

Pt/CNTs Co-Modified Tubular g-C₃N₄ for Highly Efficient Visible-Light-Driven Photodegradation of Rhodamine B

¹Junkai Wang*, ¹Jinsheng Kang, ²Zhenxia Huang and Jingyi Xing

¹*School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo, Henan Province 454003, China.*

²*College of Chemistry and Chemical Engineering, Henan Polytechnic University, Jiaozuo, Henan Province 454003, China.*

jkwang@hpu.edu.cn*

(Received on 18th December 2025, accepted in revised form 22nd May 2026)

Summary: Developing photocatalysts with multidimensional conductive networks and synergistic interfaces is a promising strategy to suppress charge carrier recombination and enhance visible-light-driven photocatalytic performance. Herein, a Pt and carbon nanotube (CNT) co-modified tubular g-C₃N₄ photocatalyst (Pt/CNT@g-C₃N₄) was successfully fabricated via an electrostatic self-assembly strategy. The introduction of CNTs constructed efficient electron transport pathways, while highly dispersed Pt nanoparticles formed stable metal–semiconductor interfaces. Their synergistic coupling broadened visible-light absorption, narrowed the bandgap, and promoted the separation and migration of photogenerated charge carriers. At the optimal composition (2 wt% Pt and 1.5 wt% CNTs), Pt/CNT@g-C₃N₄ exhibited a Rhodamine B (RhB) degradation rate constant of 0.148 min⁻¹, which was approximately 10.8 times higher than that of pristine tubular g-C₃N₄, achieving 96% pollutant removal within 20 min under simulated visible-light irradiation. In addition, the catalyst retained over 83% of its initial photocatalytic activity after five consecutive cycles, indicating good stability and reusability. Radical trapping experiments combined with electron paramagnetic resonance (EPR) measurements confirmed that ·O₂⁻ radicals were the dominant reactive species during the photocatalytic process. Moreover, the enhanced photocatalytic performance was mainly attributed to the efficient extraction and transfer of photogenerated electrons from g-C₃N₄ through two synergistic pathways mediated by Pt nanoparticles and CNTs, which effectively suppressed electron–hole recombination. This work reveals the synergistic enhancement mechanism of Pt and CNTs in tubular g-C₃N₄ systems and provides a rational strategy for designing efficient visible-light-driven photocatalysts for environmental purification.

Keywords: Photocatalysis; Graphitic carbon nitride; Pt nanoparticles; Carbon nanotubes; Electrostatic assembly.

Introduction

Water pollution, particularly the discharge of recalcitrant organic dyes, is a global environmental issue [1,2]. Semiconductor photocatalysis has garnered extensive attention in the degradation of organic pollutants due to its green nature, lack of secondary pollution, and the ability to utilize solar energy to drive redox reactions [3,4,5].

Graphitic carbon nitride (g-C₃N₄) has drawn considerable attention in the photocatalytic breakdown of pollutants. This popularity stems from its favorable band gap (~2.7 eV), robust chemical stability, ability to respond to visible light, and low production expenses [6,7,8]. That said, g-C₃N₄ faces several drawbacks: its surface area is relatively small, it absorbs light inadequately, and the photogenerated charge carriers recombine quickly. These issues lead to less-than-ideal photocatalytic effectiveness, which in turn limits its real-world uses [9,10]. As a result,

devising effective modification approaches is critical to boosting the photocatalytic capabilities of g-C₃N₄.

Current strategies to improve the photocatalytic performance of g-C₃N₄ primarily include morphological control, construction of metallic active centers, and compositing with highly conductive carbon materials. Regarding morphological control, Sun et al. [11] utilized a template-assisted approach to construct g-C₃N₄ hollow nanospheres, achieving a hydrogen production rate of 9 μmol·h⁻¹·g⁻¹, a significant improvement from almost inactive bulk g-C₃N₄. Xia et al. [12] fabricated g-C₃N₄ nanosheets through thermal peeling treatment increasing the specific surface area from 5 m²·g⁻¹ to 116 m²·g⁻¹ (~22-fold) and prolonging the carrier lifetime from 3.4 ns to 6.7 ns, which enhanced the CO₂ reduction rates to CH₄ and CH₃OH by 10-fold and 5-fold, respectively. Jiang et al. [13] fabricated hollow

*To whom all correspondence should be addressed.

tubular g-C₃N₄, increasing the surface area from 52.51 m²·g⁻¹ to 74.94 m²·g⁻¹ and increasing the RhB degradation rate by a factor of two. Wu et al. [14] developed porous tubular g-C₃N₄, with surface area and pore volume enhanced by 5.3-fold and 80-fold, respectively, resulting in a 2.44-fold increase in tetracycline degradation rate. Tong et al. [15] synthesized tubular g-C₃N₄, achieving hydrogen evolution and methyl orange degradation rate constants 2.7- and double that of the pristine g-C₃N₄.

In terms of metallic active center construction, Cao et al. [16] prepared Pt/g-C₃N₄ via electrostatic assembly, increasing the hydrogen evolution rate to 29.4 μmol·h⁻¹·g⁻¹, significantly outstripping that of pristine g-C₃N₄. Jeyalakshmi et al. [17] fabricated Pd single-atom-doped g-C₃N₄, achieving a hydrogen evolution rate of 0.24 mmol·h⁻¹·mg⁻¹ at only 0.05 wt% Pd loading, 55 times higher than conventional Pd nanoparticle/g-C₃N₄. Wang et al. [18] constructed Cu/g-C₃N₄ systems, enhancing CO production by 3.2-fold, CH₃OH by 2.3-fold, and CH₄ by 5.1-fold compared to pristine g-C₃N₄.

Regarding composites with highly conductive carbon materials, Shi et al. [19] fabricated 3% CNTs/g-C₃N₄, achieving a methyl orange degradation rate of 92.7%, compared to 62% for pristine g-C₃N₄ (~1.5-fold improvement). Liu et al. [20] prepared g-C₃N₄/CNT composites, enhancing RhB degradation by 16.2% and slightly reducing the band gap from 2.70 eV to 2.64 eV. Wang et al. [21] employed in-situ thermal polymerization to construct CNT/g-C₃N₄, achieving a RhB degradation rate constant 3.1 times higher than pristine g-C₃N₄. Xiang et al. [22] fabricated 1 wt% graphene/g-C₃N₄, achieving a hydrogen evolution rate of 451 μmol·h⁻¹·g⁻¹, approximately three times that of pristine g-C₃N₄.

These studies indicate that Pt nanoparticles exhibit excellent electron-trapping capability, while CNTs provide high conductivity and rapid charge transport, both significantly enhancing g-C₃N₄ photocatalytic activity in their respective modification systems. However, most reports focus on single modification strategies, and systematic investigations of the synergistic modification of g-C₃N₄ by Pt and CNTs are still lacking, particularly regarding the extent of photocatalytic performance enhancement, synergistic effects, and potential advantages. Therefore, exploring Pt/CNTs co-modified g-C₃N₄ systems is crucial for improving photogenerated charge transfer efficiency and achieving highly efficient photocatalytic degradation.

In this study, tubular g-C₃N₄ was prepared using urea and melamine as precursors, followed by electrostatic assembly of Pt nanoparticles and CNTs to construct co-modified photocatalysts. By leveraging the high conductivity of CNTs and the electron-trapping ability of Pt, this strategy is designed to boost the separation and transfer of photogenerated charges in g-C₃N₄. Using RhB aqueous solution as a model contaminant, the photocatalytic degradation performances of pristine, single-modified, and Pt/CNTs co-modified catalysts under visible light were systematically compared, with emphasis on the effects of CNT and Pt loadings. The Pt/CNTs co-modified catalyst exhibited a kinetic constant of 0.148 min⁻¹ for RhB degradation 10.8 fold that of pristine tubular g-C₃N₄ and achieved 96% pollutant removal under simulated sunlight within 20 min, maintaining 83% activity after three cycles. These results demonstrate a significant synergistic enhancement, laying a solid theoretical underpinning for the structural design and practical application of high-performance visible-light-responsive photocatalytic materials.

Experimental

Reagents

Urea (analytical grade) was sourced from Kemiou Chemical Reagent Co., Ltd., located in Tianjin; melamine (analytical purity grade) from Aladdin Biochemical Technology Co., Ltd., Shanghai; anhydrous ethanol (analytical grade) from Kemao Chemical Reagent Co., Ltd., Tianjin New Technology Industrial Park; Rhodamine B (RhB, analytical grade) from Aladdin-Jingchun Industrial Co., Shanghai; multi-walled carbon nanotubes (CNTs, analytical grade) from Jiangsu Xianfeng Nanomaterials Technology Co., Ltd.; and chloroplatinic acid hexahydrate (analytical purity grade) was supplied by Aladdin Biochemical Technology Co., Ltd., Shanghai.

