

Article

Durable Sulfur-Doped g-C₃N₄ Catalysts with High Performance for Rapid Rhodamine B Degradation in Organic Wastewater

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Abstract

To overcome the inherent limitations of graphitic carbon nitride (g-C₃N₄), specifically the rapid recombination of photogenerated electron–hole pairs and its confined light absorption range, a sulfur-doped g-C₃N₄ (S-g-C₃N₄) photocatalyst was developed in this work. The photocatalytic performance and its catalytic mechanism for rhodamine B (RhB) degradation were systematically investigated. Material characterization and performance tests revealed that S doping can narrow the band gap of g-C₃N₄ and effectively enhance the separation and transport efficiency of charge carriers. The as-prepared catalyst demonstrated excellent activity under simulated sunlight, achieving nearly complete degradation of 10 mg/L RhB within 15 min. Moreover, it exhibited robust stability across a pH range of 6 to 11 and in the presence of coexisting anions (Cl[−], NO₃[−], CO₃^{2−}), with negligible activity loss after five consecutive cycles. Radical trapping experiments verified that ·OH radicals served as the primary active species, with h⁺ playing a secondary role in the degradation process. This work provides practical guidance for designing durable g-C₃N₄-based photocatalysts with high performance for organic wastewater treatment.

Keywords: sulfur-doped g-C₃N₄; RhB; photocatalytic degradation

1. Introduction

Water pollution has emerged as a critical bottleneck constraining global sustainable development. Among various pollutants, industrial dye wastewater is classified as a priority-controlled water contaminant due to its high toxicity, poor biodegradability, environmental persistence, and potential carcinogenic, teratogenic, and mutagenic effects [1,2]. RhB, a typical xanthene-based cationic dye, is widely used in textile dyeing, papermaking, food coloring, and biological labeling. Even at residual concentrations as low as 0.1 mg/L in water bodies, RhB can bioaccumulate through the food chain, causing irreversible damage to the reproductive and nervous systems of aquatic organisms and posing a serious threat to human health [3,4]. Conventional treatment technologies such as physical adsorption, chemical coagulation, and traditional chemical oxidation, while capable of achieving preliminary separation or transformation of RhB, are plagued by inherent drawbacks including incomplete degradation, propensity for secondary pollution, high operational costs, and poor cycling stability. These limitations hinder their ability to meet the requirements for deep purification in complex aqueous environments [5,6].

Photocatalytic technology, which generates highly reactive radicals such as ·OH and ·O₂[−] by semiconductor materials under light irradiation, can mineralize organic pollutants into CO₂, H₂O, and small inorganic molecules. Because of its mild reaction conditions, high



Academic Editor: Enric Brillas

Received: 21 February 2026

Revised: 29 March 2026

Accepted: 30 March 2026

Published: 1 April 2026

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mineralization efficiency, environmental friendliness, as well as low energy consumption, it is regarded as one of the most promising technologies for addressing dye wastewater pollution treatment [7,8]. Among various semiconductor photocatalysts, g-C₃N₄ has attracted significant research interest in the field of environmental catalysis due to its suitable band structure, excellent chemical and thermal stability, non-metallic composition, low-cost and readily available precursors, and good environmental compatibility [9,10]. However, g-C₃N₄ still faces two key scientific challenges, which are the restricted utilization efficiency of visible light and a high recombination rate of photogenerated charges. These drawbacks lead to relatively low photocatalytic efficiency, which significantly hinders its practical engineering application in actual wastewater treatment [11,12].

To overcome these problems, researchers have developed various modification strategies to optimize the photocatalytic performance of g-C₃N₄. Constructing heterojunction structures, such as g-C₃N₄/TiO₂ [13] and g-C₃N₄/ZnIn₂S₄ [14], to promote charge carrier separation via interfacial charge transfer. Elemental doping, such as non-metal doping with S [15], P [16], or B [17], or metal ion doping with Fe [18] or Co [19], are good ways to modulate the band structure and broaden the light response range. Noble metal modification, such as with Au [20] or Ag [21], to suppress charge carrier recombination via the Schottky barrier. Among these strategies, sulfur doping has been widely investigated [22]. However, most conventional approaches rely on precursors such as thiourea or sulfur powder, which are physically mixed with the g-C₃N₄ precursor. This physical mixing often leads to non-uniform sulfur distribution due to differences in decomposition temperatures between the sulfur source and melamine, as well as volatilization losses during thermal decomposition. This kind of sulfur doping leads to substitutional doping by using S to replace lattice N, with sulfur primarily in the S^{2−} state. In this work, we adopted a different synthetic strategy. Using melamine and trithiocyanuric acid as raw materials, a supramolecular pre-assembly was formed through hydrogen bonding between the -NH₂ and -SH groups prior to thermal polymerization. This molecular-level homogeneous mixing enables sulfur to be uniformly incorporated into the tri-s-triazine framework of g-C₃N₄ in the form of C–S or N–S bonds. Additionally, during thermal decomposition, trithiocyanuric acid continuously releases sulfur-containing gases such as H₂S and CS₂, which act as in situ gas templates. The escape of these gases facilitates the formation of porous or ultrathin nanosheet structures, resulting in a carbon nitride material with increased specific surface area. This structural feature provides more adsorption sites and reaction interfaces for RhB degradation, enriches RhB molecules on the catalyst surface, and promotes multiple light scattering, thereby enhancing light absorption efficiency.

In this study, we synthesized a series of g-C₃N₄-based composite catalytic materials using a simple one-step thermal polymerization method. The crystal structure, surface chemical states, micromorphology, and optical properties of the catalysts were systematically characterized. The photocatalytic performance was evaluated via RhB degradation experiments, examining the effects of reaction conditions such as catalyst dosage, initial RhB concentration, coexisting anions, and solution pH. Furthermore, the photocatalytic reaction mechanism and kinetic behavior were elucidated. This study aims to provide a feasible approach for the structural design of g-C₃N₄-based catalysts and to develop an efficient and stable photocatalytic technology suitable for the treatment of dye wastewater.

2. Results and Discussion

2.1. Structural and Morphological Characterization

X-ray diffraction (XRD) is a crucial technique for characterizing the crystal structure, phase composition, and crystallinity of catalysts. Figure 1 presents the XRD patterns of C-g-C₃N₄, H-g-C₃N₄, S-g-C₃N₄, CC-g-C₃N₄, and ZT-g-C₃N₄.

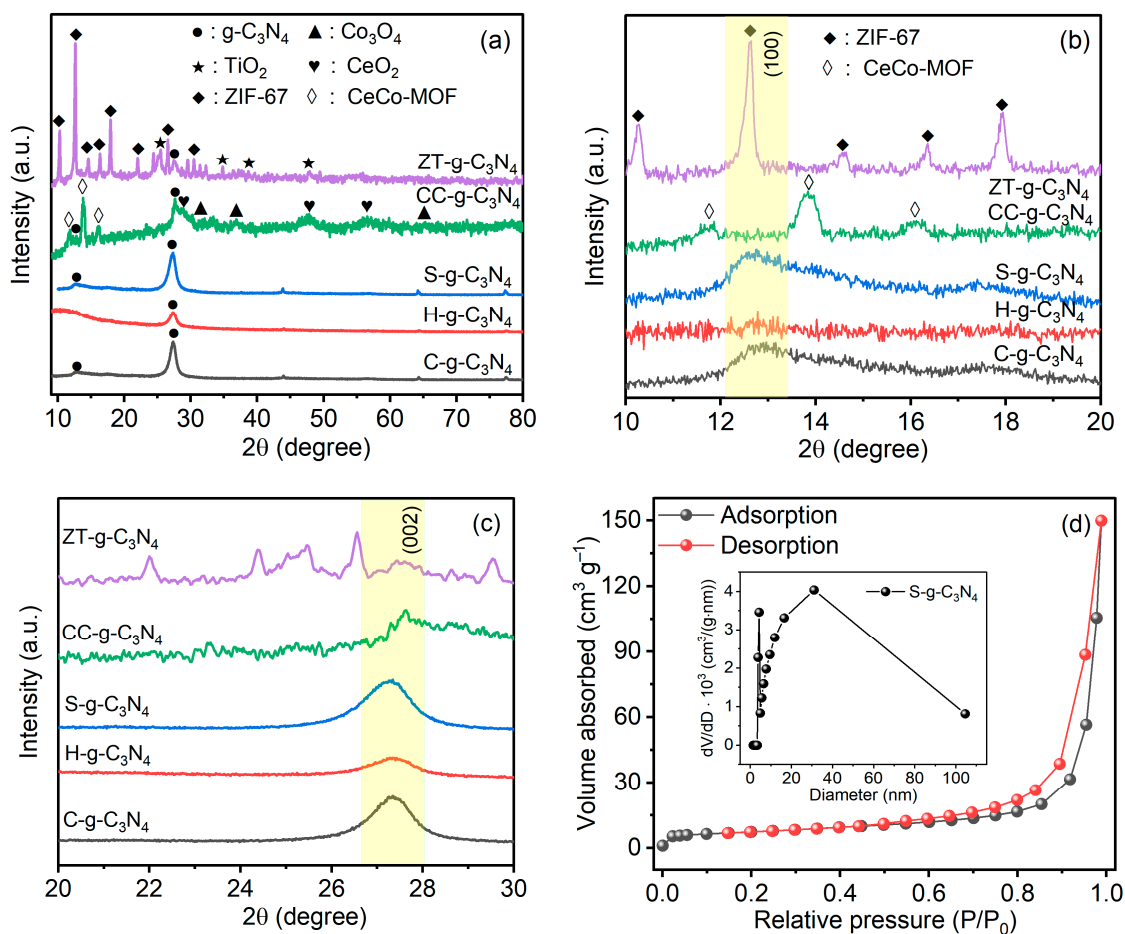


Figure 1. (a) XRD pattern and (b) magnified view of the 2θ region from 10 to 20° and (c) 20 to 30° of C-g-C₃N₄, H-g-C₃N₄, S-g-, -g-C₃N₄, and ZT-g-C₃N₄; (d) N₂ absorption–desorption isotherm and pore size distribution curve.

The XRD patterns for C-g-C₃N₄, H-g-C₃N₄ and S-g-C₃N₄ all display the characteristic diffraction peaks of graphitic carbon nitride at $2\theta = 12.8^\circ$, 27.2° , and 43.8° . The peaks at $2\theta = 12.8^\circ$ and 27.2° correspond to the (100) and (002) crystal planes of g-C₃N₄ [15] (JCPDS No. 87-1526). The diffraction peak of the (100) plane originates from the in-plane periodic arrangement of triazine ring units within the g-C₃N₄ structure, while the (002) peak is attributed to the long-range order formed by interlayer π - π stacking. This indicates the successful synthesis of g-C₃N₄ as the fundamental framework of the composite materials, maintaining its typical graphite-like layered crystal structure. The XRD peaks of the pure-phase C-g-C₃N₄ and S-g-C₃N₄ obtained by calcination are sharper, suggesting that the high-temperature treatment promotes the oriented growth of g-C₃N₄ crystals and enhances crystallinity. This is because the high-temperature environment facilitates the thorough polymerization of the melamine precursor and improves the ordering of the interlayer arrangement [23]. Compared to C-g-C₃N₄ and S-g-C₃N₄, the H-g-C₃N₄ sample exhibits broader and less intense diffraction peaks. This loss of crystallinity is attributed to the hydrothermal treatment, which can introduce structural defects and partially disrupt the long-range order of the heptazine units, leading to a more disordered framework.

For the CC-g-C₃N₄ composite, as shown in the magnified view (inset of Figure 1b,c), the g-C₃N₄ (100) peak is not clearly distinguishable, likely due to structural disruption and dilution by the MOF-derived phases. Only the (002) peak exhibits a slight shift from $\sim 27.2^\circ$ to 27.6° remains observable. These subtle changes suggest possible interfacial interactions between g-C₃N₄ and the incorporated metal oxide nanoparticles, which may exert a mild

compressive effect on the g-C₃N₄ framework. Several additional diffraction peaks are observed, indicating a multiphase composition. Peaks at 11.8°, 13.7°, and 16.0° correspond to residual CeCo-MOF, confirming partial retention of the MOF structure after calcination. Diffraction peaks at 31.3°, 36.9°, and 65.2° are indexed to the (220), (311), and (440) planes of cubic Co₃O₄ (JCPDS No. 42-1467), while peaks at 28.5°, 47.5°, and 56.3° correspond to the (111), (220), and (311) planes of cubic CeO₂ (JCPDS No. 04-0593). The coexistence of these phases confirms the successful construction of a multiphase heterojunction comprising g-C₃N₄, residual MOF, Co₃O₄, and CeO₂. The highly dispersed nature of these oxide nanoparticles on the g-C₃N₄ surface is advantageous for exposing more active sites while promoting interfacial transfer of photogenerated charge carriers.

