

Article

One-Pot In Situ Synthesis of Porous Vanadium-Doped g-C₃N₄ with Improved Photocatalytic Removal of Pharmaceutical Pollutants

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Abstract: The peroxymonosulfate (PMS)-assisted photocatalytic process has shown considerable potential for the treatment of wastewater. g-C₃N₄-based catalysts are widely applied to eliminate organic pollutants in wastewater. However, the bulk catalyst prepared by dicyandiamide has the drawback of a low surface area (10 m²/g), while the porous catalyst prepared by urea suffers from a low catalyst yield based on urea (3.5%). To address these challenges, a porous V-doped carbon nitride (V/CN) was designed through one-step thermal polymerization using urea and dicyandiamide as the carbon nitride precursor and NH₄VO₃ as the V precursor. When the ratio of urea to dicyandiamide was 10:1, the yield of V/CN was improved, while it maintained a rich porous structure with a specific surface area (64.6 m²/g). The synergetic effect of V doping and nanosheet and hollow tubular structures facilitated the separation of photogenerated carriers, leading to boosting the photocatalytic activity of g-C₃N₄ in the PMS system. V/CN(10:1) could completely degrade CBZ within 20 min, exhibiting an equivalent catalytic efficiency comparable to that of V/CN prepared by urea (V/UCN), while markedly surpassing both V/DCN and CN prepared by urea alone (UCN) in performance. This study presents an economical and effective approach for the photocatalytic degradation of pharmaceutical pollutants in aquatic environments.

Keywords: V-doped; graphitic carbon nitride; PMS activation; photocatalysis



Academic Editor: Christos Trapalis

Received: 14 January 2025

Revised: 17 February 2025

Accepted: 19 February 2025

Published: 21 February 2025

Citation: Huang, Y.; Pang, R.; Sun, S.; Chen, X.; Chen, F.; Lu, W. One-Pot In Situ Synthesis of Porous Vanadium-Doped g-C₃N₄ with Improved Photocatalytic Removal of Pharmaceutical Pollutants. *Catalysts* **2025**, *15*, 206. <https://doi.org/10.3390/catal15030206>

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1. Introduction

With the rapid acceleration of industrialization and urbanization, the emission of harmful and toxic organic pollutants has been steadily increasing, thereby posing threats to water quality and human health [1,2]. Persistent organic pollutants (POPs) constitute a category of organic compounds distinguished by their prolonged persistence in the environment, semi-volatility, and high toxicity [3–6]. These pollutants can be transported over long distances through various environmental media, such as the atmosphere, aquatic systems, and living organisms, thus presenting substantial risks to both human health and ecosystems. Carbamazepine (CBZ), a pharmaceutical compound widely used for the treatment of epilepsy and pain relief, is increasingly released into aquatic environments in large quantities [7–9]. The low biodegradability coupled with the high stability of CBZ in water poses a critical challenge in addressing water pollution. Recently, peroxymonosulfate (PMS)-assisted advanced oxidation processes (AOPs) have garnered much attention within

the field of water pollution remediation [10–15]. PMS can be activated by catalysts to generate numerous free radicals with strong redox capabilities, which can degrade various types of refractory organic pollutants. Coupling photocatalytic oxidation technology with PMS oxidation has demonstrated considerable efficacy as a treatment method for pharmaceutical pollutants in water [16,17].

Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$), as an inorganic semiconductor material, has garnered significant attention in the field of photocatalytic degradation of organic pollutants due to its non-toxic nature, environmental compatibility, and visible-light responsiveness [18–21]. The bulk $g\text{-C}_3\text{N}_4$ is typically synthesized from conventional precursors (e.g., cyanamide, dicyandiamide, and melamine) resulting in a high catalyst yield (40–60% based on the precursors). However, the bulk material exhibits a low photocatalytic efficiency, owing to its low specific surface area, weak absorption of visible light, and rapid recombination of photoexcitons [22–26]. Bulk $g\text{-C}_3\text{N}_4$ was found to activate PMS for the CBZ degradation under light irradiation; however, only a low degradation rate of 48% was achieved within 30 min with bulk $g\text{-C}_3\text{N}_4$ using PMS. To improve its photocatalytic performance, $g\text{-C}_3\text{N}_4$ nanosheets with porous structures were synthesized through using urea as a precursor. This porous catalyst possesses a large surface area ($66.3\text{ m}^2/\text{g}$); however, it suffers from a low yield of carbon nitride based on urea ($\sim 3.5\%$), which consequently increases synthesis costs. These problems may hinder their practical applications [27,28]. Therefore, it is essential to develop porous $g\text{-C}_3\text{N}_4$ -based nanocatalysts with improved yields by optimizing the precursors.

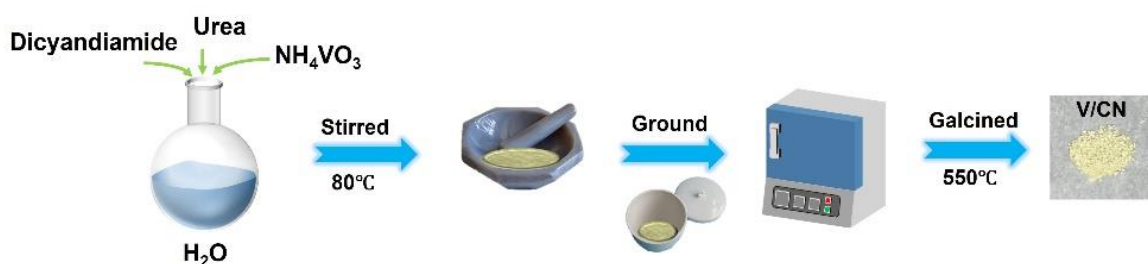
The application of porous $g\text{-C}_3\text{N}_4$ in the treatment of pharmaceutical pollutants is also limited by its low efficiency in solar energy utilization and the rapid recombination of photoexcitons [29,30]. Metal doping has emerged as an effective strategy to enhance photocatalytic performance in wastewater treatment, particularly when combined with PMS oxidation. Various metals, including Mn, Fe, and Cu, have been employed to dope into carbon nitride; however, the removal efficiency of these photocatalysts remains insufficient for practical applications [31–36]. In our previous work, vanadium oxide (VO_x) was loaded first onto porous $g\text{-C}_3\text{N}_4$ to construct a highly effective photocatalyst for the removal of refractory pharmaceutical pollutants in wastewater using PMS as an oxidant [25]. The superior activity can likely be ascribed to the diverse oxidation states and coordination polyhedral structures exhibited by VO_x species. Nevertheless, a relatively high metal content ($8\%\text{VO}_x$) was required to achieve optimized photocatalytic activity. Therefore, it is meaningful to explore the design of V-modified carbon nitride catalysts with lower V content. To date, there have been few investigations into the photocatalytic performance of V-doped materials for the removal of refractory pharmaceutical pollutants in water utilizing PMS as an oxidant [37,38].

In this study, we developed a porous vanadium-doped $g\text{-C}_3\text{N}_4$ catalyst (referred to as V/CN) to improve the PMS activation. The catalysts were synthesized through an economical and straightforward thermal polymerization method using urea and dicyandiamide as precursors for carbon nitride, alongside NH_4VO_3 serving as the vanadium source. The morphology and yield of the V/CN catalyst were tuned by varying the ratio of urea to dicyandiamide. We conducted a comprehensive characterization of the morphology and chemical structure of vanadium-doped catalysts using a variety of analytical instruments. Additionally, we investigated in detail how both morphology and V modification influenced the photocatalytic degradation of CBZ in wastewater with PMS. For the first time, V-doped CN catalysts were applied to eliminate organic pharmaceuticals from wastewater via a combination of photocatalysis and PMS oxidation. Furthermore, we proposed a mechanism for CBZ degradation with V/CN as the catalyst. Our findings provide novel insights into designing effective photocatalysts for removing pharmaceutical-contaminated water.