Catalyst Preparation

Tubular and Bulk g-C₃N₄

Tubular g-C₃N₄ (TCN) was fabricated through a one-step thermal polycondensation process, with urea and melamine serving as starting materials. 10 g of urea and 1 g of melamine were first ground thoroughly, then transferred into a crucible, and heated in a nitrogen atmosphere at a ramp rate of 5 °C·min⁻¹ up to 550 °C, where they were held for 5 h before being allowed to cool naturally. Bulk g-C₃N₄ (BCN) was synthesized under the same set of conditions, except that only melamine was used as the precursor.

Pt-Modified Tubular g-C₃N₄

Pt nanoparticles were deposited on TCN via a facile electrostatic assembly and in-situ reduction method. ISOBAM-104 (15 mg) was dispersed in 30 mL of deionized water and then agitated for 30 min to ensure complete dissolution. Chloroplatinic acid hexahydrate solution (0.137 mL, 20 mg·mL⁻¹) was added and stirred for 30 min, followed by 3.88 mg NaBH₄ to reduce Pt ions. Using 0.1 M HCl, the pH was maintained at 2-3, and 1 g·L⁻¹ NaCl was added to induce flocculation. After repeated centrifugation and washing, the Pt nanoparticles were redispersed with 0.1 g TCN, sonicated for 30 min, and reacted under the same pH conditions. After centrifugation and drying, 1wt% Pt-loaded TCN (TCN/1%Pt) was obtained. By varying the Pt precursor dosage, catalysts with 1.5wt%, 2wt%, and 2.5wt% Pt loadings were prepared (TCN/1.5%Pt, TCN/2% Pt, TCN/2.5% Pt).

CNT-Modified Tubular g-C₃N₄

CNTs were first acid-treated by dispersing 0.2 g in 30 mL concentrated H₂SO₄ and 10 mL concentrated HNO₃ at 70 °C for 6 h, followed by quenching, filtration, centrifugation, and drying. For composite formation, TCN (0.1 g) and acid-treated CNTs (5 mg) were ultrasonically dispersed in 30 mL deionized water for 30 min. The pH was set to 3-4 using 0.1 M HCl, followed by stirring the mixture for 24 h. After centrifugation and drying, TCN-wt0.5%CNTs was obtained. Using the same procedure with different CNT dosages, composites with 1wt%, 1.5wt%, 2wt%, and 2.5wt% CNTs were prepared (TCN/x%CNTs, x = 0.5-2.5).

Pt/CNTs Co-Modified Tubular g-C₃N₄

TCN/2%Pt (from Section 1.2.2) was dispersed in 30 mL deionized water (0.1 g), and adjustment of the pH to ~3 was achieved using 0.1 M HCl. Acid-treated CNTs (1.5 mg) were added, followed by 30 min ultrasonication and 24 h stirring. After centrifugation and drying, the Pt/CNTs co-modified tubular g-C₃N₄ was obtained, denoted as TCN-2%Pt/1.5%CNTs.

Material Characterization

X-ray diffraction (XRD, Smart Lab, Rigaku, Japan) identified crystalline phases over 2θ = 10-80°. Microstructure was characterized via EDS-equipped FE-SEM (Merlin Comp, Carl Zeiss). Morphology and particle size were analyzed by TEM (JEM-F200, JEOL) at 200 kV. XPS (Thermo Scientific K-Alpha, USA, Al Kα) assessed elemental composition and chemical states. UV-Vis diffuse reflectance spectra

(200–800 nm) were measured (TU-1901) with BaSO₄ as reference. Room-temperature PL spectra (UH4150, λ_{ex}=380 nm) evaluated photogenerated carrier behavior. Photocatalytic tests were run in a thermostatic beaker under a 300 W Xe lamp (CEL-HXF300-S) with a cutoff filter (λ ≥ 420 nm). The model of the instrument used for BET analysis is a Micromeritics ASAP 2460 (United States Micromeritics). Electron paramagnetic resonance (EPR) measurements were performed using an EPR200-Plus spectrometer.

Photocatalytic Performance Tests

The target pollutant selected for this work was determined to be RhB. Typically, a 10 mg portion of catalyst was added to 100 mL of RhB solution (with a concentration of 10 mg·L⁻¹) in a 300 mL double-layer beaker, and a magnetic bar was used for stirring to achieve uniform dispersion. The blend was stirred in dark environments for a duration of 30 minutes, geared toward attaining the steady adsorption-desorption equilibrium state. For visible-light exposure, a 300 W (Xe) lamp equipped with a UV cutoff filter was utilized. Throughout irradiation, 5 mL of aliquots was withdrawn every 10 minutes; after filtration with a PES syringe filter, the absorbance was measured at a wavelength of 554 nm using a UV-Vis spectrophotometer. Standard curves were constructed using RhB solutions of 1-10 μg·mL⁻¹. The initial concentration (C₀) was 10 μg·mL⁻¹, and concentrations at different times (C_t) were recorded to calculate degradation efficiency (C₀/C_t). For kinetic analysis, the post-dark equilibrium concentration was taken as the initial value to fit the reaction curve passing through the origin. After photocatalytic tests, catalysts were recovered by centrifugation, washed with water and ethanol, dried under vacuum at 60 °C, and reused for three consecutive cycles under identical conditions to evaluate stability.

Results and Discussion

Structural Characterization and Photocatalytic Performance of Tubular and Bulk g-C₃N₄ Photocatalysts

BCN and TCN were synthesized following the protocol outlined in Section 1.2.1. XRD analysis (Fig. 1a) indicates that both samples exhibit distinct diffraction peaks at 2θ = 13.1° (100 plane) and 27.3° (002 plane). The former peak is associated with the in-plane periodic arrangement of tri-s-triazine units, while the latter corresponds to the layered stacked conjugated aromatic framework. These findings align with results reported in earlier studies [23]

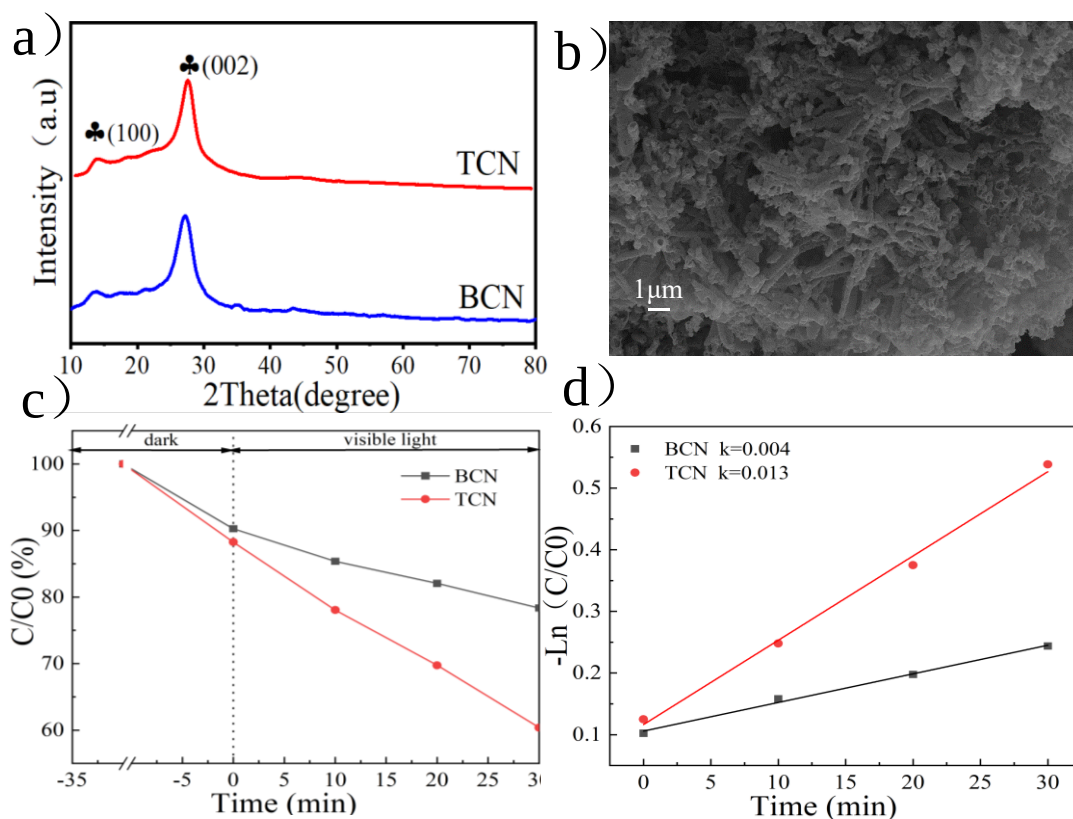


Fig. 1: Characterization and photocatalytic performance of BCN and TCN: (a) XRD patterns; (b) SEM images of TCN; (c) Visible-light-driven photocatalytic degradation of RhB; and (d) corresponding first-order kinetic fitting curves.