For the prepared ZT-g-C₃N₄ composite composed of ZIF-67, TiO₂, and g-C₃N₄, similar to the CC-g-C₃N₄ composite, the (002) diffraction peaks of g-C₃N₄ become broad. Meanwhile, the pattern exhibits sharp characteristic diffraction peaks at $2\theta = 10.2^\circ$, 12.6° , and 17.9° , which match well with the (002), (112), and (200) crystal planes of standard ZIF-67 (CCDC Deposition Number 67-1073). These peaks are hallmark features of the rhombic dodecahedral topology of ZIF-67, confirming its successful integration with g-C₃N₄ and TiO₂ [24,25]. Additionally, a series of diffraction peaks appearing at $2\theta = 29.5^\circ$, 30.5° , 31.4° , 32.3° , and 34.8° are all attributable to ZIF-67, further confirming its high crystallinity. These peaks are sharp and show no significant shift, indicating that the crystal structure of ZIF-67 remained intact during the composite formation, preserving good crystalline integrity. The high crystallinity of ZIF-67 is closely related to its unique porous structure and surface active sites, which can provide ample channels for reactant adsorption and interfaces for charge transfer in photocatalytic reactions [26]. Concurrently, the absence of impurity-related diffraction peaks in the pattern suggests that no unwanted chemical reactions occurred during the composite synthesis. The components are likely combined through physical interactions or weak chemical bonding, which helps preserve their respective structural advantages.

Figure 2 illustrates the morphological characteristics of the synthesized materials. As shown in Figure 2b, the C-g-C₃N₄ sample exhibits a flaky structure with dimensions around 1 μm . Its surface is covered with agglomerates of nanoparticles (approximately 50–100 nm in size), which adhere to each other, forming rough surface regions. The H-g-C₃N₄ sample Figure 2c displays vesicle-like or petal-like aggregates formed by the curling and aggregation of thin lamellar units. The individual lamellae are remarkably thin (<50 nm) and show significant curling and folding, with some regions forming “hollow vesicle” structures measuring about 100–300 nm in size, which is a typical product of the hydrothermal environment.

The S-g-C₃N₄ sample presents a morphology of stacked, curled nanosheets with porous and wrinkled features. Statistical analysis of SEM images (Figure S4a) reveals that the sample yielding a particle size distribution of 10 ± 3 nm (Figure S4d), and the individual sheets have an average thickness of 40 ± 3 nm (Figure S4e). They curl and stack together to form aggregates with interlayer pores ranging from 50 to 200 nm in size. N₂ adsorption–desorption isotherms show a pore size distribution centered at 31 nm (Figure 1c). This structure retains the typical layered characteristics of g-C₃N₄, but sulfur doping facilitates sheet curling and prevents excessive agglomeration. Furthermore, the presence of fine protrusions and depressions on the surface suggests that the introduction of sulfur atoms may have altered the growth interface of g-C₃N₄, increasing surface defects and active sites. Compared to the flat layered structure of pristine g-C₃N₄, sulfur doping induces sheet curling and pore formation, likely because the intercalation of sulfur atoms expands the interlayer distance and disrupts some interlayer forces, making the sheets more prone to curling and creating pores during stacking.

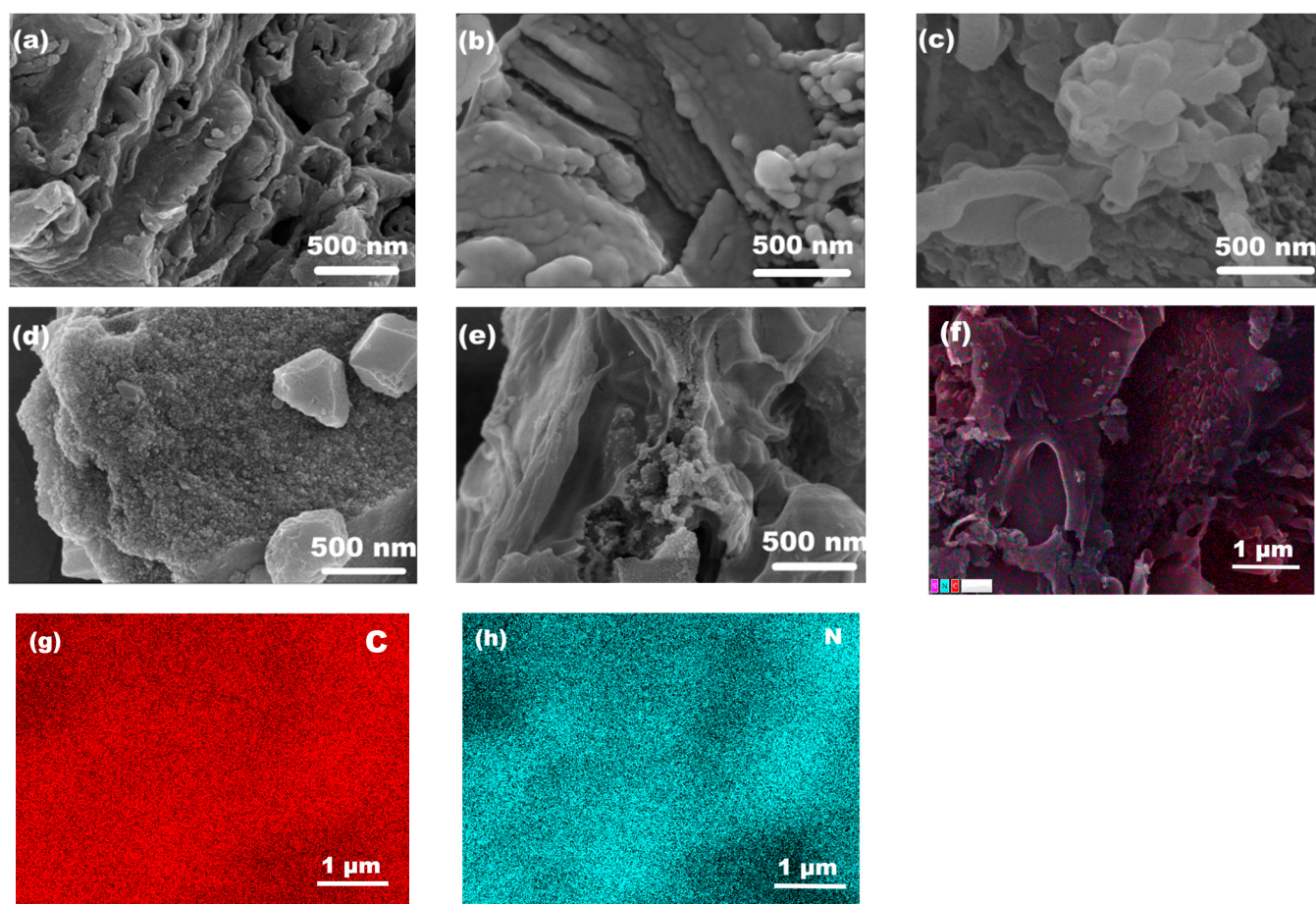


Figure 2. SEM images of (a) S-g-C₃N₄, (b) C-g-C₃N₄, (c) H-g-C₃N₄, (d) ZT-g-C₃N₄, (e) CC-g-C₃N₄, and EDS elemental mapping images of S-g-C₃N₄ (f–h).

The ZT-g-C₃N₄ sample (Figure 2d) exhibits a heterogeneous structure with two distinct components. The matrix consists of agglomerated rough nanoparticles with an average size of 15 ± 3 nm (based on 100 particle counts from Figure 2d), with an uneven, porous surface, corresponding to the composite phase of g-C₃N₄ and TiO₂. Well-defined cubic particles with edge lengths of 250 to 350 nm are attached to this matrix, representing the characteristic cubic morphology of ZIF-67. The intact cubic structure of ZIF-67 indicates that the composite synthesis conditions were mild, preserving the intrinsic morphology and properties of each component and combining the morphological and porous advantages of ZIF-67 with the photocatalytic activity of g-C₃N₄ and TiO₂.

The CC-g-C₃N₄ sample (Figure 2e) shows a biphasic composite structure. It retains the typical curled layered features of g-C₃N₄, while nanoparticle agglomerates (average size: 12 ± 4 nm, based on 30 particle counts from Figure 2f), corresponding to the CeCoO_x component, are uniformly attached to the surface and within the pores of the layered framework. The uniform dispersion of CeCoO_x as nanoparticles ensures more sufficient interfacial contact with the substrate, leading to more pronounced heterojunction effects.

The EDS elemental mapping of S-g-C₃N₄ (Figure 2f–h) reveals that the C signal is distributed continuously across the entire aggregate, aligning perfectly with its morphology. This indicates that carbon is the dominant element, uniformly distributed without significant deficiency, consistent with the matrix characteristics of S-g-C₃N₄. The N signal completely overlaps with the C distribution area and shows uniform intensity, confirming nitrogen as another primary element. Together with carbon, it forms the basic C–N network skeleton of S-g-C₃N₄, with no local deficiency or enrichment of N, suggesting a structurally

intact matrix. Due to the low sulfur doping concentration, EDS mapping was insufficient to resolve the spatial distribution of sulfur. Therefore, XPS analysis was used to confirm the incorporation of sulfur into the $g\text{-C}_3\text{N}_4$ framework. This distribution state facilitates the modulation of the electronic structure of $g\text{-C}_3\text{N}_4$ by sulfur, providing a structural foundation for enhancing properties such as photocatalytic performance.

To obtain clearer insights into the sample morphology, TEM analysis was performed. Figure 3 presents the TEM images of S- $g\text{-C}_3\text{N}_4$, C- $g\text{-C}_3\text{N}_4$, H- $g\text{-C}_3\text{N}_4$, ZT- $g\text{-C}_3\text{N}_4$, and CC- $g\text{-C}_3\text{N}_4$. As shown in panel (Figure 3b), the C- $g\text{-C}_3\text{N}_4$ sample appears as thick layered aggregates with a size of about $1\ \mu\text{m}$ (Figure 3b). Some pores with an average size of about $40 \times 15\ \text{nm}$ (Figure S4g). In contrast, the H- $g\text{-C}_3\text{N}_4$ sample (Figure 3c) displays ultrathin, discrete, “wrinkled vesicle-like” nanosheets with thicknesses of only $13 \pm 2\ \text{nm}$ (Figure S4i, based on 20 measurements from Figure 3c). These sheets are more dispersed without significant agglomeration, and some are curled to form hollow vesicle structures with an average size of $350 \times 135\ \text{nm}$. The mild hydrothermal environment limits sheet agglomeration, promoting the growth of $g\text{-C}_3\text{N}_4$ as ultrathin discrete sheets, while surface tension induces curling into vesicles, creating a hierarchical porous structure.

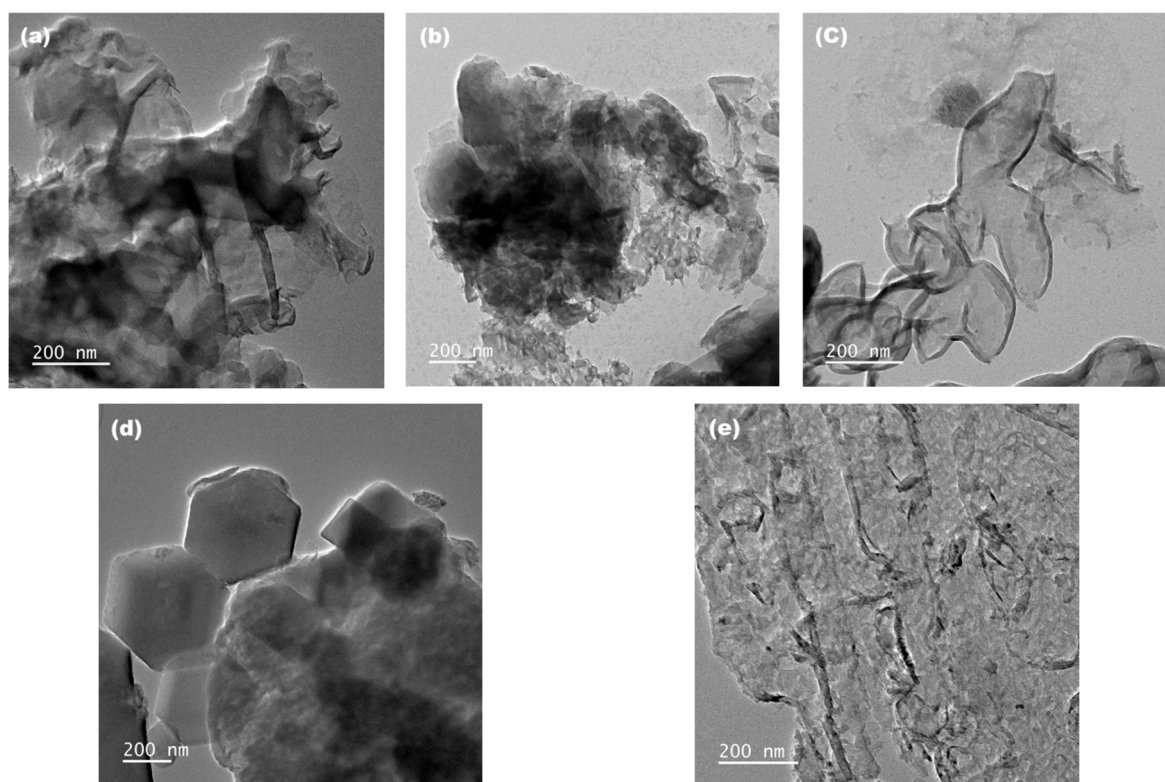


Figure 3. TEM images of (a) S- $g\text{-C}_3\text{N}_4$, (b) C- $g\text{-C}_3\text{N}_4$, (c) H- $g\text{-C}_3\text{N}_4$, (d) ZT- $g\text{-C}_3\text{N}_4$, and (e) CC- $g\text{-C}_3\text{N}_4$.