2. Results and Discussion

2.1. Fabrication Process of V/CN Catalysts

The V-doped $g\text{-C}_3\text{N}_4$ was fabricated through a one-step thermal polymerization method, using urea and dicyandiamide as precursors for carbon nitride, while ammonium metavanadate (NH_4VO_3) served as the vanadium precursor. The preparation route is illustrated in Scheme 1. In the initial stage, urea, dicyandiamide, and NH_4VO_3 were thoroughly mixed in an aqueous solution. This mixture was stirred at 80°C to facilitate water removal, and a V-containing complex was obtained, which was subsequently pyrolyzed at 550°C in air. During this process, the V-containing complex underwent polymerization to form graphitic carbon nitride, with vanadium species being immobilized within the $g\text{-C}_3\text{N}_4$ matrix by forming a V-N_x structure simultaneously. Concurrently, abundant gases (e.g., NH_3 , NO , and CO) were generated, resulting in significant volume expansion. As a result of these processes, fluffy V-doped carbon nitride nanosheets were produced. The obtained carbon nitride and V-doped samples were denoted as $\text{CN}(x:y)$ and $\text{V/CN}(x:y)$, where $x:y$ represents the mass ratio of urea to dicyandiamide. The carbon nitride and V-doped samples synthesized from urea alone are referred to as UCN and V/UCN , while those derived solely from dicyandiamide are designated as DCN and V/DCN , respectively. The mass fraction of the initial mass of V to the total mass of V-doped carbon nitride catalyst was about 3%.



Scheme 1. A synthetic route diagram of the V/CN catalyst.

2.2. Characterizations of V/CN Catalysts

The influence of vanadium doping and different precursors for carbon nitride on the catalyst yield based on precursors is presented in Table S1. The yields for UCN, $\text{CN}(10:1)$, and DCN were 3.5%, 7.4%, and 62.6%, respectively, while the yields for V/UCN , $\text{V/CN}(10:1)$, and V/DCN were 3.7%, 7.9%, and 45%. These results indicated that the introduction of dicyandiamide into urea could significantly enhance the yield of carbon nitride. Furthermore, it appeared that vanadium doping did not have a notable impact on the yield. The impact of vanadium doping and different precursors for carbon nitride on the porous structure of $g\text{-C}_3\text{N}_4$ -based catalysts was investigated through N_2 sorption measurement. As illustrated in Figure 1a, all samples exhibited typical IV adsorption isotherms accompanied by H3-type hysteresis loops, which implied the presence of mesoporous structures [26,39]. The BJH pore size analysis presented in Figure 1b revealed that pore size distributions for V/DCN , V/UCN , $\text{V/CN}(10:1)$, and $\text{CN}(10:1)$ were similar; moreover, these samples displayed a wide range of pore sizes, predominantly concentrated between 0 and 60 nm. Specifically, the average pore sizes for $\text{CN}(10:1)$ and $\text{V/CN}(10:1)$ were found to be 13.5 nm and 12.9 nm, respectively. A summary of the specific surface areas and pore volumes for these catalysts is provided in Table S1. The specific surface areas measured for DCN, UCN, and $\text{CN}(10:1)$ were found to be $6.7\text{ m}^2/\text{g}$, $66.3\text{ m}^2/\text{g}$, and $44.7\text{ m}^2/\text{g}$, respectively; notably, the specific surface area of UCN was nearly ten times greater than that of DCN, while that of $\text{CN}(10:1)$ increased up to approximately 6.7 times compared with DCN. This indicated that using urea as a precursor facilitated the formation of a nanosheet