SEM images reveal that BCN displays a typical bulk layered structure with graphite-like stacking (Fig. S1), whereas TCN exhibits a loose, porous tubular morphology (Fig. 1b). The formation mechanism of TCN can be attributed to the decomposition of urea and melamine during calcination, which releases large amounts of NH_3 and CO_2 gases, creating porous nanosheets. With further heating under N_2 flow, these porous nanosheets curl to form hollow tubular structures.

The N_2 adsorption-desorption isotherms and pore size distribution curves of BCN and TCN are shown in Fig. S2. As presented in Fig. S2a, both samples exhibit typical type-IV adsorption isotherms with obvious hysteresis loops at high relative pressure, indicating the existence of mesoporous structures. Compared with BCN, TCN shows a significantly enhanced N_2 adsorption capacity and a much larger specific surface area. The BET surface area increases from $13.85 \text{ m}^2 \text{ g}^{-1}$ for BCN to $97.5 \text{ m}^2 \text{ g}^{-1}$ for TCN, suggesting that the tubular structure effectively

promotes the exposure of active surface sites.

The pore size distribution curves in Fig. S2b further confirm the mesoporous characteristics of the samples, with average pore diameters of 31.94 and 32.18 nm for BCN and TCN, respectively. Moreover, TCN exhibits a broader pore distribution and higher pore volume than BCN, which can facilitate mass transfer and provide more accessible active sites during the photocatalytic process.

Using RhB, ($\lambda_{\text{max}} = 554 \text{ nm}$) as a model organic dye, the photocatalytic activity of the samples was assessed. As shown in Fig. 1c, TCN exhibits higher adsorption capacity (11.74%) than BCN (9.73%). After 30 minutes of visible-light irradiation, TCN achieved a degradation efficiency of 78.36%-notably higher than BCN (60.37%). Kinetic analysis (Fig. 1d) indicates that the apparent first-order rate constant (k) of TCN is 0.0136 min^{-1} , approximately 2.94 times greater than the value of BCN (0.0046 min^{-1}).

In summary, although BCN and TCN share similar crystalline structures, their morphologies differ significantly. The porous tubular structure of TCN not only enhances adsorption capacity but also provides more accessible reactive sites, resulting in markedly improved photocatalytic degradation efficiency. These results show that controlling the morphology of g-C₃N₄ is a valid strategy to boost its photocatalytic activity.

Structural Characterization and Photocatalytic Performance of CNTs Modified TCN Photocatalysts

TCN-CNT composites with different CNT loadings (0.5-2.5 wt%) were prepared as described in Section 1.2.2. XRD patterns (Fig. 2a) show that TCN and TCN-CNT samples exhibit a characteristic g-C₃N₄ (002) peak at 27.3°, corresponding to the long-range stacking of conjugated aromatic layers [24]. A typical CNT diffraction peak is observed at 26.1°, attributed to the graphitic sp² structure. With increasing CNT content, the peak intensity slightly increases, likely due to the overlap of CNT and g-C₃N₄ signals.

SEM images (Fig. 2b-f) reveal the morphology of TCN-CNT composites. Acid-treated CNTs retain their one-dimensional tubular structure (Fig. S3) [25]. At low CNT content (0.5 wt%, Fig. 2e), CNTs are well-dispersed along the tubular TCN framework. With increasing CNT loading to 1.5 wt% (Fig. 2c), a more interconnected three-dimensional CNT network forms, with TCN uniformly anchored on the network. However, at higher loadings (2.5 wt%, Fig. 2f), CNT aggregation becomes evident, leading to phase separation and reduced interfacial contact.

Photocatalytic degradation experiments of RhB under visible light (Fig. 2g) show that the adsorption capacity of TCN-CNT composites increases with CNT addition. The photocatalytic activity initially increases and then decreases with CNT content, reaching a maximum at 1.5 wt%. The degradation kinetics follow a pseudo-first-order model (Fig. 2h), with the rate constant *k* for TCN/1.5% CNT reaching 0.0578 min⁻¹, 4.2 times that of pristine TCN (0.0136 min⁻¹) and 5.35 times that of BCN.

These results indicate that CNTs serve as a

conductive heterostructure, preventing dense stacking of TCN and generating a more porous morphology that increases the specific available reactive sites and surface area. Optimal CNT content ensures intimate interfacial contact between TCN and CNTs, facilitating efficient transfer of photogenerated electrons. Excessive CNT loading leads to aggregation, reducing effective heterojunction interfaces and partially blocking active sites, which negatively affects photocatalytic performance [26].

Structural Characterization and Photocatalytic Performance of Pt-Modified TCN Photocatalysts

Pt-modified TCN (TCN/Pt) photocatalysts with different Pt loadings were prepared according to the method described in Section 1.2.3. XRD characterization (Fig. 3a) demonstrated that all composites retained the characteristic diffraction peaks of g-C₃N₄ at 2θ values of 13.1° and 27.3°, with these peaks corresponding to the repeated triazine units and long-range planar aromatic stacking, respectively [27]. Compared with pure TCN, the incorporation of Pt nanoparticles failed to bring about notable alterations in the crystal structure or conjugated framework of g-C₃N₄. When the Pt loading was low (1-1.5wt%), no obvious diffraction peaks of metallic Pt were observed in the XRD patterns due to the weak signal from the low Pt content; at higher loadings (2-2.5wt%), the Pt (111) peak at 39.8° became apparent, while the (002) peak of g-C₃N₄ remained unchanged and no new peaks appeared, indicating that Pt was mainly deposited on the surface without causing lattice distortion or forming new crystalline phases [28].

To further confirm the successful loading and elemental distribution of Pt nanoparticles, EDS analysis was performed on the TCN/2%Pt sample (Fig. 3b-f). The results showed that C and N were uniformly distributed throughout the sample, corresponding to the TCN matrix, while Pt appeared as discrete and well-dispersed dots without significant large aggregates, demonstrating the homogeneous surface distribution of Pt nanoparticles on TCN.