The S- $g\text{-C}_3\text{N}_4$ sample (Figure 3a) shows aggregates of thin, curled nanosheets. Statistical analysis of TEM images reveals an average sheet thickness of $25 \pm 4\ \text{nm}$ (Figure S4h), which is comparable to that of H- $g\text{-C}_3\text{N}_4$. The sheet thickness is comparable to that in (Figure 3c), with obvious wrinkles at the edges. The sheets are stacked together but not severely agglomerated. Compared to the flat layers of pristine $g\text{-C}_3\text{N}_4$, sulfur doping makes the sheets more prone to curling and thinning. This structure is beneficial for increasing the specific surface area and introducing defect sites. N_2 adsorption–desorption measurements (Figure 1c) confirm this structural evolution, with S- $g\text{-C}_3\text{N}_4$ exhibiting a BET surface area of $25.58\ \text{m}^2/\text{g}$. The corresponding pore size distribution (Barrett–Joyner–Halenda method) shows a broad peak centered at approximately $31\ \text{nm}$ (inset of Figure 1c), consistent with

the TEM observations. The thin curled sheets shorten the transport path for photogenerated charge carriers, which is favorable for charge separation in photocatalysis. The ZT-g-C₃N₄ sample (Figure 3d) exhibits a heterogeneous structure composed of a matrix and cubic particles. ZIF-67 retains its own cubic morphology while forming intimate interfacial contact with g-C₃N₄ and TiO₂. The CC-g-C₃N₄ sample (Figure 3e) displays a composite structure combining a layered framework with nanoparticles, which is consistent with the SEM observations.

Figure 4 displays the XPS spectra of C-g-C₃N₄ and S-g-C₃N₄. As shown in the C 1s spectrum (Figure 4a), three peaks located at 288.2 eV, 284.8 eV, and 286.2 eV are observed for C-g-C₃N₄, corresponding to sp²-hybridized carbon atoms (N-C=N), adventitious carbon (C-C/C-H), and C-NH_x (x = 1, 2), respectively. For S-g-C₃N₄, in addition to the peak for sp²-hybridized carbon (N-C=N) at 288.2 eV, the intensity of the adventitious carbon (C-C/C-H) peak at 284.8 eV is significantly enhanced. Meanwhile, new peaks emerge at 289.7 eV and 290.4 eV. This is primarily attributed to the different electronegativity between S and N atoms. After S substitutes for N sites, the electron cloud density of the surrounding C atoms increases, resulting in a slight shift in their peaks. Furthermore, a new peak appears around 285.6 eV, indicating the formation of C-S-C bonds.

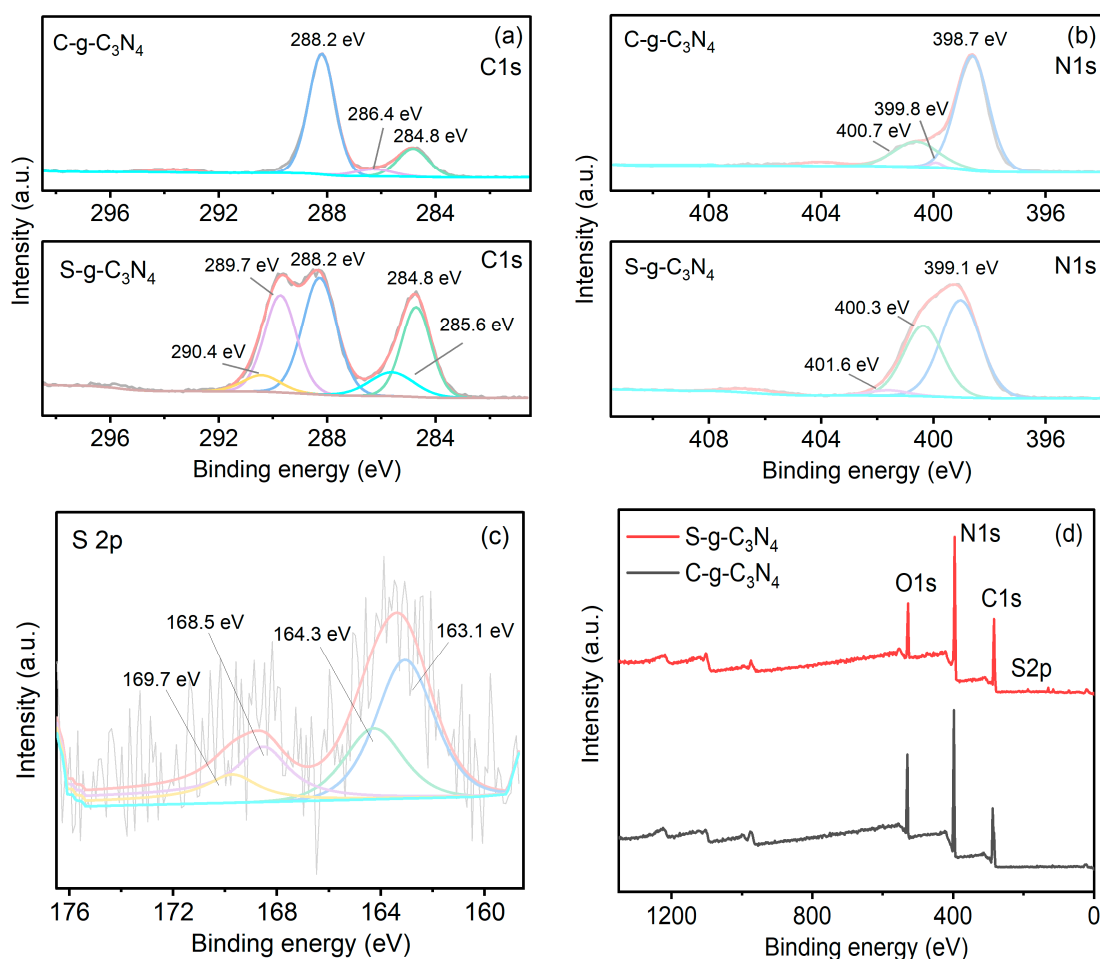


Figure 4. XPS pattern of C-g-C₃N₄ and S-g-C₃N₄. (a) High-resolution C 1s spectra; (b) High-resolution N 1s spectra; (c) High-resolution S 2p spectrum of S-g-C₃N₄; (d) Survey spectra. The black lines represent experimental data, the red solid lines represent the fitted curves, the light blue solid lines represent the Shirley background.

For the N 1s spectrum (Figure 4b), three peaks are identified for C-g-C₃N₄. The peak observed at 398.7 eV corresponds to sp²-hybridized pyridinic nitrogen (C-N=C) within

the triazine or heptazine ring structures, and the signal at 399.8 eV is ascribed to tertiary nitrogen (N-(C)₃) at ring junction sites or amino-containing nitrogen (C-N-H) present at the edges of the catalyst. And the peak at 400.7 eV is attributed to amino or protonated amino groups (-NH₂, -NH₃⁺), typically associated with surface-adsorbed water or molecules. Similar spectra are obtained for H-g-C₃N₄ (Figure S1).

For S-g-C₃N₄, the N 1s peaks shift overall to 399.1 eV, 400.3 eV, and 401.6 eV. Concurrently, the peak area of pyridinic nitrogen (399.1 eV) decreases, which is mainly due to the substitution of lattice N by S. These results confirm the successful doping of S into g-C₃N₄, where S substitutes for lattice N and forms C-S-C bonds. To clarify the nature of sulfur incorporation in the S-g-C₃N₄ sample, XPS S 2p spectrum was carefully analyzed following standard peak-fitting protocols (Figure 4c). The spectrum was deconvoluted with spin-orbit splitting constraints. The fitted peaks at 163.1 eV and 164.3 eV are attributed to the S 2p_{3/2} and S 2p_{1/2} components of C-S bonds, indicating that sulfur is incorporated into the g-C₃N₄ framework by substituting lattice nitrogen. An additional doublet at 168.5 eV and 169.7 eV corresponds to oxidized sulfur species (C-SO_x), likely formed at the edges or defect sites. No peaks corresponding to S-S or metal-S bonds were detected, confirming that sulfur is chemically bonded within the carbon nitride network rather than existing as physically adsorbed species or separate sulfur phases. Based on these assignments, the sulfur incorporation in this work is predominantly substitutional, with a minor fraction present as surface-bound oxidized species.

The XPS spectrum of CC-g-C₃N₄ is shown in Figure S2. The C 1s spectrum of CC-g-C₃N₄ was calibrated at 284.80 eV. The peak at 285.09 eV is assigned to C-O or C-N bonds, while the peak at 288.16 eV corresponds to O=C-N groups in the g-C₃N₄ framework, confirming the presence of graphitic carbon nitride. The N 1s spectrum was deconvoluted into three peaks with consistent FWHM. The peak at 397.54 eV is assigned to sp²-hybridized nitrogen (C=N-C) in the triazine units of g-C₃N₄. The peak at 398.38 eV corresponds to pyridinic/structural nitrogen in the g-C₃N₄ framework. The peak at 400.09 eV is attributed to bridging N-(C)₃ groups or terminal N-H defects. This fitting is consistent with the typical structure of graphitic carbon nitride. The O 1s spectrum with peak at 529.23 eV is assigned to lattice oxygen (O²⁻) in Co₃O₄ and CeO₂. The peak at 530.53 eV corresponds to oxygen vacancies and surface hydroxyl groups (M-OH), which favor charge separation. The peak at 532.07 eV is attributed to adsorbed oxygen or surface adsorbed water. The Co 2p spectrum was deconvoluted into six peaks consistent with the Co₃O₄ spinel structure. The peaks at 778.20, 779.83 eV (2p_{3/2}) and 793.02, 794.70 eV (2p_{3/2}) are assigned to Co³⁺ in octahedral sites. The peak at 784.40 eV (2p_{3/2}) corresponds to Co²⁺ in tetrahedral sites. The satellite peak at 800.55 eV is characteristic of Co²⁺ in cobalt oxides. The Ce 3d XPS spectrum (Figure S2e) reveals the coexistence of Ce(IV) and Ce(III) species, originating from CeO₂ and the residual CeCo-MOF, respectively. The peaks at 881.59 eV, 878.45 eV, 901.61 eV, and 912.54 eV are characteristic of Ce(IV) in CeO₂, while the peaks at 884.53 eV, 896.83 eV, and 903.96 eV correspond to Ce(III) species associated with the CeCo-MOF. The presence of both Ce(IV) and Ce(III) peaks confirms that the CeCo-MOF structure is partially retained after calcination, consistent with the XRD results (Figure 1). The binding energies are in good agreement with literature values for CeO₂ (Ce 3d_{5/2} at ~882 eV, Ce 3d_{3/2} at ~900 eV) and Ce(III)-based MOFs.

For ZT-g-C₃N₄ (Figure S3), the C 1s spectrum of ZT-g-C₃N₄ was calibrated at 284.84 eV (adventitious carbon). The peak at 286.10 eV is assigned to C-O or C-N bonds, while the peak at 288.06 eV corresponds to O=C-N groups in the g-C₃N₄ framework, confirming the presence of graphitic carbon nitride. All peaks were fitted with uniform FWHM to ensure physical validity. The N 1s spectrum was deconvoluted into three peaks characteristic of g-C₃N₄. The dominant peak at 397.49 eV is attributed to sp²-hybridized nitrogen (C=N-C) in

triazine units. The peak at 399.89 eV corresponds to bridging nitrogen (N-(C)₃) connecting adjacent triazine units, and the weak peak at 398.60 eV reflects fine structural features. This fitting aligns with the standard g-C₃N₄ structure. The Ti 2p_{3/2} located at 459.51 eV and Ti 2p_{1/2} at 465.17 eV. The Co 2p XPS spectrum of ZT-g-C₃N₄ was fitted with four peaks corresponding to the Co 2p_{3/2} and Co 2p_{1/2} doublet and their characteristic satellites. The Co 2p_{3/2} main peak at 781.41 eV and the corresponding Co 2p_{1/2} peak at 796.89 eV exhibit a spin–orbit splitting of 15.5 eV, which is consistent with literature values for Co²⁺ in ZIF-67. The satellite peaks at 786.35 eV and 802.01 eV, with energy separations of 5.0 eV and 5.1 eV from their respective main peaks, are characteristic of high-spin Co²⁺ species. These results confirm that the ZIF-67 structure is preserved during composite formation with g-C₃N₄ and TiO₂, which is consistent with the XRD analysis (Figure 1).