with porous structure, which enhanced the number of active sites [40]. After vanadium modification, the specific surface areas of V/DCN, V/UCN, and V/CN(10:1) increased to $20.3 \text{ m}^2/\text{g}$, $100.6 \text{ m}^2/\text{g}$, and $64.6 \text{ m}^2/\text{g}$, respectively. This indicated that V doping may have partially interfered with the thermal polymerization process of urea and dicyandiamide, thereby modifying the charge distribution on the carbon nitride plane. This alteration may have reduced the electrostatic repulsion on the surface of carbon nitride and decreased its lateral dimensions [41,42]. Consequently, it could facilitate the formation of smaller nanosheets and more porous structures, which in turn exposed a greater number of active sites. This enhancement would promote substrate diffusion from the solvent to both the inner and outer surfaces of the catalyst, thereby effectively participating in photocatalytic reactions. Notably, when the mass ratio of urea to dicyandiamide was 10:1, the yield of the V-doped sample (7.9%) could increase by one fold, compared with V/UCN (3.7%), but it still maintained a rich porous structure with a high surface area ($64.6 \text{ m}^2/\text{g}$).

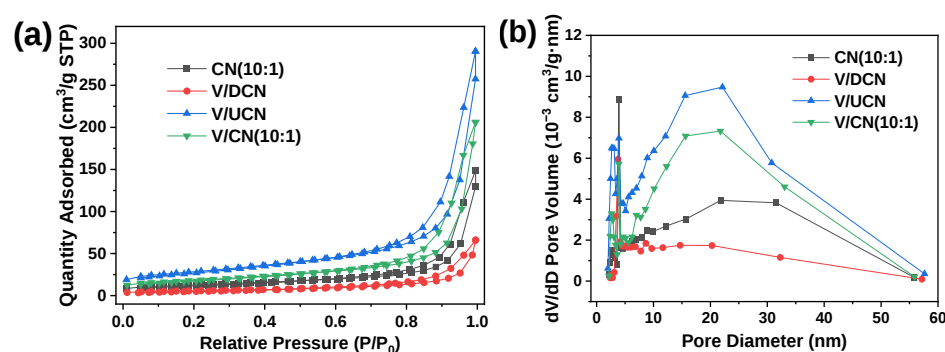


Figure 1. (a) N_2 adsorption/desorption curves and (b) BJH pore size distribution of CN(10:1), V/DCN, V/UCN, and V/CN(10:1).

The influences of different precursors for carbon nitride on the morphologies of V-doped carbon nitride were characterized using SEM. As illustrated in Figure 2a,b, the V/DCN exhibited a dense structure, composed of numerous particles ranging from tens to hundreds of micrometers. In contrast, Figure 2c,d reveal that V/UCN displayed a porous folded nanosheet stacking morphology characterized by high porosity, resembling UCN. Furthermore, as shown in Figure 2e,f, both lamellar and hollow tubular structures were observed in the V/CN(10:1) sample. The nanosheets with porous structures formed through thermal polymerization of urea were retained; however, part of the lamellae curled to create a more ordered hollow tube structure by the introduction of dicyandiamide [43]. SEM mapping for V/CN(10:1), presented in Figure 2g, confirmed that the elements C, N, O, and V were uniformly distributed throughout the carbon nitride structure. The V content in V/CN(10:1), determined by EDS and inductively coupled plasma optical emission spectroscopy (ICP-OES), was found to be 1.96% (Figure S1) and 2.35%, respectively. Figure 3 presents the TEM images of CN(10:1) and V/CN(10:1). As illustrated in Figure 3a–c, the CN(10:1) sample supported the stacked nanosheets characterized by a porous structure. In contrast, Figure 3d,e reveal that V/CN(10:1) primarily consisted of smaller nanosheet stacks. The HR-TEM image in Figure 3f reflects the presence of the (002) plane of carbon nitride with lattice spacings of about 0.329 nm. Notably, no discernible metal or metal oxide nanoparticles were detected in the HRTEM image, suggesting the absence of metallic V or vanadium oxides within V/CN(10:1). Consequently, combined with SEM mapping results, it can be hypothesized that vanadium may have been incorporated into the carbon nitride framework.