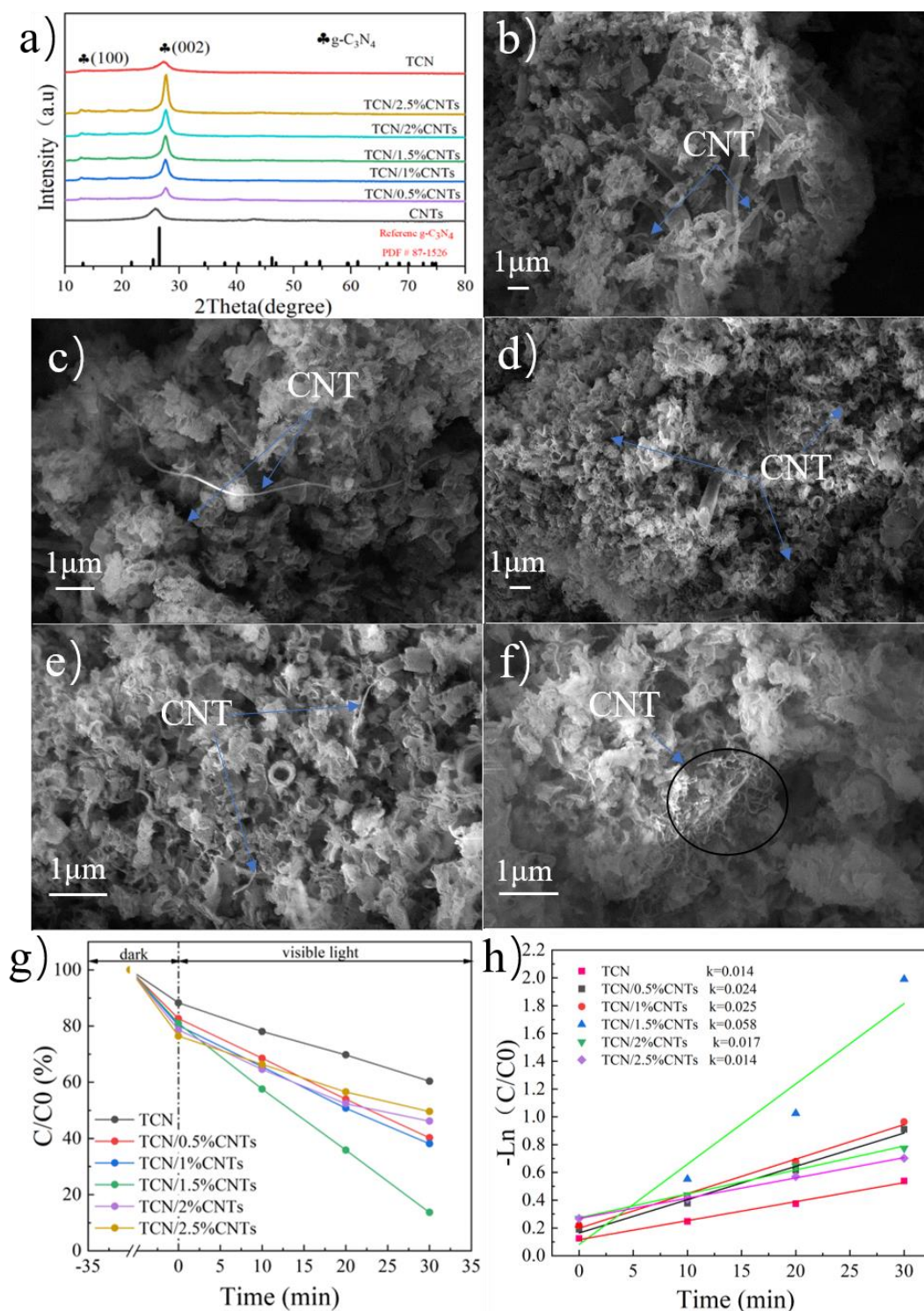


Fig. 2 (a): XRD patterns of TCN and TCN–CNT (0.5–2.5%) photocatalysts; (b–f) SEM images of TCN–CNT (0.5–2.5%); (g) visible-light photocatalytic performances of TCN and TCN–CNT (0.5–2.5%); and (h) first-order kinetic curves of RhB degradation over TCN–CNT (0.5–2.5%).

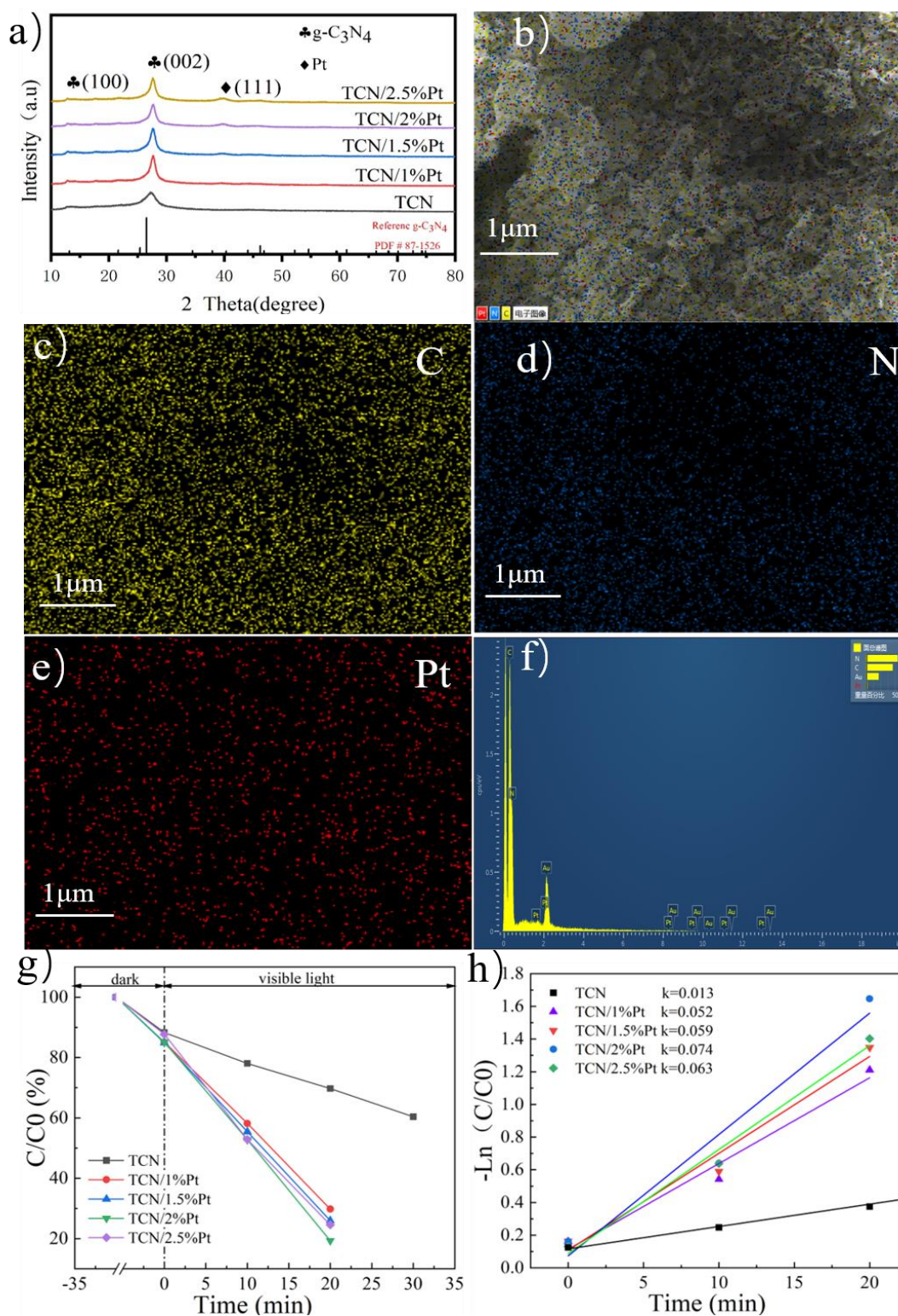


Fig. 3: (a) XRD patterns of TCN and TCN–Pt (1-2.5%) photocatalysts; (b-f) EDS spectrum and elemental mapping images of TCN-2%Pt; (g) visible-light photocatalytic performances of TCN and TCN-Pt (1-2.5%); and (h) first-order kinetic curves of RhB degradation over TCN-Pt (1-2.5%).

Photocatalytic tests (Fig. 3g) revealed that Pt loading significantly enhanced the RhB degradation activity of TCN. During the dark adsorption stage, the addition of Pt slightly improved the adsorption capacity. After 30 min of visible-light irradiation, the degradation efficiency of pure TCN was approximately 40%, whereas even with only 1% Pt loading, the RhB degradation reached ~70% within 20 min. Increasing the Pt content to 2% further enhanced the catalytic activity, with TCN/2%Pt achieving ~85% degradation within 20 min, showing the best performance. However, a further increase to 2.5wt% Pt resulted in slightly decreased activity, indicating an optimal loading amount of 2wt% for this system. Pseudo-first-order kinetic analysis (Fig. 3h) gave rate constants (k) of 0.013, 0.052, 0.059, 0.074, and 0.063 min^{-1} for TCN, TCN/1%Pt, TCN/1.5%Pt, TCN/2%Pt,

and TCN/2.5%Pt, respectively. The reaction rate of TCN-2wt% Pt was 5.4 times that of TCN and 16.1 times that of BCN.

In summary, the TCN was decorated with a uniform dispersion of Pt nanoparticles without altering its original crystal structure. The well-dispersed Pt serves as highly efficient electron trapping sites, promoting the transfer of photogenerated electrons from TCN to Pt and suppressing electron-hole recombination, thereby significantly enhancing photocatalytic degradation performance. However, an excessive amount of Pt may result in agglomeration, thereby decreasing the quantity of active sites and even potentially impeding light absorption—an effect that exerts an adverse impact on catalytic activity.