Figure 5a,b presents the UV–Vis absorption spectra of C-g-C₃N₄, H-g-C₃N₄, S-g-C₃N₄, CC-g-C₃N₄, and ZT-g-C₃N₄. As shown in Figure 5a, the absorption edge of C-g-C₃N₄ is located near 460 nm, which is characteristic of the typical bandgap of g-C₃N₄. For H-g-C₃N₄, the absorption edge is blue-shifted compared to C-g-C₃N₄, consistent with its larger bandgap (Figure 5b, 2.95 eV vs. 2.53 eV). This blue-shift is attributed to the hydrothermal treatment, which alters the crystallinity and nanostructure of g-C₃N₄, leading to a widening of the bandgap. Notably, despite the blue-shifted bandgap, H-g-C₃N₄ exhibits slightly enhanced absorption in the region of 200–400 nm and 450–600 nm compared to C-g-C₃N₄. This apparent contradiction can be possibly explained by two factors. First, the hydrothermal treatment introduces sub-bandgap defect states within the bandgap, which act as additional absorption centers in the visible light region. Second, the unique vesicle-like nanosheet structure of H-g-C₃N₄ (Figure 2c) significantly increases the specific surface area and enhances light scattering, leading to higher overall absorption intensity despite the blue-shifted absorption edge. These combined effects result in enhanced visible light absorption even with a widened bandgap.

It is well established that g-C₃N₄ is an indirect semiconductor [13]. Therefore, the band gap energies (E_g) of all samples were estimated from Tauc plots constructed using the Kubelka–Munk function transformed according to the indirect transition mode, i.e., plotting $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$). The absorption edge of S-g-C₃N₄ shows a slight red shift, indicating that S doping introduces impurity energy levels and reduces the bandgap to approximately 2.48 eV (Figure 5b). The substitution of N atoms in g-C₃N₄ by S atoms, whose 3p orbital energy level lies between the p orbitals of C and N, introduces impurity states within the bandgap, thereby lowering the energy required for electron transitions.

For CC-g-C₃N₄, the absorption edge is significantly red-shifted to ~580 nm, with further enhanced absorption in the visible region. The introduction of intermediate energy levels from the d-orbitals of Ce/Co contributes to this bandgap narrowing. Similarly, the absorption edge of ZT-g-C₃N₄ is red-shifted to ~600 nm, exhibiting strong absorption across the 500–700 nm visible range. The composite of ZIF-67 and TiO₂ not only forms heterojunctions but also introduces the broad-spectrum response of TiO₂, collectively narrowing the bandgap and enabling wide-spectrum light absorption. The bandgaps of C-g-C₃N₄, H-g-C₃N₄, CC-g-C₃N₄, and ZT-g-C₃N₄ were determined to be 2.50 eV, 2.63 eV, 2.21 eV, and 2.95 eV, respectively, from their corresponding Tauc plots (Figure 5b). It should be noted that the bandgap of H-g-C₃N₄ (2.95 eV) represents a slight red-shift compared to pristine g-C₃N₄, consistent with its slightly enhanced visible light absorption observed in Figure 5a.

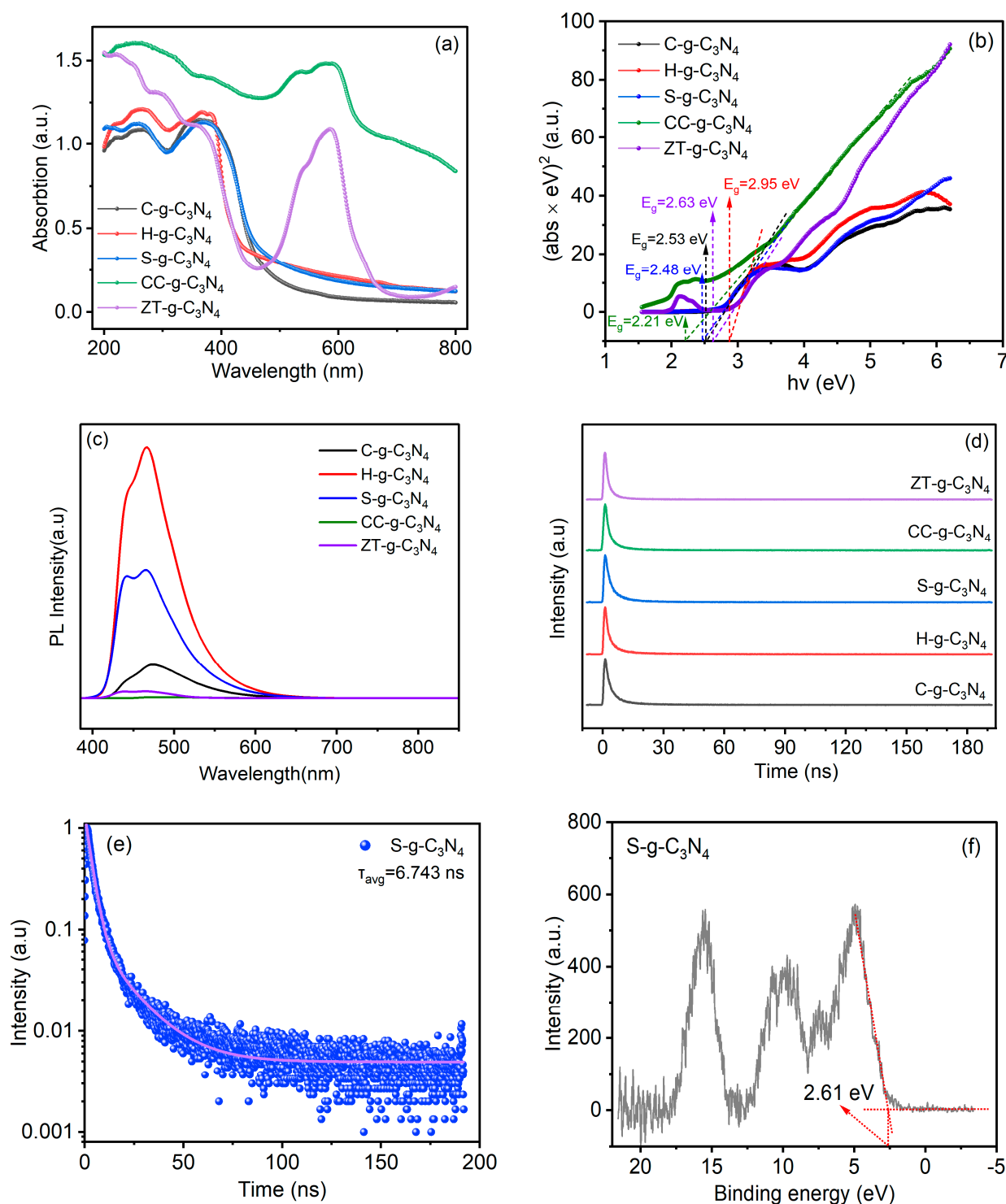


Figure 5. (a) UV–Vis absorption spectra, (b) Tauc plots, (c) photoluminescence (PL) spectra, and (d) average fluorescence lifetime decay curves of C-g-C₃N₄, H-g-C₃N₄, S-g-C₃N₄, CC-g-C₃N₄, and ZT-g-C₃N₄. (e) TRPL decay curves and (f) valence-band XPS spectra of S-g-C₃N₄.

To further investigate the defect states in H-g-C₃N₄, PL spectroscopy was performed. As shown in Figure 5c, H-g-C₃N₄ exhibits a significantly higher PL intensity compared to C-g-C₃N₄, indicating a higher density of defect states that facilitate radiative recombination. These defect states, likely introduced during the hydrothermal treatment, are consistent with the observed sub-bandgap absorption in the visible region (Figure 5a). While these defects contribute to enhanced visible light absorption, they also act as recombination

centers for photogenerated charge carriers, leading to the lower photocatalytic activity of H-g-C₃N₄ (Figure 6a).

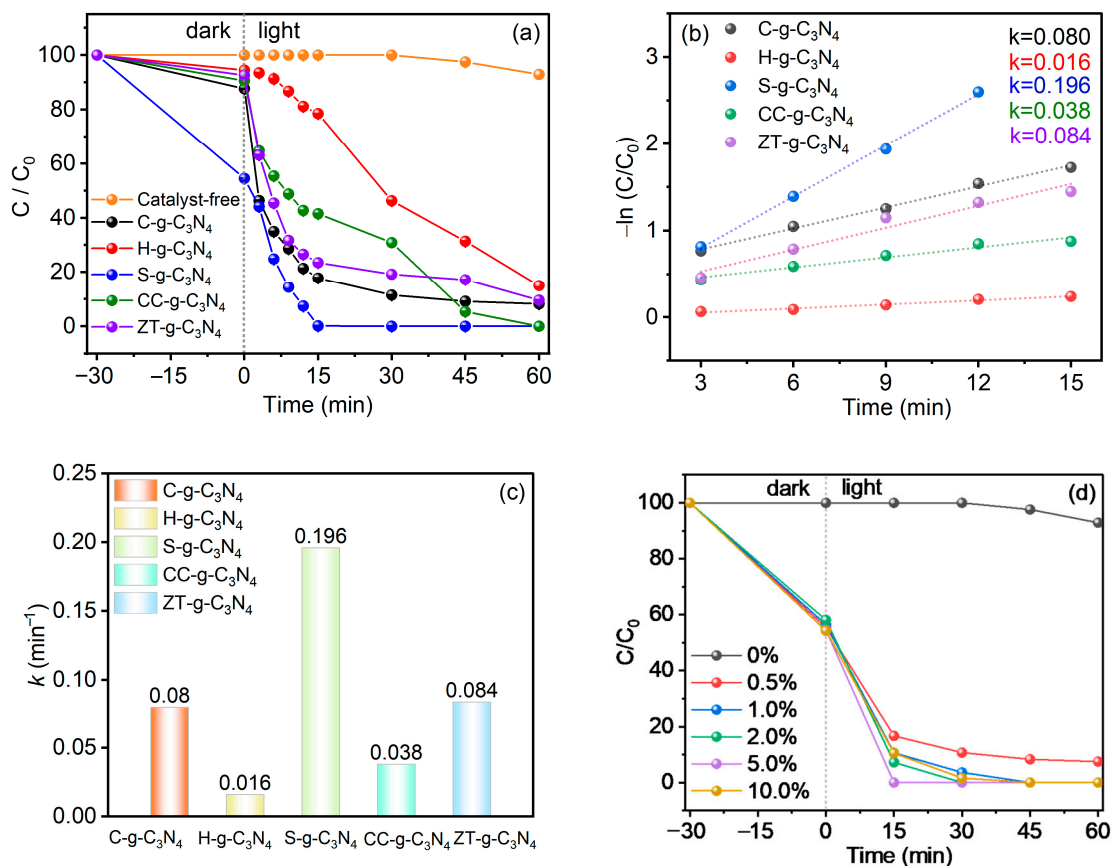


Figure 6. The RhB degradation performance curve: (a) degradation ratio of different catalysts, (b) Pseudo-first-order kinetics fitting curves for RhB degradation over different catalysts, (c) pseudo-first-order rate constants k value of different catalysts, and (d) degradation ratio of catalysts with different sulfur doping content.

2.2. Photocatalytic Performance Evaluation

The photocatalytic performances of S-g-C₃N₄, ZT-g-C₃N₄, C-g-C₃N₄, CC-g-C₃N₄ and H-g-C₃N₄ were assessed via the degradation of RhB under simulated solar light irradiation (Figure 6). All degradation experiments were performed in triplicate to ensure reproducibility. The reported data represent mean values, and error bars in the figures indicate standard deviations. The degradation ratio is defined as C/C_0 , where C and C_0 represent the residual and initial concentrations of RhB, respectively.

As shown in Figure 6a, the reaction suspension was first stirred in darkness for 30 min to establish the equilibrium between adsorption and desorption. All degradation experiments were performed in triplicate, and the data points in Figure 6a represent mean values with error bars indicating standard deviations. After 60 min of irradiation, the self-degradation of RhB in the absence of any catalyst was negligible. S-g-C₃N₄ demonstrated the most superior activity, achieving nearly 100% degradation within 15 min. CC-g-C₃N₄ showed a degradation efficiency of only 59.02% at the 30 min mark, which increased significantly to 94.46% at 45 min. C-g-C₃N₄ achieved 91.78% degradation at 60 min, while H-g-C₃N₄ and ZT-g-C₃N₄ reached 84.97% and 90.35%, respectively. Based on the final degradation efficiencies after 60 min of irradiation, the performances ranked as follows: S-g-C₃N₄ (100%) $\approx$ CC-g-C₃N₄ (100%) > C-g-C₃N₄ (91.78%) > ZT-g-C₃N₄ (90.35%) > H-g-C₃N₄ (84.97%). Among all tested materials, S-g-C₃N₄ exhibited the strongest capability

ity for photocatalytic RhB degradation. These results collectively indicate that these four catalysts all possess favorable degradation performance.