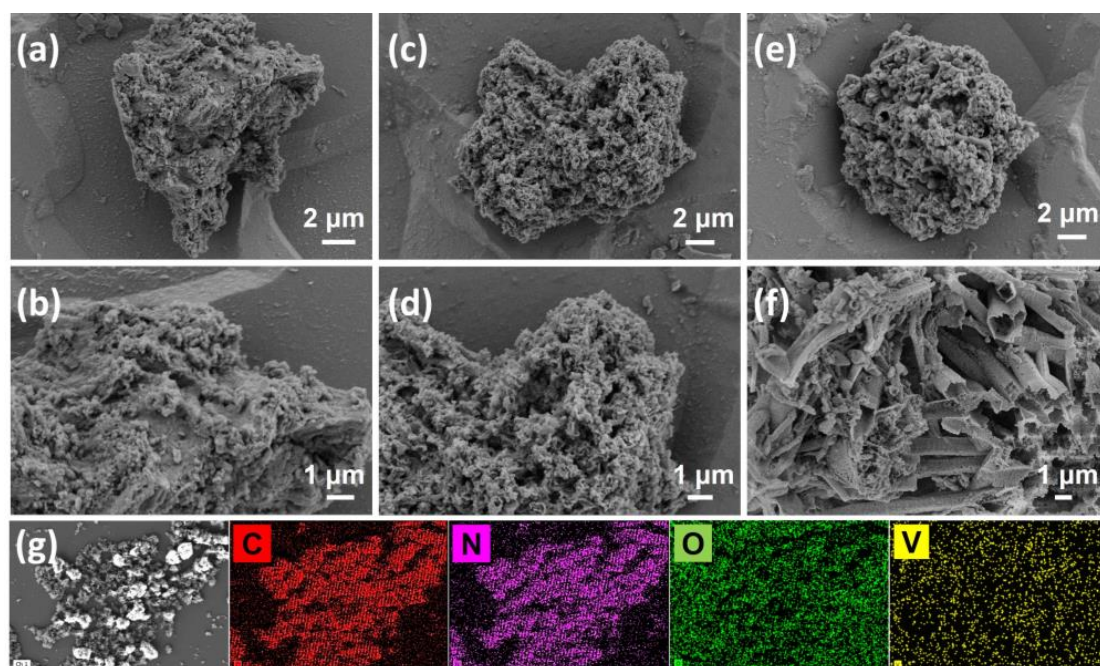


Figure 2. SEM images of (a,b) V/DCN, (c,d) V/UCN, and (e,f) V/CN(10:1) at different magnifications and (g) STEM mapping images of V/CN(10:1) (C, N, O, V elements).