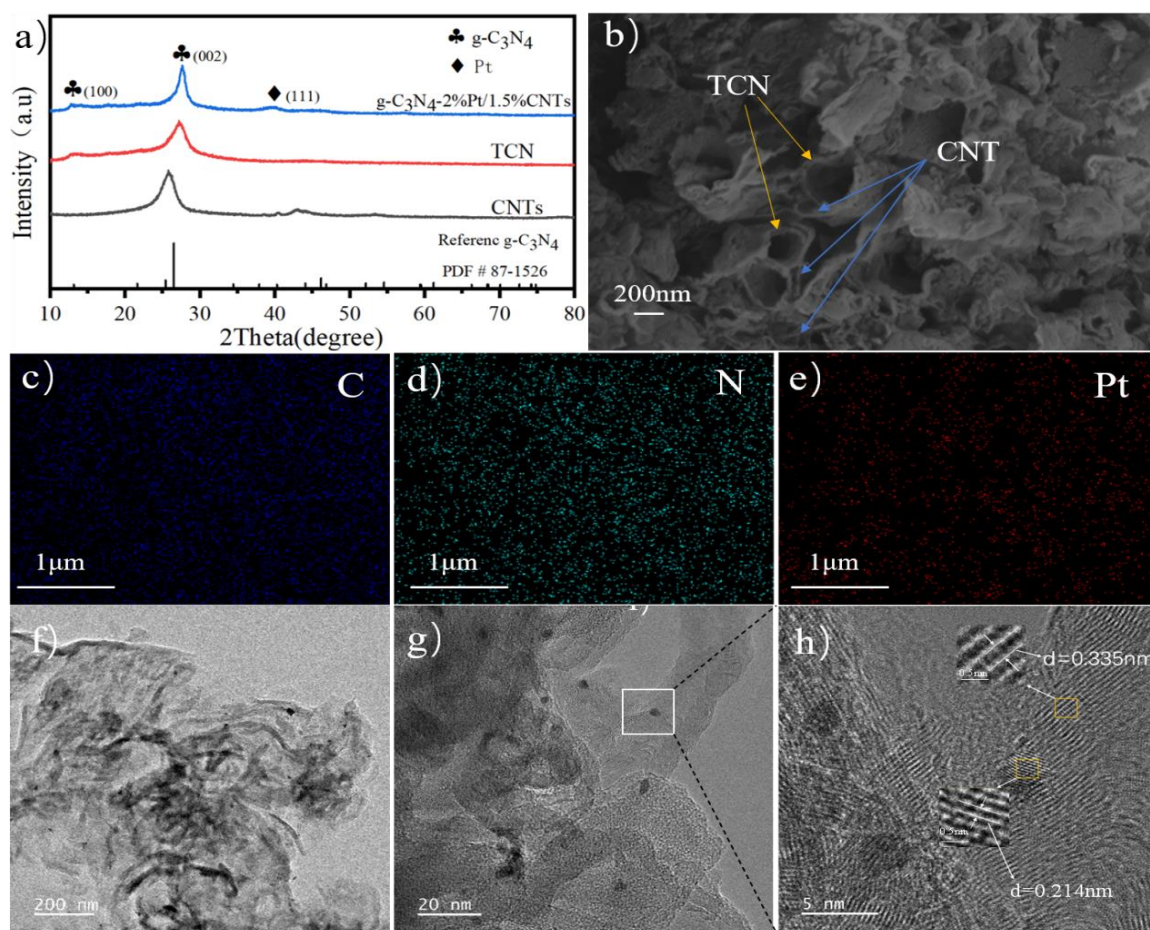


Fig. 4: (a) XRD patterns of CNT, TCN, and TCN-2%Pt/1.5%CNT photocatalysts; (b) SEM images of TCN-2%Pt/1.5%CNT; (c-e) corresponding EDS mapping images; (f-g) TEM and (h) HRTEM images of the TCN-2%Pt/1.5%CNT sample.

Structural Characterization and Photocatalytic Performance of CNTs/Pt Co-Modified TCN Photocatalysts

The ternary composite photocatalyst TCN-2%Pt/1.5%CNT was prepared according to the method described in Section 1.2.4. XRD analysis (Fig. 4a) showed an enhanced intensity of the (002) peak, along with a clear Pt (111) reflection, indicating the successful incorporation of Pt nanoparticles and CNTs into the TCN framework.

SEM images (Fig. 4b) revealed that the CNTs were well dispersed within the tubular structure of TCN, forming a tight interfacial contact with TCN, confirming effective composite formation. EDS mapping (Fig. 4c-e) demonstrated that Pt was uniformly distributed on the TCN surface without obvious aggregation, further confirming the successful loading of Pt and CNTs onto TCN.

TEM analysis (Fig. 4f-h) indicated that the CNTs were homogeneously dispersed within TCN without noticeable aggregation, owing to the acid-pretreated CNTs, which facilitated uniform integration with TCN. Pt nanoparticles exhibited a spherical morphology and were evenly distributed on the TCN surface. Through HRTEM observations, a lattice spacing value of 0.214 nm was identified for the Pt nanoparticles, and this spacing corresponds to the Pt (111) crystal plane. [29].

Fourier-transform infrared (FTIR) spectroscopy (Fig. S4) showed that the characteristic absorption peaks of the composite were essentially the same as those of TCN, this suggests that the introduction of CNTs and Pt failed to modify the chemical structure of TCN. Characteristic peaks at 1537, 1462, 1408, 1318, and 1238 cm^{-1} are assigned to the stretching vibrations of C–N and C=N heterocycles; the peak at 810 cm^{-1} is ascribed to the bending vibration of triazine rings, while a broad band in the range of 3000–3500 cm^{-1} corresponds to the stretching vibrations of residual N–H groups [30,31].

Photocatalytic tests (Fig. 5a-b) indicated that pure TCN exhibited relatively low RhB degradation efficiency, whereas the introduction of 1.5%CNT and 2%Pt significantly enhanced photocatalytic activity. Under visible light irradiation, the ternary composite

TCN-2%Pt/1.5%CNT achieves approximately 96% degradation efficiency of RhB within 20 minutes, while pure BCN-2%Pt/1.5%CNT only reaches a degradation rate of 84% over the same period. This indicates that the tubular structure exerts a remarkable influence on the photocatalytic performance of the material. Pseudo-first-order kinetic analysis revealed that the rate constants (k) for TCN, TCN-1.5%CNT, TCN-2%Pt, TCN-2%Pt/1.5%CNT and BCN-2%Pt/1.5%CNT were 0.013, 0.055, 0.071, 0.141 and 0.081 min^{-1} , respectively, with corresponding R^2 (coefficient of determination) values of 0.995, 0.949, 0.967, 0.916, and 0.957, respectively. Among them, the TCN-2%Pt/1.5%CNT composite exhibited the highest degradation rate, which is approximately 10.8 times higher than that of pristine TCN, indicating its superior photocatalytic performance. Reusability tests over five cycles (Fig. 5c) demonstrated that TCN-2%Pt/1.5%CNT maintained over 83% of its initial activity, and nearly complete RhB degradation was still achieved within 30 min in each cycle, confirming its stable and durable photocatalytic performance.

Mechanistic Insights into the Photocatalytic Enhancement of TCN by CNTs/Pt Co-Modification

To delve further into the mechanism behind the enhanced photocatalytic performance of CNT and Pt co-modified TCN, a series of optical, electronic, and reactive analyses were conducted.

As exhibited in the UV–Vis diffuse reflectance spectra (Fig. 6a), pristine TCN exhibits an absorption edge at approximately 440 nm, while the ternary composite TCN-2%Pt/1.5%CNT displays a distinct redshift to about 443 nm, along with markedly enhanced light-harvesting capability in the visible region (400–700 nm). This redshift and enhancement can be ascribed to the synergistic effects between the three-dimensional porous tubular structure and the heterointerfaces among CNTs, Pt nanoparticles, and TCN. The porous architecture affords a high specific surface area and high-efficiency mass-transfer pathways, while the introduction of CNTs and Pt promotes the directional migration and separation of photogenerated charge carriers through favorable band alignment. The band gaps estimated from Tauc plot are 2.83 eV for TCN and 2.75 eV for the ternary composite (Fig. 6b), indicating a slightly narrowed band gap that is beneficial for enhanced visible-light absorption.

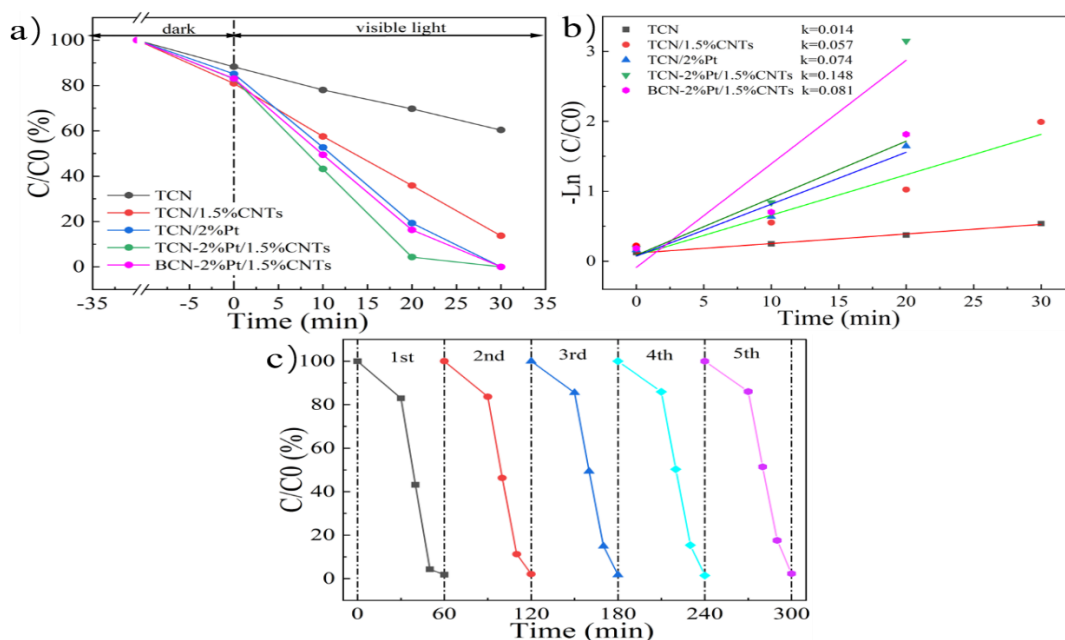


Fig. 5: (a) Visible-light photocatalytic performances of TCN, TCN-1.5%CNT, TCN-2%Pt, TCN-2%Pt/1.5%CNT and BCN-2%Pt/1.5%CNT; (b) first-order kinetic curves of RhB degradation; and (c) reusability of the TCN-2%Pt/1.5%CNT catalyst.

