1.08 and 1.52 eV, respectively.⁵⁶ TiO_2 had a limited absorption range in the UV light area and no response in the visible region due to the broad band gap. However, the coating





Scheme 2 Proposed mechanism in PTCN fibers for photocatalytic H₂ evolution and RhB degradation. Under visible light irradiation, P-TiO₂ had no photocatalytic response, due to its broad band gap. While in the core/shell PTCN composite, photogenerated electrons in the g-C₃N₄ shell could transfer to the P-TiO₂ core rapidly through the heterojunction, thereby realizing effective electron–hole separation. For the H₂-evolution process, electrons accumulate on Pt particles and participate in the water splitting reaction. For the RhB degradation reaction, the photogenerated holes and the superoxide radicals derived from the dissolved O₂ are responsible for RhB degradation.

of a continuous g-C₃N₄ layer on P-TiO₂ fibers to construct the PTCN heterojunction could broaden its light absorption range. Under visible light conditions, the photo-induced electrons separate, with the holes rapidly leaping to the g-C₃N₄ CB, and then transiting to the CB of TiO₂ readily through the TiO₂/g-C₃N₄ heterojunction in PTCN. The fast separate and transfer of the electrons inhibit the recombination of carriers efficiently. As the reaction progresses, more electrons gather in the TiO₂ CB and more holes stay in g-C₃N₄ VB. In the process of photocatalytic water splitting, electrons accumulate on the cocatalyst and reduce H⁺ to H₂. Photogenerated holes in g-C₃N₄ VB oxidize TEOA to CO₂ and H₂O. Moreover, during the RhB photodegradation process, a portion of dissolved O₂ is reduced by electrons to create superoxide radicals with a high oxidation ability in the CB of g-C₃N₄. According to the active species trapping experiments, the photoexcited holes together with superoxide radicals acted as reactive species to decompose RhB into its degradation products. As a consequence, the strong heterojunction between g-C₃N₄ and TiO₂ together with the intimate core/shell fiber structure facilitate the transport of photoexcited carriers. The unique TiO₂/g-C₃N₄ core/shell structure and the TiO₂/g-C₃N₄ heterojunction produce a synergistic effect to the photocatalytic efficiency in the PTCN composite.

4 Conclusions

TiO₂@g-C₃N₄ core/shell fibers were fabricated by a template-assisted electrospinning method together with a solution infiltration process. In the synthesis process, the porous structure of the TiO₂ fibers enabled CY solution to readily immerse into the abundant nanopores and nanocavities to build a continuous and close-contacted TiO₂ core/g-C₃N₄ shell structure. The strong heterojunction between TiO₂ and g-C₃N₄ accelerated the separation and transfer of photoexcited electrons and holes rapidly. In addition, the intimate core/shell structure provided a rapid transmission channel for carriers as well. The

synergistic effect of the strong heterojunction and intimate core/shell structure of the PTCN composite photocatalyst led to a significant improvement in the photocatalytic performance. PTCN-90% exhibited the highest performance in H₂ generation and RhB degradation. This work offers a fresh insight in designing and synthesizing multi-structure heterojunction photocatalysts for extensive applications in the field of green and sustainable new energy.

Conflicts of interest

There are no conflicts to declare.

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