Kinetic analysis was performed by fitting the initial degradation stage (0–15 min) to the pseudo-first-order model: $\ln(C_0/C) = kt$, where k is the apparent rate constant. This interval was chosen because it yields excellent linear fits ($R^2 > 0.95$ for all samples) and represents the intrinsic photocatalytic activity before the accumulation of intermediates affects the kinetics. Both pseudo-first-order and pseudo-second-order kinetic models were evaluated for all samples (Table S1). While the pseudo-second-order model generally gave better R^2 values for most samples, H-g-C₃N₄ showed an unacceptably poor fit ($R^2 = 0.46$). Therefore, to maintain consistent model comparison across all catalysts, the pseudo-first-order model was adopted. This model yields acceptable R^2 for all samples, enabling reliable comparison of their photocatalytic activities.

As shown in Figure 6b, the apparent pseudo-first-order rate constants (k) for RhB degradation were determined. The catalysts can be ranked according to their k values as follows: S-g-C₃N₄ (0.196 min^{-1}) > ZT-g-C₃N₄ (0.084 min^{-1}) > C-g-C₃N₄ (0.080 min^{-1}) > CC-g-C₃N₄ (0.038 min^{-1}) > H-g-C₃N₄ (0.016 min^{-1}). This kinetic analysis further confirms the superior activity of S-g-C₃N₄.

To benchmark the performance of our S-g-C₃N₄ against recent literature, we compared its photocatalytic activity with previously reported S-doped g-C₃N₄ and other modified g-C₃N₄ photocatalysts under normalized conditions. As summarized in Table S1, the comparison takes into account key parameters such as catalyst dosage, pollutant concentration, light source, and the apparent rate constant (k) per unit mass of catalyst. Our S-g-C₃N₄ exhibits a rate constant of 0.196 min^{-1} . This value is competitive with or superior to recently reported S-g-C₃N₄ systems and some other modified g-C₃N₄ photocatalysts under comparable conditions.

To investigate the influence of S doping content on photocatalytic activity, a series of S-g-C₃N₄ samples with varying S concentrations were prepared and evaluated for RhB degradation. As shown in Figure 6d, the degradation efficiency exhibits a volcanic trend with increasing S content. It initially enhances progressively, reaches an optimum at a moderate doping level, and then slightly declines upon further increase. This phenomenon can be attributed to the dual role of S doping in modifying the physicochemical properties of g-C₃N₄. At low to moderate doping levels, S atoms are incorporated into the g-C₃N₄ lattice by substituting N atoms or occupying interstitial sites. This substitution introduces impurity energy levels within the bandgap, effectively narrowing the band gap, enabling more efficient utilization of solar energy. Moreover, S doping creates lattice defects that act as charge trapping centers, prolonging the lifetime of photogenerated electrons and holes and suppressing their recombination. However, at excessive doping levels, the photocatalytic performance declines. This deterioration can be explained by the excessive S atoms may act as recombination centers for photogenerated electron–hole pairs rather than separation promoters. When the doping concentration exceeds the optimal threshold, the impurity sites become too abundant, trapping charge carriers and facilitating their recombination before they can participate in surface redox reactions [27]. Furthermore, excessive S incorporation could lead to the formation of undesirable by-products or surface passivation layers that block active sites. Therefore, the S-g-C₃N₄ with moderate S content exhibits the highest photocatalytic activity due to the synergistic optimization of light absorption, charge separation efficiency, and surface active sites.

To elucidate the influence of catalyst dosage on photocatalytic activity, Figure 7a investigates the photocatalytic degradation behavior of RhB under different catalyst loadings. The initial RhB concentration was fixed at 10 mg/L , and the catalyst dosage was set at 0, 10, 20, and 30 mg . The results show that during the dark adsorption period (0–15 min), the

adsorption of RhB significantly increased with higher catalyst dosages. This is attributed to the greater number of adsorption sites provided by the larger amount of catalyst. In the subsequent photodegradation stage (after 15 min of irradiation), the RhB concentration continued to decrease upon light exposure. A positive correlation was found between the catalyst dosage and the RhB degradation efficiency. The group with 10 mg of catalyst exhibited a relatively slow degradation rate, whereas near-complete degradation of RhB was achieved within 60 min in the group with 30 mg of catalyst. The concentration of RhB in the blank control group (0 mg catalyst) showed no significant change, confirming that the RhB degradation is predominantly driven by the photocatalytic action of the catalyst, effectively ruling out interference factors such as self-degradation. These findings indicate that increasing the catalyst dosage provides more photocatalytic active sites while simultaneously enhancing the adsorption and enrichment of RhB molecules. These two effects work synergistically to improve the overall photocatalytic degradation efficiency.

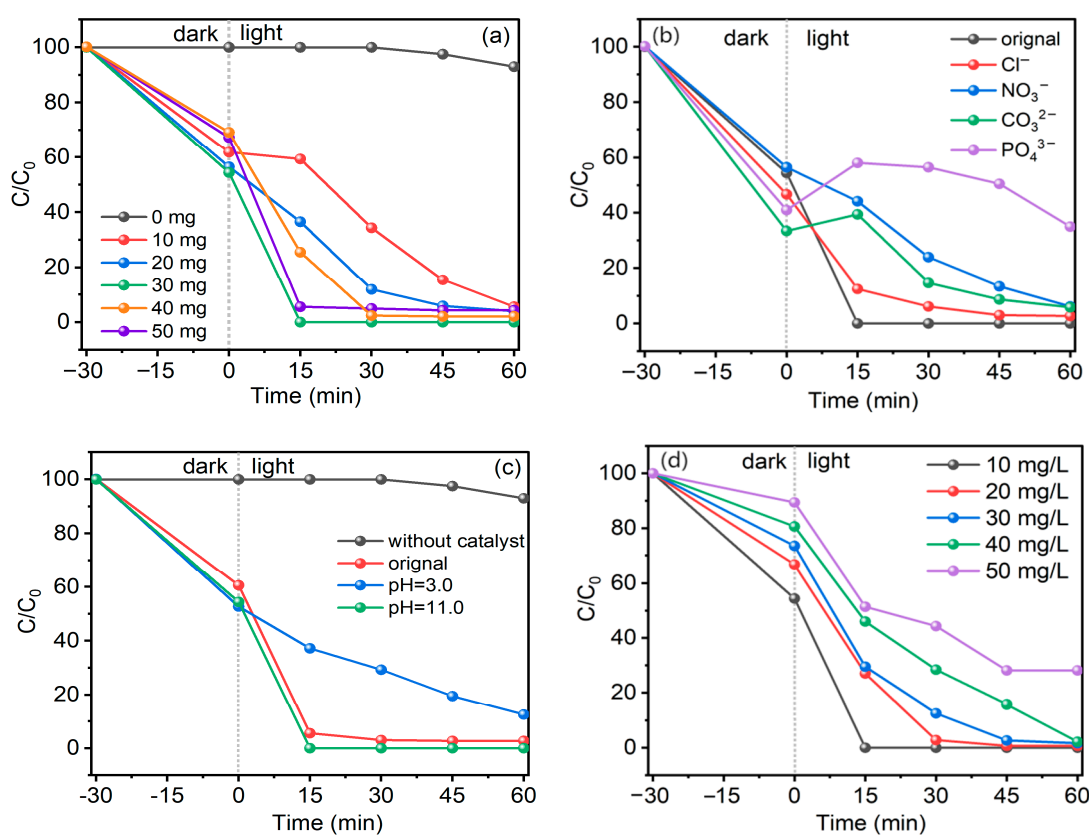


Figure 7. Effects of (a) catalyst dosage, (b) coexisting ions, (c) pH value, and (d) initial RhB concentration on photocatalytic degradation.

To simulate the influence of coexisting anions in actual wastewater on the photocatalytic degradation of RhB, experiments were conducted with a fixed initial RhB concentration of 10 mg/L and a catalyst dosage of 30 mg. Equal concentrations of Cl^- , NO_3^- , CO_3^{2-} and PO_4^{3-} (added in the form of their sodium salts) were separately introduced into the system. A control group without additional ions was used for comparison, and their degradation performance under simulated sunlight was evaluated (Figure 7b). The results indicate that during the dark adsorption stage (−30 to 0 min), the adsorption behavior of RhB in all anion-containing groups (Cl^- , NO_3^- , CO_3^{2-} and PO_4^{3-}) was nearly identical to that of the control group without added anions. This suggests that none of the tested anions significantly compete with RhB for adsorption sites on the catalyst surface under dark conditions, including PO_4^{3-} . Upon illumination, the degradation profiles of

the Cl^- , NO_3^- and CO_3^{2-} groups remained close to that of the control group, achieving near-complete degradation of RhB within 60 min. This indicates that these three anions have little influence on the photocatalytic activity of the catalyst under the tested conditions. In contrast, the PO_4^{3-} group exhibited a distinct behavior: a rapid increase in RhB concentration was observed immediately after light irradiation, indicating photo-induced desorption of RhB from the catalyst surface. This desorption is likely caused by changes in surface charge upon photogeneration of electron–hole pairs, which disrupts the interaction between phosphate-adsorbed catalyst and RhB molecules. Following this initial desorption, the degradation rate slowed significantly, and the final degradation efficiency after 60 min was much lower than that of the other groups.

To clarify the influence of solution pH on the photocatalytic degradation of RhB, experiments were conducted with a fixed initial RhB concentration of 10 mg/L and a catalyst dosage of 30 mg. Four groups were established for comparison: a blank control (no catalyst), the original pH, pH = 3 (acidic), and pH = 11 (alkaline). Their degradation performance under simulated sunlight is compared in Figure 7c. The results show that during the dark adsorption stage, the RhB concentration decreased significantly in the original pH, pH = 3, and pH = 11 groups, far exceeding the blank control. However, the adsorption capacity under acidic conditions was notably lower than that under the original and alkaline pH, indicating that the acidic environment weakened the catalyst's adsorption capability for RhB. In the photodegradation stage, the RhB concentration decreased rapidly and continuously under both the original and alkaline pH conditions, achieving nearly complete degradation within 60 min. In contrast, under acidic conditions, the degradation rate slowed noticeably after illumination began, resulting in a final degradation efficiency much lower than the other two conditions. For the blank control group, the RhB concentration showed no significant change, ruling out interference from self-degradation and confirming that the degradation process is primarily driven by the photocatalyst.

The underlying reasons for this phenomenon may be as follows. Under acidic conditions, RhB exists in a cationic form. If the catalyst surface is positively charged in an acidic environment, electrostatic repulsion would weaken RhB adsorption. Conversely, in an alkaline environment, the occurrence of electrostatic interaction between RhB and the catalyst surface is more likely, thereby enhancing the cooperative effect of adsorption and degradation processes. Furthermore, under acidic conditions, the generation of reactive oxygen species (such as hydroxyl radicals, $\cdot\text{OH}$) on the catalyst surface may be inhibited, and the separation efficiency of photogenerated charge carriers could be affected, thereby leading to reduced catalytic degradation performance.

The initial concentration of the target pollutant stands as a critical parameter for the practical implementation of photocatalytic technology. In this experiment, with the catalyst dosage fixed at 30 mg, the effect of the initial RhB concentration of 10, 20, 30, 40, and 50 mg/L on the degradation performance was investigated (Figure 7d). The results indicate that in the low-concentration range (10–30 mg/L), there was no significant difference in the amount of RhB adsorbed during the dark adsorption stage across different concentrations, and the degradation rates after illumination were similar. Specifically, the groups with 10, 20, and 30 mg/L all achieved near-complete degradation of RhB within 45 min. This demonstrates that the catalyst is endowed with ample active sites and favorable light utilization efficiency, and fluctuations in concentration exert minimal influence on the degradation result. In the high-concentration range (40–50 mg/L), the degradation rate began to slow for the 40 mg/L group, and a significant decline in degradation efficiency was observed for the 50 mg/L group, with incomplete degradation even after 60 min, showing a clear concentration inhibition effect. This can be attributed to the following reasons in the low-concentration range: the number of accessible active sites over the catalytic material

and the generation of photogenerated charge carriers can match the degradation demand for RhB, meaning solution transparency is good, and the catalyst receives sufficient photons. Simultaneously, the number of RhB molecules does not exceed the capacity of the active sites and reactive oxygen species, resulting in stable degradation efficiency.

When the concentration increases to 40–50 mg/L, the deeper color of the RhB solution enhances the shielding of simulated sunlight, leading to a decrease in the photon flux reaching the catalyst surface and a reduction in the generation of photogenerated electron–hole pairs. Excessive RhB molecules and intermediates generated in the initial stage simultaneously compete for the limited active sites on the catalyst surface and for reactive species (e.g., $\cdot\text{OH}$, h^+) in the solution, significantly reducing the probability of effective reactions. Furthermore, the high concentration of RhB may alter the interfacial potential of the solution, weakening the catalyst's adsorption capacity for RhB and further decreasing the degradation efficiency. Therefore, diluting the pollutant to a suitable concentration is economically practical, with 10 mg/L identified as the optimal RhB concentration in this study.