PL spectroscopy (Fig. 6c) further corroborates this conclusion. The pristine TCN displays a prominent emission peak centered at 450 nm, while the fluorescence intensity of TCN-2%Pt/1.5%CNT is significantly quenched and slightly blue-shifted after Pt and CNT incorporation, indicating that electron-hole recombination is effectively suppressed. This behavior suggests that Pt nanoparticles act as efficient electron-trapping centers, capturing photogenerated electrons directly, while CNTs function as conductive pathways to rapidly extract electrons from the TCN, thereby further reducing recombination probability and prolonging carrier lifetime.

XPS analysis (Fig. 7) indicates electronic interactions and charge redistribution among Pt, CNTs, and g-C₃N₄. In the C 1s spectrum (Fig. 7b), the sp²-C peak shows a slight shift (from 288.0 eV for TCN to ≈ 288.1 eV for TCN-2%Pt/1.5%CNT), suggesting minor electron redistribution and possible electronic coupling between CNTs and the N=C-N units of TCN[32,33,34,35]. The slight changes in the binding energies are observed for the N=C-N and N-(C)₃ components in the N 1s spectrum (Fig. 7c) further imply that a portion of the photogenerated electrons may be transferred to Pt d orbitals, while CNTs facilitate electron transport [16,36,37]. In addition, the

Pt 4f peaks (Fig. 7d) shift slightly toward lower binding energy, consistent with metal-support interactions that help to stabilize Pt nanoparticles as electron-sink sites and improve separation of photogenerated charge carriers[38].

The reactive species involved in the photocatalytic process were further investigated through radical-trapping experiments (Fig. 8). The addition of p-benzoquinone (BQ), a scavenger of superoxide radicals, markedly suppressed the degradation of RhB, demonstrating that $\cdot O_2^-$ is the dominant reactive species in this system. In contrast, the introduction of EDTA-2Na caused negligible changes in the degradation efficiency, indicating that photogenerated holes (h^+_{VB}) play a minor role. Interestingly, the photocatalytic activity exhibited a slight enhancement upon the addition of tert-butanol (t-BuOH). This behavior suggests that although a small amount of $\cdot OH$ may be formed, $\cdot OH$ does not serve as a primary oxidant. Instead, quenching $\cdot OH$ effectively suppresses competing side reactions, allowing a larger fraction of photogenerated electrons to participate in the reduction of O₂ to $\cdot O_2^-$, thereby improving the overall reaction efficiency.

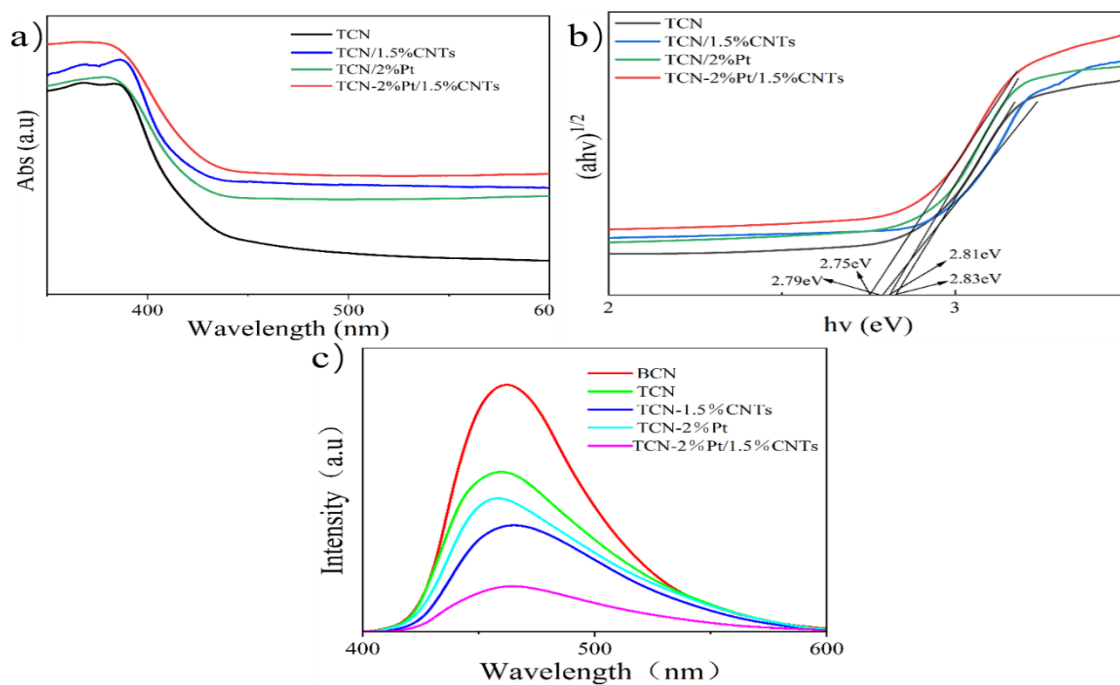


Fig. 6: (a) UV-Vis diffuse reflectance spectra and (b) energy bandgap spectra of TCN, TCN-1.5%CNT, TCN-2%Pt, and TCN-2%Pt/1.5%CNT photocatalysts; and (c) PL emission spectra of BCN, TCN, TCN-1.5%CNT, TCN-2%Pt, and TCN-2%Pt/1.5%CNT photocatalysts.

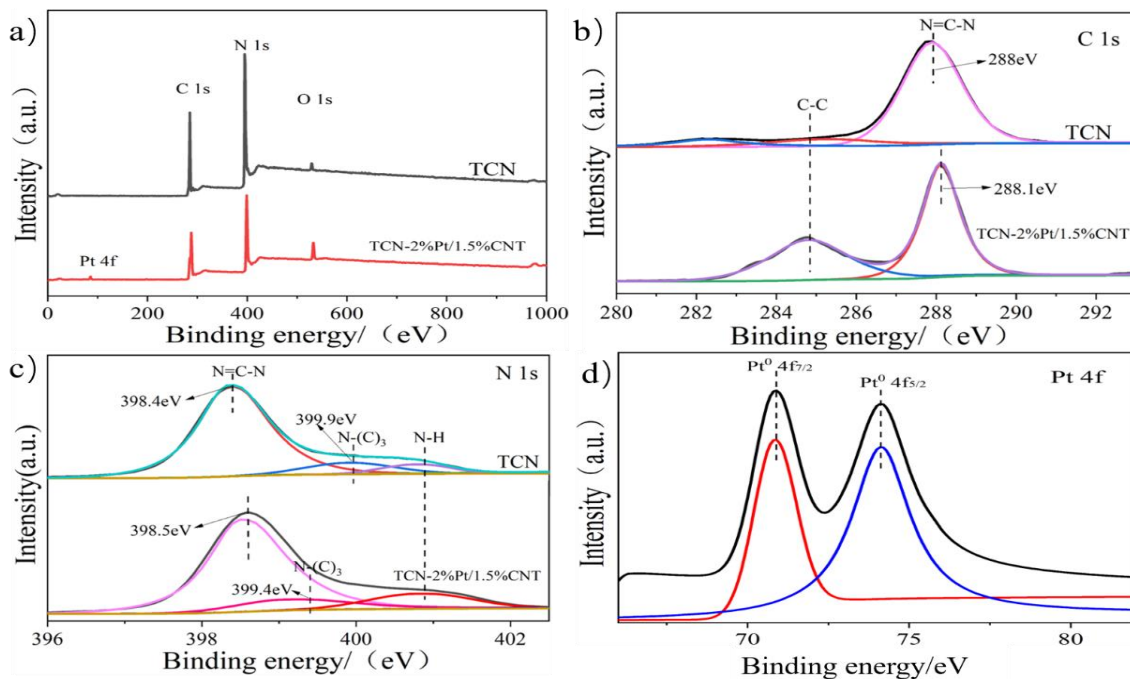


Fig. 7: XPS spectra of TCN and TCN-2%Pt/1.5%CNT samples: (a) survey spectrum; (b) C 1s; (c) N 1s; and (d) Pt 4f.