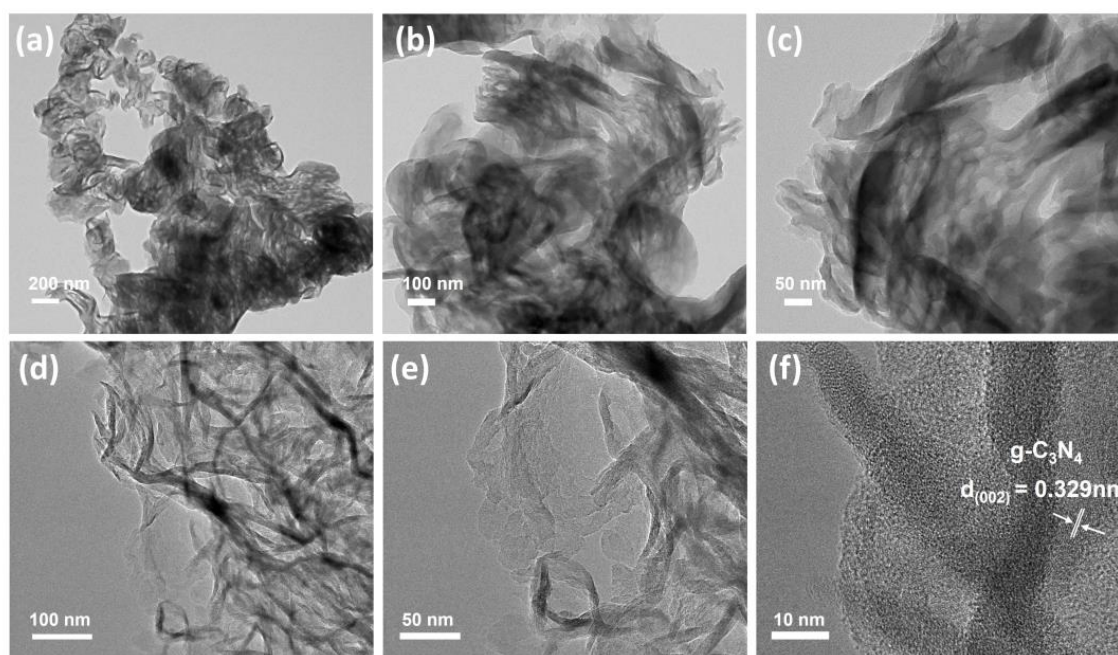


Figure 3. TEM images of (a–c) CN(10:1) and (d,e) V/CN(10:1) and (f) HRTEM images of V/CN(10:1).

The chemical structure of the V/CN materials was characterized by XRD and FTIR. The XRD patterns for various g-C₃N₄ samples, including V-doped g-C₃N₄, are presented in Figure 4a. Distinct peaks were observed at $2\theta = 13.1^\circ$ and 27.4° in all samples, belonging to the (100) and (002) planes of carbon nitride, respectively [44]. Notably, the intensity of the (002) peak for CN(10:1) and DCN exhibited a significant enhancement compared with UCN. The possible reason was that the introduction of dicyandiamide helped the improvement of the regular stacking of the aromatic rings, thereby leading to an increased degree of crystallization [45]. A similar trend was also noted in the V-doped samples. Furthermore, the intensity of the (002) peak for V/CN(10:1) was weaker than that for

CN(10:1), which could be ascribed to incomplete polymerization within the graphitic layer, as well as disruptions in stacking caused by vanadium doping [46,47]. Importantly, no discernible peaks corresponding to metallic V or VO_x species were detected; this finding further supported the notion that vanadium atoms may be uniformly embedded into the polymer backbone. Figure 4b shows the FT-IR spectra of UCN, DCN, CN(10:1), and V/CN(10:1). All the samples had several similar adsorption bands at 3100–3500, 1200–1650, and 810 cm^{-1} , attributed to the stretching vibrations of amino groups, $\text{C}=\text{N}/\text{C}-\text{N}-\text{C}$ groups, and the s-triazine ring, respectively [47]. The intensity of the broad peak in the range of 3000–3500 cm^{-1} exhibited a significant increase after V doping, indicating that the amount of amino groups had risen as a result of this doping process.

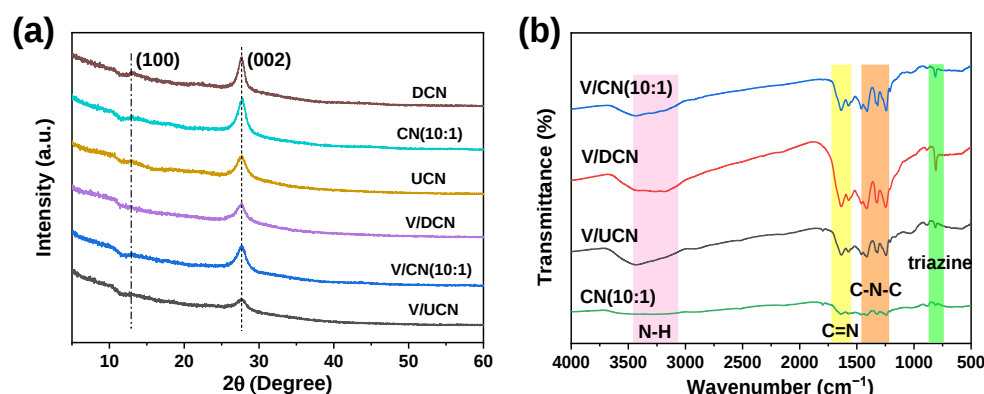


Figure 4. (a) XRD patterns and (b) FT-IR spectra of different catalysts.