To figure out the dominant active species that participate in the photocatalytic degradation of RhB on S-g- C_3N_4 , trapping experiments were conducted by introducing different radical scavengers. Isopropanol (IPA) was used for hydroxyl radicals ($\cdot\text{OH}$), disodium ethylenediaminetetraacetate (EDTA-2Na) for holes (h^+), ascorbic acid (AA) for superoxide radicals ($\cdot\text{O}_2^-$), and silver nitrate (AgNO_3) for electrons (e^-). The results are presented in Figure 8.

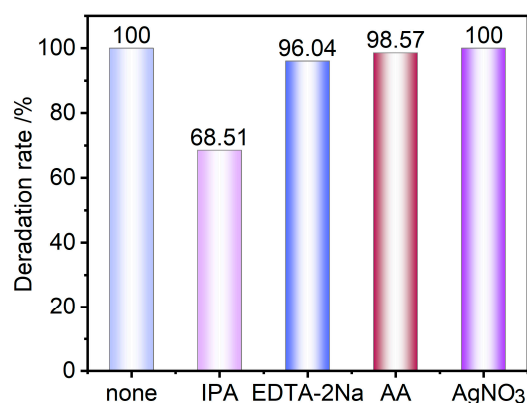


Figure 8. Effect of active species scavengers on the degradation efficiency of RhB.

As shown in Figure 8, the degradation efficiency of RhB decreased significantly upon the addition of IPA, the $\cdot\text{OH}$ scavenger. This indicates that IPA effectively captured the $\cdot\text{OH}$ generated in the system and concurrently demonstrates the efficient separation of photogenerated electron–hole pairs (e^- – h^+) on the catalyst surface. The addition of EDTA-2Na, the h^+ scavenger, led to only a slight reduction in degradation efficiency, suggesting that h^+ plays a secondary role in the reaction. In contrast, the effects of AA ($\cdot\text{O}_2^-$ scavenger) and AgNO_3 (e^- scavenger) on the degradation efficiency were negligible.

Therefore, it can be concluded that $\cdot\text{OH}$ serves as the dominant reactive species in the photocatalytic degradation process of RhB using S-g- C_3N_4 as the catalyst, while h^+ participates partially. The roles of $\cdot\text{O}_2^-$ and e^- are not significant in this system.

To evaluate the cycling stability of the catalyst, five consecutive photocatalytic degradation cycles of RhB were performed on the target sample. The results are presented in Figure 9a. As shown in Figure 9a, the S-g- C_3N_4 catalyst maintained high degradation efficiency throughout five consecutive cycles. In each cycle, near-complete removal of RhB was achieved within 60 min of irradiation. However, a gradual decrease in the degradation

rate was observed from the fifth cycle with slightly slower kinetics compared to the first cycle. Specifically, while the first cycle achieved complete degradation within 15 min, the fifth cycle required approximately 30 min to reach similar removal efficiency. Despite this slowdown in rate, the final degradation efficiency after 60 min remained 100% in all five cycles.

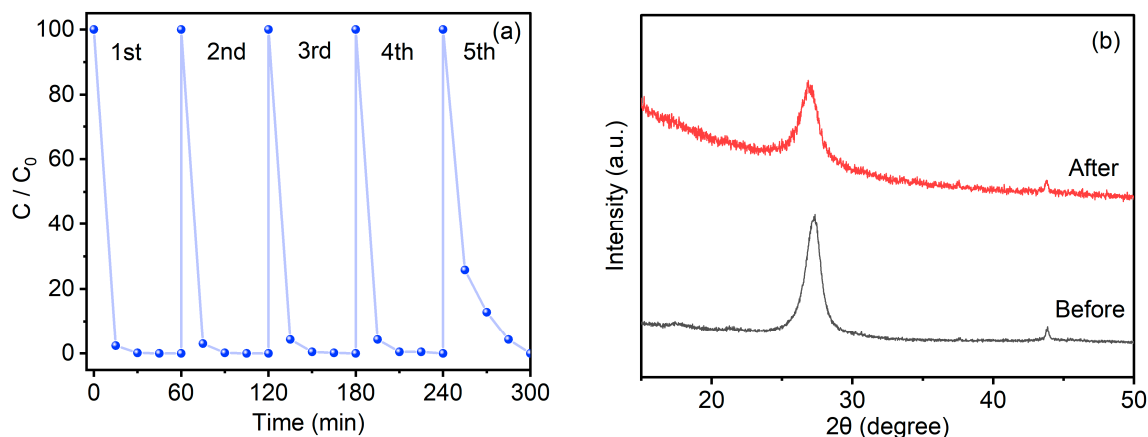


Figure 9. Schematic diagram of the cyclic stability of S-g-C₃N₄ used for RhB degradation (a) and XRD patterns of S-g-C₃N₄ before and after the photocatalytic cycles (b).

The XRD patterns of S-g-C₃N₄ before and after the photocatalytic cycles are shown in Figure 9b. Comparison of the XRD patterns before and after five reaction cycles reveals that the positions and intensities of the characteristic diffraction peaks remain essentially unchanged, indicating that the crystal structure of S-g-C₃N₄ is well-preserved during photocatalysis. No additional peaks corresponding to secondary phases or structural decomposition products were observed, confirming that the bulk structure of the catalyst is stable under the reaction conditions.

To investigate whether sulfur leaching occurs during the photocatalytic process, the reaction solution after five cycles was collected and analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Table S4). The concentration of leached sulfur in the solution was found to be below 0.1 ppm, which is near the detection limit and negligible compared to the total sulfur content in the catalyst. This result confirms that the doped sulfur atoms are tightly bound within the g-C₃N₄ framework and do not leach into the solution during photocatalysis. The strong chemical bonding of sulfur in the form of C–S and N–S bonds, as evidenced by XPS analysis (Figure 4c), contributes to this excellent stability against leaching.

The as-prepared S-g-C₃N₄ composite exhibited exceptional photocatalytic activity for the degradation of RhB under simulated sunlight. Nearly 100% of RhB was decomposed within 15 min, demonstrating a degradation efficiency superior to that of pristine g-C₃N₄ and many reported results (Table S3) [26,28–41]. This activity can be primarily attributed to the effective S doping, which optimizes the band structure and enhances charge carrier separation. Furthermore, the catalyst maintained its high activity over multiple cycles, indicating not only high efficiency but also robust stability.

Total organic carbon (TOC) removal is a critical parameter to evaluate the mineralization efficiency of organic pollutants, distinguishing complete degradation to CO₂ and H₂O from mere decolorization. Due to instrument availability constraints, direct TOC measurements were not conducted in the present work, which will be systematically investigated in future studies. However, indirect evidence from radical trapping experiments and catalyst reusability tests supports the mineralization capability of S-g-C₃N₄.

As shown in Figure 8, radical trapping experiments revealed that $\cdot\text{OH}$ and h^+ are the primary reactive species responsible for RhB degradation. These species, particularly $\cdot\text{OH}$, are known to effectively attack and break down aromatic rings, leading to the deep mineralization of organic pollutants into CO_2 and H_2O . The generation of $\cdot\text{OH}$, which has a high oxidation potential ($E^0 = +2.8 \text{ V vs. NHE}$), suggests that the degradation process extends beyond chromophore cleavage to complete mineralization.

Furthermore, the catalyst exhibited excellent stability over five consecutive cycles (Figure 9), with only a slight decline in activity. This indicates that the active sites are not easily poisoned or blocked by accumulated intermediates—a strong indicator of efficient mineralization. If the degradation process were primarily driven by decolorization without mineralization, the accumulation of intermediate products on the catalyst surface would likely lead to rapid deactivation in subsequent cycles. The sustained high activity over multiple cycles thus indirectly supports the occurrence of effective mineralization.

2.3. Photoelectrochemical Characterization

To gain deeper insight into the charge carrier dynamics, time-resolved photoluminescence (TRPL) measurements were performed on pristine $\text{g-C}_3\text{N}_4$ - and $\text{g-C}_3\text{N}_4$ -based samples. As shown in Figure S6, PL spectroscopy, including emission (PL Em) and excitation (PL Ex) spectra, was employed to investigate the separation and migration behavior of photogenerated charge carriers in various modified $\text{g-C}_3\text{N}_4$ samples. The PL Ex spectra reveal that all samples exhibit excitation peaks centered at 350–450 nm with a main peak around 400 nm, consistent with the intrinsic bandgap ($\sim 2.7 \text{ eV}$) of $\text{g-C}_3\text{N}_4$, indicating their effective photoresponse range covers the UV–visible region. Among them, $\text{H-g-C}_3\text{N}_4$ and $\text{S-g-C}_3\text{N}_4$ show higher excitation intensity, suggesting superior light absorption ability. Notably, $\text{S-g-C}_3\text{N}_4$ displays a distinct shoulder peak at 420–430 nm, implying that S doping introduces shallow defect levels and further broadens the photoresponse range.

The PL emission spectra demonstrate that $\text{H-g-C}_3\text{N}_4$ exhibits the strongest emission peak, indicating the fastest recombination rate of photogenerated electron–hole pairs, which aligns with its lowest photocatalytic degradation activity. After modification, the PL intensities of $\text{S-g-C}_3\text{N}_4$, $\text{C-g-C}_3\text{N}_4$, $\text{ZT-g-C}_3\text{N}_4$, and $\text{CC-g-C}_3\text{N}_4$ are significantly reduced, confirming that the modification strategies effectively suppress carrier recombination. It is noteworthy that although $\text{ZT-g-C}_3\text{N}_4$ and $\text{CC-g-C}_3\text{N}_4$ show near-baseline PL intensity with the best charge separation ability, their catalytic activity is lower than that of $\text{S-g-C}_3\text{N}_4$. This can be attributed to overly deep defect levels, which lead to “irreversible trapping” of charge carriers, preventing them from effectively participating in surface reactions. Combined with PL spectra and radical trapping experiments, $\text{S-g-C}_3\text{N}_4$ achieves a balance between high light absorption efficiency and moderate charge separation efficiency: it not only broadens the photoresponse range and enhances photon capture via S doping, but also moderately suppresses carrier recombination, allowing more electrons and holes to migrate to the surface to reduce O_2 to $\cdot\text{O}_2^-$ and oxidize $\text{H}_2\text{O}/\text{OH}^-$ to $\cdot\text{OH}$, respectively, ultimately exhibiting the optimal RhB photocatalytic degradation activity.

The separation and migration efficiency of photogenerated charge carriers represents a critical factor governing photocatalytic performance. In this study, the charge carrier behavior of different materials was systematically evaluated through transient photocurrent response and electrochemical impedance spectroscopy (EIS) and TRPL.

Figure 10a presents the transient photocurrent analysis results of $\text{S-g-C}_3\text{N}_4$, $\text{ZT-g-C}_3\text{N}_4$, $\text{C-g-C}_3\text{N}_4$, $\text{CC-g-C}_3\text{N}_4$, and $\text{H-g-C}_3\text{N}_4$ samples. Transient photocurrent intensity is a direct reflection of the separation efficiency of photogenerated carriers. The $\text{C-g-C}_3\text{N}_4$ and $\text{H-g-C}_3\text{N}_4$ exhibited relatively low photocurrent density, which indicates a high likelihood of photogenerated electron–hole pair recombination. In contrast, $\text{S-g-C}_3\text{N}_4$

showed a significantly higher photocurrent density than the pristine g-C₃N₄, demonstrating that S doping markedly improved charge carrier separation efficiency. This improvement is consistent with the prolonged charge carrier lifetime observed in TRPL measurements (Figure S6), confirming that sulfur doping effectively suppresses radiative recombination. This improvement is attributed to the impurity energy levels introduced by S atoms, which can act as charge transfer mediators, facilitating the directional separation of photogenerated electrons and holes while reducing their recombination. Furthermore, ZT-g-C₃N₄ and CC-g-C₃N₄ also exhibited relatively large current densities. This can be ascribed to the strengthened interfacial charge transfer facilitated by their respective heterojunction structures.