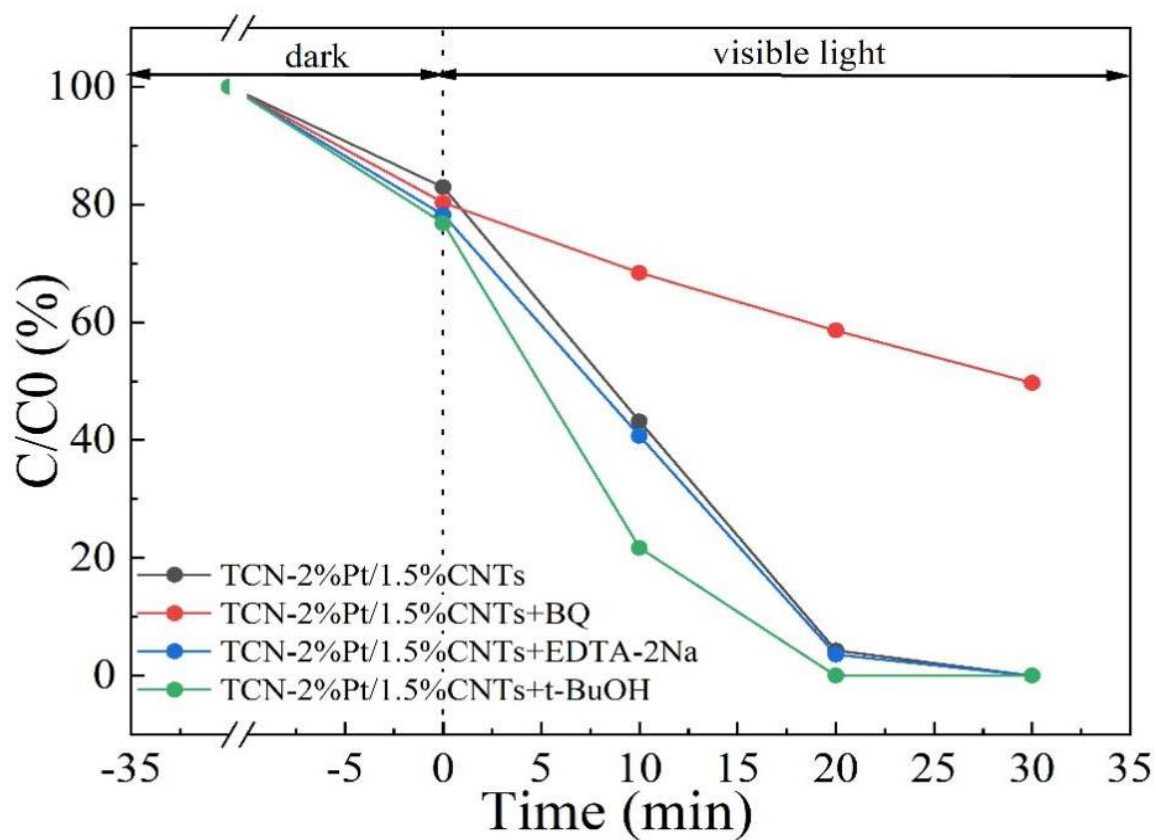


Fig. 8: Influence of various scavengers on the visible-light photocatalytic degradation of RhB over the TCN-2%Pt/1.5%CNT catalyst.

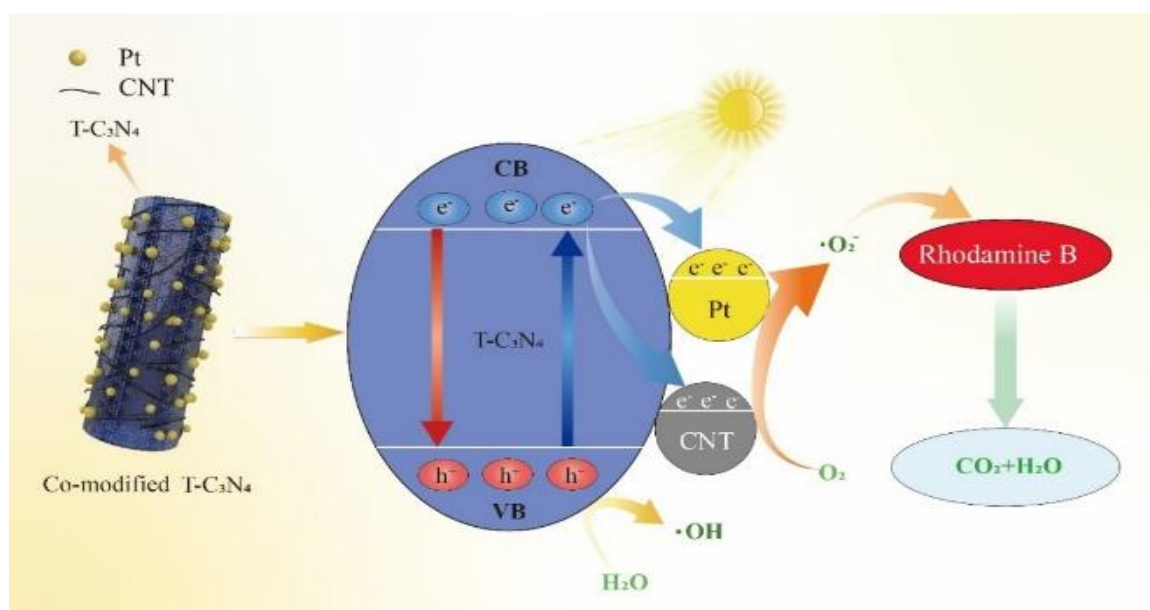


Fig. 9: Mechanism diagram of RhB degradation by TCN-2%Pt/1.5%CNT.

Electron paramagnetic resonance (EPR) measurements with DMPO as the spin-trapping agent were also performed to identify the reactive oxygen species generated during the photocatalytic process. As shown in Fig. S5, no obvious EPR signal was observed under dark conditions, whereas characteristic DMPO- $\cdot\text{O}_2^-$ signals appeared clearly under visible-light irradiation, indicating that superoxide radicals ($\cdot\text{O}_2^-$) were generated during the photocatalytic reaction. The results suggest that $\cdot\text{O}_2^-$ plays an important role in the photocatalytic degradation process.

These results indicate that the enhanced photocatalytic performance of the TCN-2%Pt/1.5%CNT ternary composite originates from the synergistic interaction among Pt nanoparticles, CNTs, and tubular g- C_3N_4 (Fig. 9). Pt nanoparticles act as efficient electron acceptors and active sites for oxygen reduction, while CNTs provide conductive pathways that facilitate charge migration and suppress electron-hole recombination. Through this cooperative effect, the separation and utilization of photogenerated charge carriers are significantly improved, leading to enhanced formation of reactive oxygen species, particularly $\cdot\text{O}_2^-$.

Conclusion

A Pt/CNTs co-modified TCN photocatalyst was successfully constructed through electrostatic self-assembly. CNTs built an internal conductive network, while Pt nanoparticles formed efficient heterointerfaces, together enhancing visible-light absorption and promoting charge separation.

For the optimal TCN-2%Pt/1.5%CNT sample, the RhB degradation rate constant reached 0.148 min^{-1} , which was 10.8-fold higher than that of pure TCN; demonstrating a clear synergistic effect. Radical scavenging results, combined with EPR measurements, indicated that $\cdot\text{O}_2^-$ was the dominant reactive species. The improved performance arose from a synergistic electron-transfer process, in which Pt acted as an electron-trapping center and CNTs served as conductive pathways, jointly accelerating electron extraction and suppressing recombination.

Overall, this work clarifies the cooperative roles of Pt and CNTs in enhancing photocatalytic activity and provides insights for the rational design of high-efficiency visible-light-driven photocatalysts.

Acknowledgments

The authors acknowledge that this study was funded by the National Natural Science Foundation of China (Grant No.52102017).