XPS was conducted to elucidate the surface composition and chemical states of the g- C_3N_4 -based catalysts. The full spectrum presented in Figure 5a indicates that the g- C_3N_4 samples primarily consisted of C, N, and O elements, whereas V-doped carbon nitride contained C, N, O, and V elements. The C 1s spectra shown in Figure 5b revealed three peaks at 284.6 eV, 286.4 eV, and 288.2 eV for all samples; these corresponded to the graphite C–C bond, the C–O/C–N bond, and the C–N=C bond, respectively [48]. Notably, the atomic ratio of C to N increased from 1.12 for CN(10:1) to 1.14 for V/CN(10:1), suggesting that V doping resulted in a partial loss of nitrogen atoms within the carbon nitride framework, thereby introducing a small amount of nitrogen vacancies. The N 1s spectra depicted in Figure 5c could be deconvoluted into four peaks at 398.7 eV, 400.1 eV, 401 eV, and 404.4 eV; these were attributed to sp^2 N (C–N=C) and sp^3 N–(C)₃ groups, amino functional groups (C–N–H), and π -excitation bonds, respectively [49]. In comparison with CN(10:1), both the C–N=C peak and the C–N–H peak in V/CN(10:1) exhibited shifts of 0.1–0.2 V toward higher binding energies. This phenomenon may be ascribed to a decrease in electron density around N atoms due to V–N bond formation [50,51]. Compared with the undoped sample, the V/CN(10:1) sample exhibited a slight increase in the peak intensity of C–N–H groups. This observation may be associated with the formation of smaller nanosheets by V doping. Furthermore, analysis of the V 2p spectra illustrated in Figure 5d revealed four peaks; specifically, two peaks located at 524.4 eV and 516.8 eV were associated with vanadium in the V(V) state, while two other peaks at 523.3 eV and 516.0 eV corresponded to vanadium in the V(IV) state [25]. The ratios of V(V)/V(IV) observed for V/DCN, V/CN(10:1), and V/UCN were approximately 5.1, 2.0, and 3.5, respectively. The aforementioned analyses confirmed that V species existed in the form of V (V) and V (IV). The V atoms were doped within the carbon nitride structure through the V–N bonds.