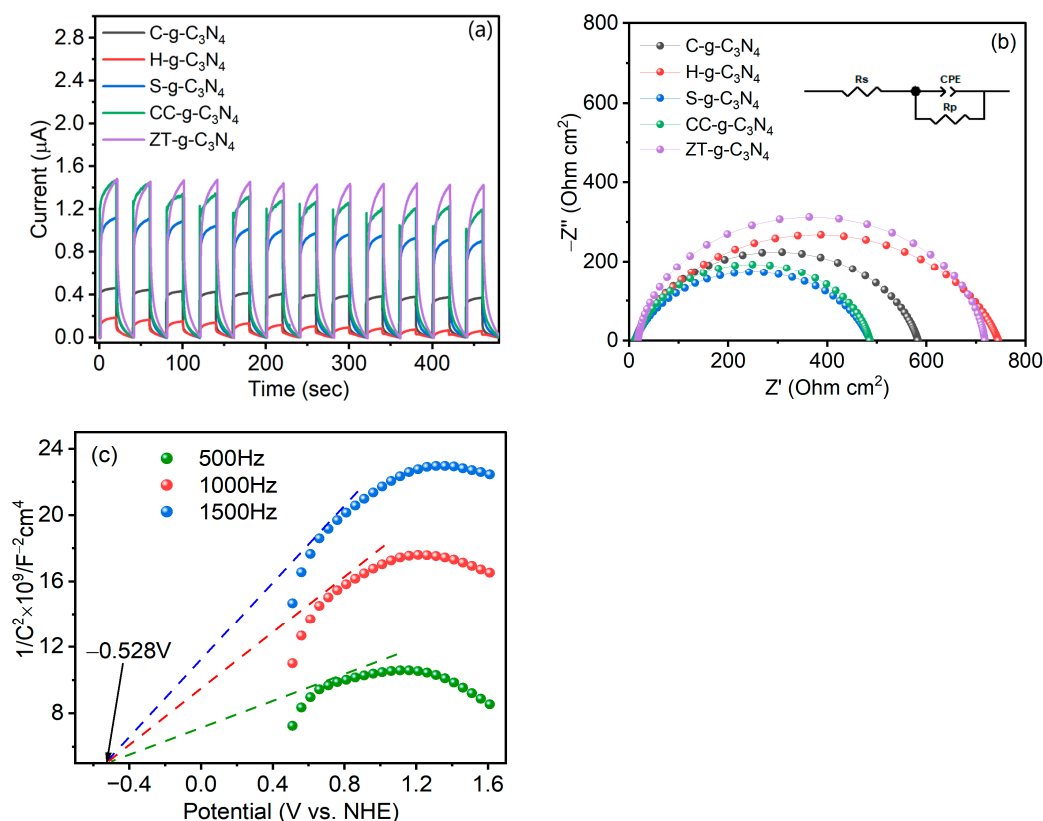


Figure 10. (a) Transient photocurrent response, (b) electrochemical impedance spectroscopy (EIS) plots of the C-g-C₃N₄, H-g-C₃N₄, S-g-C₃N₄, CC-g-C₃N₄, and ZT-g-C₃N₄ composites, and (c) Schottky plot of the S-g-C₃N₄.

Figure 10b presents the EIS Nyquist plots of the S-g-C₃N₄, ZT-g-C₃N₄, C-g-C₃N₄, CC-g-C₃N₄, and H-g-C₃N₄ samples. The plots measured over a frequency range of 100 kHz to 0.1 Hz. The whole plots and a magnified view of the 0–150 Ω range are provided in Figure S7. The arc radius of the semicircle in the EIS profile is indicative of the interfacial charge transfer resistance. S-g-C₃N₄ exhibits the smallest semicircle radius, indicating the lowest charge transfer resistance. This is consistent with its highest photocurrent density among the g-C₃N₄ series (Figure 10a) and its superior photocatalytic activity (Figure 6a), confirming that sulfur doping effectively reduces charge transfer resistance and enhances charge separation efficiency. ZT-g-C₃N₄ presents an interesting case: it exhibits a high photocurrent density (Figure 10a) but a relatively large EIS semicircle radius. This apparent contradiction can be explained by considering the different physical processes probed by these techniques. The high photocurrent indicates efficient bulk charge separation, facilitated by the heterojunctions formed between g-C₃N₄, TiO₂, and ZIF-67. However, the large EIS arc suggests high interfacial charge transfer resistance,

likely due to non-ideal band alignment at the heterojunction interfaces, creating additional barriers for charge transfer to the electrode. Furthermore, multiple interfaces in the ternary composite that introduce cumulative impedance. These results collectively demonstrate that bulk charge separation efficiency and interfacial charge transfer are not necessarily correlated with photocatalytic activity. The overall photocatalytic performance depends on a combination of factors, including charge transport properties, band edge positions, and surface chemical environment. For S-g-C₃N₄, the optimal combination of moderate bulk separation, low interfacial resistance, and favorable band edge positions yields the highest photocatalytic activity.

To determine the flat band potential and charge carrier type of the samples, Mott-Schottky measurements were performed at frequencies of 500, 1000, and 1500 Hz in 0.5 M Na₂SO₄ (pH = 7) using an Ag/AgCl reference electrode. The results are presented in Figure 10c, and the key parameters for S-g-C₃N₄ are summarized here. As shown in Figure 10c, the Mott-Schottky plots of S-g-C₃N₄ exhibit positive slopes across all measured frequencies, confirming that S-g-C₃N₄ is an n-type semiconductor. The flat band potential (E_{fb}) was determined from the x-intercept of the linear region of the $1/C^2$ vs. potential plot. For S-g-C₃N₄, the flat band potential is -0.528 V vs. NHE. For n-type semiconductors, the conduction band minimum (CBM) is typically 0.1–0.2 V more negative than the flat band potential. Therefore, the CBM of S-g-C₃N₄ is estimated to be approximately -0.63 V vs. NHE. Combining this with the band gap energy ($E_g = 2.48$ eV) obtained from the Tauc plot (Figure 5b), the valence band maximum (VBM) is calculated to be $+1.85$ V vs. NHE ($CBM + E_g = -0.63 + 2.48 = +1.85$ V). The Mott-Schottky plots for C-g-C₃N₄, H-g-C₃N₄, CC-g-C₃N₄, and ZT-g-C₃N₄ are provided in Figure S5.

2.4. Proposed Photocatalytic Mechanism

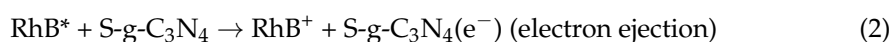
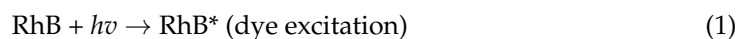
Finally, based on our experimental data and relevant literature, we analyzed the catalytic mechanism of S-g-C₃N₄. The band edge positions have important implications for the photocatalytic mechanism. As discussed above, the CBM of S-g-C₃N₄ at -0.63 V vs. NHE is sufficiently negative to reduce O₂ to $\cdot O_2^-$ ($E^0(O_2/O_2^-) = -0.33$ V vs. NHE), which is thermodynamically favorable. However, the VBM at $+1.85$ V vs. NHE is slightly lower than the thermodynamic potential for direct oxidation of OH[−] to $\cdot OH$ (approximately $+1.99$ V vs. NHE at neutral pH). This suggests that the $\cdot OH$ radicals detected in radical trapping experiments (Figure 8) are likely generated via an indirect pathway involving $\cdot O_2^-$ and H₂O₂ intermediates, rather than direct hole oxidation. This interpretation is consistent with the radical trapping results, where the $\cdot OH$ scavenger (IPA) almost completely inhibited the reaction, while the $\cdot O_2^-$ scavenger (AA) showed measurable but less pronounced inhibition, indicating that $\cdot OH$ is the dominant reactive species.

Pristine g-C₃N₄ primarily absorbs blue-green light with wavelengths below 460 nm [27]. Sulfur doping significantly optimizes its band structure through atomic orbital hybridization and lattice defect modulation. Orbital hybridization between the 3p orbitals of S atoms and the 2p orbitals of C/N species in g-C₃N₄ induces impurity energy levels in the bandgap, thus reducing the bandgap width to around 2.48 eV. This enables the utilization of a broader spectrum of solar energy to excite electron-hole (e^- - h^+) pairs.

Beyond band gap narrowing, sulfur doping influences charge transfer pathways primarily through the introduction of mid-gap states that serve as electron traps. The replacement of N atoms by larger S atoms in the g-C₃N₄ lattice introduces structural distortion and creates localized defect states within the band gap. These mid-gap states act as temporary trapping sites for photogenerated electrons, effectively separating them from the holes remaining in the valence band. This spatial separation prolongs the lifetime

of charge carriers, as directly evidenced by TRPL measurements (Figure S6), where S-g-C₃N₄ exhibits a significantly longer average fluorescence lifetime (6.7 ns) compared to pristine g-C₃N₄ (5.4 ns). The trapped electrons can then be transferred to adsorbed O₂ molecules to form superoxide radicals ($\cdot\text{O}_2^-$), while the accumulated holes participate in direct oxidation or react with H₂O/OH⁻ to generate hydroxyl radicals ($\cdot\text{OH}$). This charge separation and transfer mechanism is further supported by the transient photocurrent response (Figure 10a), where S-g-C₃N₄ exhibits a photocurrent density 2–3 times higher than pristine g-C₃N₄, and by EIS analysis (Figure 10b), which shows a reduced charge transfer resistance for S-g-C₃N₄.

Thermodynamic analysis shows that the VBM of S-g-C₃N₄ (+1.85 V vs. NHE) is insufficient to directly oxidize H₂O/OH⁻ to $\cdot\text{OH}$ (requires > +1.99 V vs. NHE). More importantly, as shown in Figure 8, the degradation efficiency remains >95% even when e⁻, h⁺, and $\cdot\text{O}_2^-$ are scavenged. If the classical mechanism were operative, blocking these species would halt the reaction. Therefore, the classical mechanism cannot explain the experimental observations. Based on the radical trapping results and band structure analysis, the classical semiconductor photocatalysis mechanism is invalid for explaining RhB degradation over S-g-C₃N₄. Instead, we propose a dye-sensitized photocatalysis mechanism.



RhB molecules adsorbed on the S-g-C₃N₄ surface are excited by visible light to form RhB* (excited state). The excited RhB* injects electrons into the conduction band of S-g-C₃N₄. These injected electrons can be transferred to adsorbed O₂ to form reactive oxygen species. The oxidized RhB⁺ species undergo degradation through subsequent reactions. Based on the above analysis, the photocatalytic mechanism of S-g-C₃N₄ is proposed as illustrated in Figure 11.

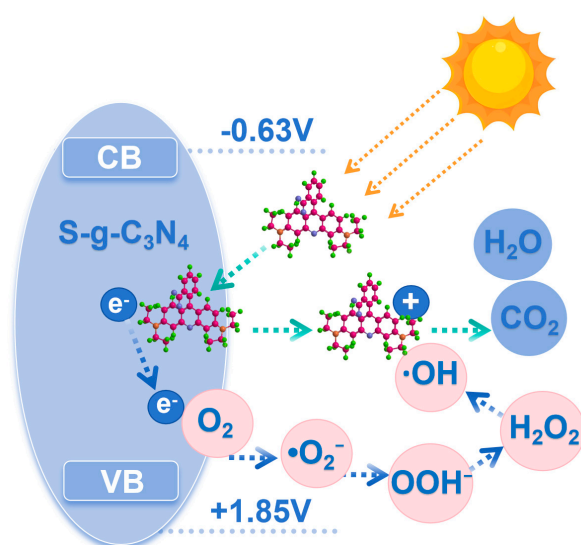


Figure 11. Schematic illustration of the S-g-C₃N₄ photocatalytic mechanism. In the figure, the orange arrow represents sunlight, the green arrow denotes the degradation route of RhB, and the blue arrow indicates the transformation pathway of reactive oxidative species.

3. Materials and Methods

3.1. Materials and Reagents

Melamine and 2-Methylimidazole are from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Phosphoric acid (H_3PO_4), Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Cerium nitrate heptahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 7\text{H}_2\text{O}$), Titanium dioxide (TiO_2) and Anhydrous ethanol are from Shanghai Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Trithiocyanuric acid and rhodamine B (RhB) were supplied by Shandong Keyuan Biochemical Co., Ltd. (Shandong, China). Methanol was sourced from Tianjin Damao Chemical Reagent Factory (Tianjin, China).

3.2. Synthesis Methods

Two types of pristine g- C_3N_4 were prepared using different methods. For C-g- C_3N_4 , 5 g of melamine was placed in an alumina crucible with a cover and heated in a tube furnace to 550 °C at a ramp rate of 2 °C/min under static air. The temperature was maintained at 550 °C for 2 h, and then the product was naturally cooled to room temperature. The resulting yellow solid was ground into a fine powder for further use.

For H-g- C_3N_4 , 750 mg of melamine was dispersed in 75 mL of deionized water followed by the addition of 530 μL of H_3PO_4 . The mixture was stirred magnetically for 1 h until the melamine was completely dissolved. The suspension was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 10 h. After naturally cooling to room temperature, the obtained precipitate was collected by centrifugation, washed several times with deionized water and ethanol, and dried at 80 °C overnight. The dried product was then calcined under the same conditions as C-g- C_3N_4 (550 °C, 2 h, ramp rate 5 °C/min) to obtain H-g- C_3N_4 .