References

1. PR Gogate, M Sivakumar and AB Pandit, Destruction of Rhodamine B using novel sonochemical reactor with capacity of 7.5 l, Sep Purif Technol, **34**, 13, (2004)
2. B Neppolian, HC Choi and S Sakthivel, Solar/UV-induced photocatalytic degradation of three commercial textile dyes, J. Hazard Mater, **89**, 303, (2002)
3. S Wang, J Li and R Li, Controllable synthesis of peryleneimide-based nanocrystals as bifunctional photocatalyst for water splitting, J. Colloid Interface Sci, **699**, 13, (2025)
4. N Meghana, V Zimba and J Nayak, Enhanced ammonia gas sensing properties of hexagonal phase graphitic carbon nitride in moist atmosphere in the near room temperature ambience, Mater Lett, **403**, 3, (2026)
5. H Jing, M Luan and W Li, Porous g- C_3N_4 synthesized via trithiocyanuric acid-assisted two-step thermal treatment for efficient photocatalytic H_2 evolution, Mater Lett, **400**, 4, (2025)
6. J Wang and S Wang, A critical review on graphitic carbon nitride (g- C_3N_4)-based materials: Preparation, modification and environmental application, Coord Chem Rev, **453**, 214338, (2022)
7. S Hou, X Gao and X Lv, Decade Milestone Advancement of Defect-Engineered g- C_3N_4 for Solar Catalytic Applications, Nanomicro Lett., **16**, 70, (2024)
8. X Ji, B Xu and H Zhang, Dimensional Nanoarchitectonics of g- C_3N_4 /Co Nanocomposites for Photo- and Electro-Chemical Applications, ACS Appl. Nano Mater., **5**, 11731, (2022)
9. M Pourmadadi, E Rahmani and MM Eshaghi, Graphitic carbon nitride (g- C_3N_4) synthesis methods, surface functionalization, and drug delivery applications: A review, J. Drug Deliv Sci Technol, **79**, 104001, (2023)
10. B Yuan, J Wei and T Hu, Simple synthesis of g- C_3N_4 /rGO hybrid catalyst for the photocatalytic degradation of rhodamine B, Chin J. Catal, **36**, 1009, (2015)
11. J Sun, J Zhang and M Zhang, Bioinspired hollow semiconductor nanospheres as photosynthetic nanoparticles, Nat. Commun., **3**, 1139, (2012)

12. P Xia, B Zhu and J Yu, Ultra-thin nanosheet assemblies of graphitic carbon nitride for enhanced photocatalytic CO₂ reduction, *J. Mater. Chem. A Mater*, **5**, 3230, (2017)
13. Z Jiang, X Zhang and HS Chen, Formation of g-C₃N₄ Nanotubes towards Superior Photocatalysis Performance, *ChemCatChem*, **11**, 4558, (2019)
14. T Wu, Z Liu and B Shao, Enhanced piezo-photocatalytic degradation of organic pollutants by cambered wall lamellar structure of porous tubular g-C₃N₄, *Nano Energy*, **120**, 109137, (2024)
15. Z Tong, D Yang and Y Sun, Tubular g-C₃N₄ Isotype Heterojunction: Enhanced Visible-Light Photocatalytic Activity through Cooperative Manipulation of Oriented Electron and Hole Transfer, *Small*, **12**, 4093, (2016)
16. S Cao, J Jiang and B Zhu, Shape-dependent photocatalytic hydrogen evolution activity over a Pt nanoparticle coupled g-C₃N₄ photocatalyst, *Phys Chem Chem Phys*, **18**, 19457, (2016)
17. V Jeyalakshmi, S Wu and S Qin, Pd single atoms on g-C₃N₄ photocatalysts: minimum loading for maximum activity, *Chem. Sci.*, **16**, 4788, (2025)
18. J Wang, T Heil and B Zhu, A Single Cu-Center Containing Enzyme-Mimic Enabling Full Photosynthesis under CO₂ Reduction, *ACS Nano*, **14**, 8584, (2020)
19. Z Shi, L Rao and P Wang, The photocatalytic activity and purification performance of g-C₃N₄/carbon nanotubes composite photocatalyst in underwater environment, *Environ Sci Pollut Res Int*, **29**, 83981, (2022)
20. G Liu, M Liao and Z Zhang, Enhanced photodegradation performance of Rhodamine B with g-C₃N₄ modified by carbon nanotubes, *Sep Purif Technol*, **244**, 116618, (2020)
21. P Wang, Z Li and Z Yingmei, Synthesis of Carbon Nanotubes Modified g-C₃N₄ Photocatalysts for Enhanced Photocatalytic Degradation Activity, *Chin J Inorg Chem*, **35**, 217, (2019)
22. Q Xiang, J Yu and M Jaroniec, Preparation and Enhanced Visible-Light Photocatalytic H₂ - Production Activity of Graphene/C₃N₄ Composites, *The Journal of Physical Chemistry C*, **115**, 7355, (2011)
23. S Raha and M Ahmaruzzaman, Facile fabrication of g-C₃N₄ supported Fe₃O₄ nanoparticles/ZnO nanorods: A superlative visible light responsive architecture for express degradation of pantoprazole, *Chem Eng J.*, **387**, 18, (2020)
24. C Feng, Z Chen and J Jing, Significantly enhanced photocatalytic hydrogen production performance of g-C₃N₄/CNTs/CdZnS with carbon nanotubes as the electron mediators, *J. Mater Sci Technol*, **80**, 75, (2021)
25. K Wang, M Li and Y Liu, Effect of acidification conditions on the properties of carbon nanotube fibers, *Appl Surf Sci*, **292**, 469, (2014)
26. L Song, X Kang and S Zhang, CNT/g-C₃N₄ photocatalysts with enhanced hydrogen evolution ability for water splitting based on a noncovalent interaction, *Int J. Energy Res*, **42**, 1649, (2018)
27. Y Zhu, T Wang and T Xu, Size effect of Pt co-catalyst on photocatalytic efficiency of g-C₃N₄ for hydrogen evolution, *Appl Surf Sci*, **464**, 36, (2019)
28. S Li, H Yin and X Kan, Potential of transition metal atoms embedded in buckled monolayer g-C₃N₄ as single-atom catalysts, *Phys Chem Chem Phys*, **19**, 30069, (2017)
29. R Devivaraprasad, R Ramesh and N Naresh, Oxygen Reduction Reaction and Peroxide Generation on Shape-Controlled and Polycrystalline Platinum Nanoparticles in Acidic and Alkaline Electrolytes, *Langmuir*, **30**, 8995, (2014)
30. J Gao, Y Wang and S Zhou, A Facile One - Step Synthesis of Fe - Doped g-C₃N₄ Nanosheets and Their Improved Visible - Light Photocatalytic Performance, *ChemCatChem*, **9**, 1708, (2017)
31. N Sun, Y Liang and X Ma, Reduced Oxygenated g-C₃N₄ with Abundant Nitrogen Vacancies for Visible - Light Photocatalytic Applications, *Chemistry*, **23**, 15466, (2017)
32. J Lang, M Liu and Y Su, Fabrication of the hetero structured CsTaWO₆ / Au / g-C₃N₄ hybrid photocatalyst with enhanced performance of photocatalytic hydrogen production from water, *Appl Surf Sci*, **358**, 252, (2015)
33. J Yu, S Wang and B Cheng, Noble metal-free Ni (OH)₂ - g-C₃N₄ composite photocatalyst with enhanced visible-light photocatalytic H₂ - production activity, *Catal. Sci. Technol.*, **3**, 1782, (2013)
34. S Cao, Y Yuan and J Barber, Noble-metal-free g-C₃N₄ / Ni (dmgh)₂ composite for efficient photocatalytic hydrogen evolution under visible light irradiation, *Appl Surf Sci*, **319**, 344, (2014)
35. K Wang, Q Li and B Liu, Sulfur-doped g-C₃N₄ with enhanced photocatalytic CO₂ -reduction performance, *Appl Catal B*, **176**, 44, (2015)
36. J Wen, J Xie and Z Yang, Fabricating the Robust g-C₃N₄ Nanosheets / Carbons / NiS Multiple Heterojunctions for Enhanced Photocatalytic H₂ Generation : An Insight into the Trifunctional Roles of Nanocarbons, *ACS Sustain. Chem. Eng.*, **5**, 2224, (2017)

37. L Ge and C Han, Synthesis of MWNTs / g-C₃N₄ composite photocatalysts with efficient visible light photocatalytic hydrogen evolution activity, *Appl Catal B*, **117**, 268, (2012)
38. X Yang,X Liu and X Meng, Self-assembly of highly dispersed Pt and PtRu nanoparticles on perylene diimide derivatives functionalized carbon nanotubes as enhanced catalysts for methanol electro-oxidation, *J. Power Sources*, **240**, 536, (2013)