S-g- C_3N_4 was synthesized via a calcination method using melamine and trithiocyanuric acid as precursors. Specifically, 630 mg of melamine and 60 mg of trithiocyanuric acid with 1 mL water were thoroughly ground in an agate mortar for 15 min to ensure homogeneous mixing. The mixture was transferred to an alumina crucible with a cover and heated in a tube furnace to 550 °C at a ramp rate of 2 °C/min under static air. The temperature was maintained at 550 °C for 2 h, after which the product was naturally cooled to room temperature. The resulting S-g- C_3N_4 powder was collected and used without further purification. The sulfur doping content was optimized by varying the amount of trithiocyanuric acid (6, 12, 24 and 120 mg) while keeping the melamine amount constant at 630 mg. The detailed synthesis flowchart is shown in Figure 12.

The CeCoOx/g- C_3N_4 composite (CC-g- C_3N_4) was prepared using a metal–organic framework (MOF)-derived method. First, 0.1455 g $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.932 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 4 mL of methanol. Separately, 200 mg of as-prepared C-g- C_3N_4 was dispersed in 50 mL of methanol by ultrasonication for 2 h. The metal nitrate solution was then added to the g- C_3N_4 dispersion under vigorous stirring. Subsequently, 13 mL of methanol containing 1.2315 g of 2-methylimidazole was slowly added dropwise. The mixture was stirred at room temperature for 24 h to allow for MOF growth. The resulting precipitate was collected by centrifugation, washed several times with methanol, and dried at 60 °C overnight. Finally, the obtained powder was calcined at 400 °C for 2 h with a ramp rate of 2 °C/min under air atmosphere to convert the CeCo-MOF precursor to CeCoOx, yielding the CC-g- C_3N_4 composite.

The ZIF-67/g- C_3N_4 - TiO_2 (ZT-g- C_3N_4) composite was synthesized through an in situ growth method. First, 0.1 g of as-prepared C-g- C_3N_4 - TiO_2 composite was dispersed in 40 mL of methanol by ultrasonication for 2 h. Then, 0.657 g 2-methylimidazole and 0.582 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added to the dispersion, maintaining a molar ratio of 1:4. The mixture was magnetically stirred for 2 h and then allowed to age at room temperature for

24 h. The resulting solid was collected by centrifugation, washed with anhydrous ethanol three times, and dried in an electric thermostatic drying oven at 60 °C for 12 h. The obtained product was denoted as ZT-g-C₃N₄.

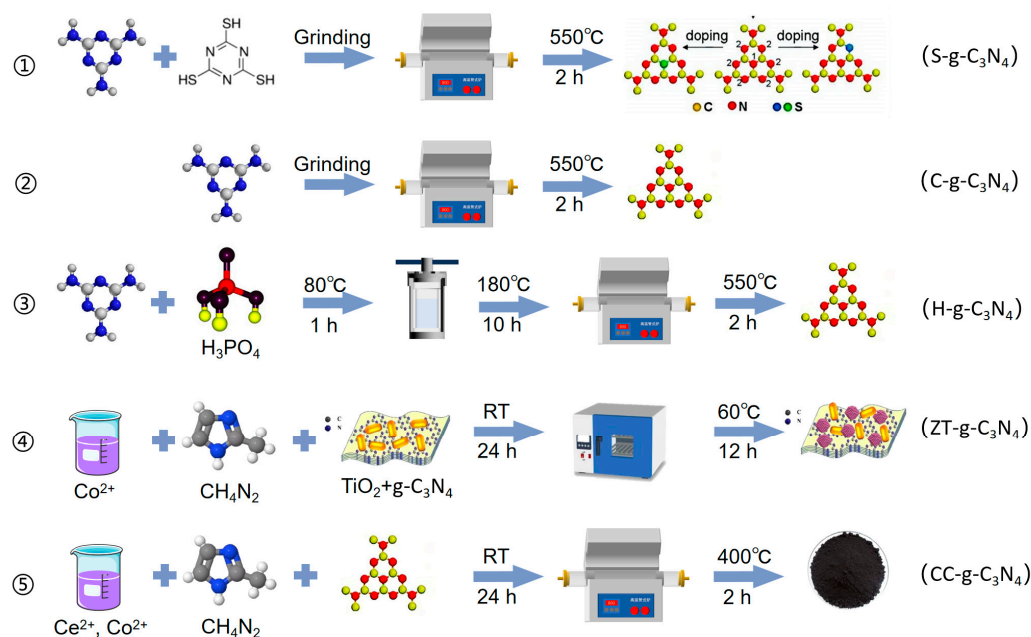


Figure 12. Schematic diagram of the preparation process of g-C₃N₄-based catalysts.

3.3. Structural Characterization

The crystalline phase composition was investigated by X-ray diffraction (XRD, SHIMADZU LabX XRD-6100, Shimadzu, Kyoto, Japan) with Cu K α radiation ($\lambda = 0.15418$ nm), a step size of 0.05°, and operating parameters of 40 kV and 30 mA. Scanning electron microscopy (SEM, Sigma 300, Carl Zeiss, Oberkochen, Germany) and transmission electron microscopy (TEM, JEM-F200, equipped with an Ultim Max 80 EDS detector, JEOL Ltd., Kyoto, Japan) was used to examine the surface morphology of the samples. The specific surface area and pore structure of the powder samples were analyzed by Brunauer–Emmett–Teller (BET) method using a surface area and porosity analyzer (ASAP 2460, Micromeritics, Norcross, GA, USA). The light absorption properties of the solid samples were measured, and the bandgap energy was calculated based on data obtained from ultraviolet–visible spectrophotometry (UV–Vis, UV3600i Plus, Shimadzu, Kyoto, Japan) in the wavelength range of 200–800 nm. The elemental composition and chemical valence states were characterized by X-ray photoelectron spectroscopy (XPS, Scientific K-Alpha, Thermo Fisher Scientific, Waltham, MA, USA). The concentrations of leached sulfur were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 5110, Agilent Technologies, Santa Clara, CA, USA). Time-resolved photoluminescence (TRPL, FLS1000, Edinburgh Instruments, Livingston, UK) decay spectra were recorded using a fluorescence spectrophotometer equipped with a pulsed laser. The decay curves were fitted with a bi-exponential function: $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where τ_1 and τ_2 are the fast and slow decay lifetimes, and A_1 and A_2 are the corresponding amplitudes. The average lifetime (τ_{avg}) was calculated using the equation:

$$\tau_{\text{avg}} = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2) \quad (6)$$

3.4. Photocatalytic Activity Measurement

The photocatalytic performance was evaluated by monitoring the degradation of Rhodamine B (RhB). In a typical procedure, 30 mg of the photocatalyst was dispersed

into 30 mL of an aqueous RhB solution to obtain a RhB solution with a concentration of 10 mg/L. In order to establish an adsorption–desorption equilibrium, the suspension was stirred in the dark for 30 min firstly. Subsequently, the solution was irradiated under a 300 W xenon lamp. During the 60 min irradiation period, 2 mL aliquots of the suspension were sampled at 15 min intervals. Each aliquot was immediately filtered through a syringe filter, and the absorbance of the filtrate was measured at 553 nm.

The RhB concentration corresponding to the measured absorbance was determined using a pre-established calibration curve, expressed by the equation: $y = 0.0316x + 0.0025$ ($R^2 = 0.9998$), where y is the absorbance of the solution and x is the RhB concentration (mg/L). The degradation efficiency (η , %) of RhB was then calculated according to Equation (7):

$$\eta = (1 - C/C_0) \times 100 \quad (7)$$

where C_0/C is the relative concentration, C_0 is the initial concentration and C is the concentration at time t of RhB (mg/L), respectively.

3.5. Radical and Charge Carrier Trapping Experiments

To pinpoint the dominant core active species responsible for the photocatalytic degradation of RhB over g-C₃N₄, trapping experiments were conducted within the aforementioned photocatalytic system. Specific scavengers were introduced at a concentration of 1 mmol/L: silver nitrate (AgNO₃) for electrons (e[−]), disodium ethylenediaminetetraacetate (EDTA-2Na) for holes (h⁺), isopropanol (IPA) for hydroxyl radicals (·OH), and ascorbic acid (AA) for superoxide radicals (·O₂[−]). The subsequent variation in the degradation efficiency of RhB upon the addition of each scavenger was monitored to determine the contribution of the corresponding reactive species.

4. Conclusions

In this study, a series of g-C₃N₄-based photocatalysts (C-g-C₃N₄, H-g-C₃N₄, S-g-C₃N₄, CC-g-C₃N₄, and ZT-g-C₃N₄) were successfully synthesized. Among them, S-g-C₃N₄ exhibited the optimal photocatalytic activity for RhB degradation, achieving nearly complete removal within 15 min under simulated sunlight, with a rate constant (0.196 min^{−1}) significantly higher than that of pristine g-C₃N₄. Sulfur doping via melamine and trithiocyanuric acid reactions enabled uniform substitutional doping (C-S bonds) into the g-C₃N₄ framework, inducing the formation of curled porous nanosheets with enhanced surface area and active sites. Band structure analysis by Mott–Schottky and VB-XPS revealed a conduction band minimum of −0.63 V vs. RHE and a valence band maximum of +1.85 V vs. RHE. Transient photocurrent, EIS, and TRPL measurements confirmed that S-g-C₃N₄ exhibits enhanced charge separation and prolonged carrier lifetime (6.7 ns vs. 5.4 ns for pristine g-C₃N₄), attributed to S-induced mid-gap states that act as electron traps. The catalyst demonstrated good adaptability across pH 6–11 and in the presence of common coexisting anions (Cl[−], NO₃[−], CO₃^{2−}), with excellent structural and chemical stability over five cycles. Post-reaction characterization confirmed preserved crystal structure and morphology, with negligible sulfur leaching (<0.1 ppm). This work provides understanding of sulfur incorporation, offering insights for the rational design of high-performance g-C₃N₄-based photocatalysts for wastewater treatment.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16040316/s1>, Figure S1: XPS pattern of H-g-C₃N₄; Figure S2: XPS pattern of CC-g-C₃N₄. (a) High-resolution C 1s spectra; (b) High-resolution N 1s spectra; (c) High-resolution O 1s spectra; (d) High-resolution Co 2p spectra; (e) High-resolution Ce 3d spectra; (f) Survey spectra; Figure S3: XPS pattern of ZT-g-C₃N₄. (a) High-resolution C 1s spectra;

(b) High-resolution N 1s spectra; (c) High-resolution Ti 2p spectra; (d) High-resolution Co 2p spectra; (e) Survey spectra.; Figure S4: SEM photo of (a) S-g-C₃N₄, (b) ZT-g-C₃N₄, Frequency distribution of (c) particle size (based on 100 particle counts from Figure S4a), (d) layer thickness (based on 50 particle counts from Figure 2a), Frequency distribution of particle size of (e) ZT-g-C₃N₄ (based on 100 particle counts from Figure 2d), (f) CC-g-C₃N₄ (based on 30 particle counts from Figure 2e), and TEM photo of (g) C-g-C₃N₄, sheet thickness of (h) S-g-C₃N₄ (based on 20 sheet counts from Figure 2a), and (i) H-g-C₃N₄ (based on 20 sheet counts from Figure 2c); Figure S5: Mott-Schottky plot of (a) C-g-C₃N₄, (b) H-g-C₃N₄, (c) CC-g-C₃N₄ and (d) ZT-g-C₃N₄; Figure S6: TRPL plot of (a) C-g-C₃N₄, (b) H-g-C₃N₄, (c) CC-g-C₃N₄ and (d) ZT-g-C₃N₄; Figure S7: EIS plots for all samples (a) over a wider frequency range and (b) A magnified view of the range of 0 to 150 ohm·cm²; Table S1: Pseudo-first-order and pseudo-second-order kinetic rate constants (k_1 and k_2), correlation coefficients (R^2), and standard deviations (SD) for RhB degradation over different samples (0 to 15 min); Table S2: Pseudo-first-order and pseudo-second-order kinetic rate constants (k_1 and k_2), correlation coefficients (R^2), and standard deviations (SD) for RhB degradation over different samples (0 to 60 min); Table S3: The comparison of the photocatalyst with the reported works; Table S4: ICP-OES results of sulfur in the reaction solution after five cycles.

Author Contributions: Conceptualization, H.L. and Z.H.; methodology, X.L. and Y.C.; software, X.P.; validation, X.L., J.H. and J.H.; formal analysis, H.L.; investigation, X.L. and Y.C.; resources, X.L., X.P. and J.H.; data curation, X.L., X.P. and J.H.; writing—original draft preparation, X.L., X.P., J.H. and W.T.; writing—review and editing, H.L.; visualization, X.L.; supervision, H.L. and Z.H.; project administration, H.L.; funding acquisition, H.L. and Z.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Guangdong Province Undergraduate Innovation and Entrepreneurship Training Program, grant number 2024012DCXM and Characteristics and Innovation Project of Universities in Guangdong Province (Natural Science), grant number 2023KTSCX178. The APC was funded by Beijing Institute of Technology, Zhuhai first class major program.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding authors.

Acknowledgments: During the preparation of this manuscript, the authors used DeepSeek-V3.2 for the purposes of language improvement. The authors have reviewed and edited the output and take full responsibility for the content of this publication.

Conflicts of Interest: The authors declare no conflicts of interest.

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