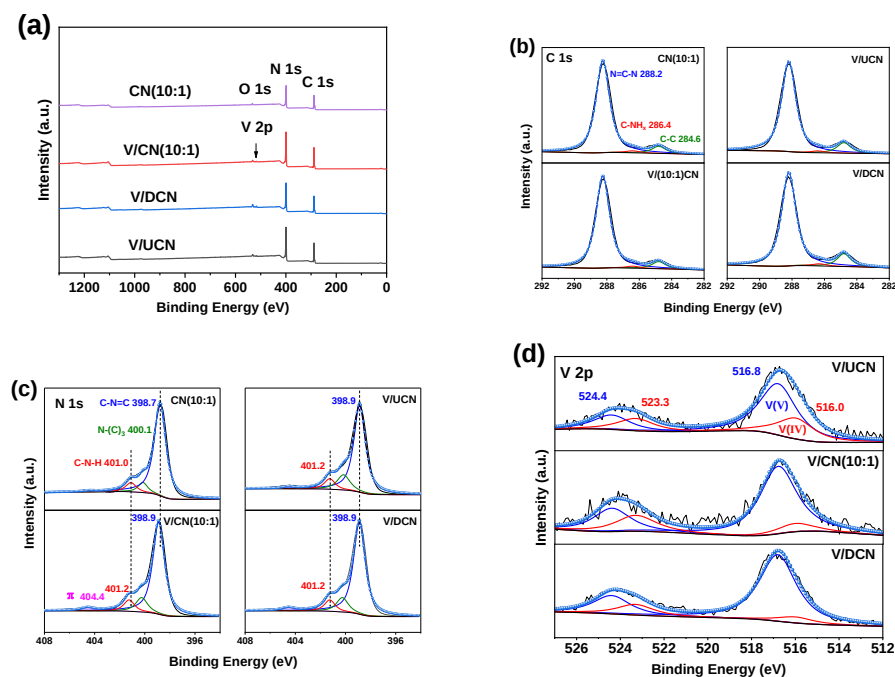


Figure 5. (a) XPS full spectrum, (b) C 1s spectra, (c) N 1s spectra, and (d) V 2p spectra of different carbon nitride and V-doped samples.

UV–vis diffuse reflection spectra were utilized to investigate the optical absorption properties of the samples. As shown in Figure 6, all samples displayed significant absorption in the visible light region, with the absorption edge predominantly located around 460 nm. Notably, compared with UCN and CN(10:1), the absorption edge of DCN displayed a red shift. This phenomenon may be ascribed to the quantum size effect associated with nanosheets in UCN and CN(10:1). Additionally, a color change from light yellow to yellow was observed for UCN, CN(10:1), and DCN. Vanadium doping boosted obviously the light absorption intensity of V/DCN within the wavelength range of 400–750 nm, thereby improving its light harvesting efficiency. Additionally, vanadium modification led to a slight increase in light absorption intensity within the range of 438–600 nm for V/CN(10:1), which may be attributed to the formation of V–N_x bonds. Furthermore, compared with CN(10:1), a slight blue shift in the absorption edge was observed in V/CN(10:1), indicating that the nanosheets in the vanadium-doped sample were smaller [51].

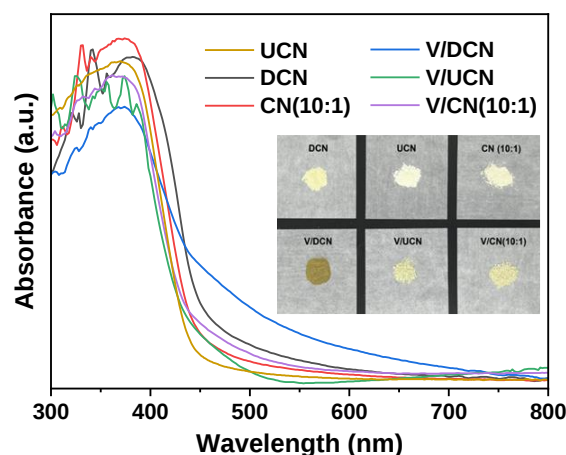


Figure 6. Ultraviolet-visible diffuse reflection spectra of different carbon nitrides and V-doped carbon nitrides.

Transient photocurrent (TPC) analyses were conducted on g-C₃N₄-based catalysts to investigate the behaviors of photogenerated electron–hole separation and transfer. Figure 7a illustrates the photocurrent responses of various carbon nitride and V-doped samples. The current density of V/CN(10:1) was found to be 3.4, 1.4, and 2.1 times higher than those of CN(10:1), V/UCN, and V/DCN, respectively. This enhancement in photocurrent density confirmed that V doping and nanosheet and hollow tubular structures significantly promoted the rapid separation of charge carriers. It was likely that the interaction between nitrogen and vanadium atoms through V–N_x bonds enhanced both the e[−]/h⁺ separation efficiency and charge transfer rate. Furthermore, the larger specific surface area of V/CN(10:1) along with its nanosheet and hollow tube structure provided abundant active sites for interaction with reactants while facilitating their transport through interconnected channels within the catalyst. Figure 7b presents the electrochemical impedance spectroscopy (EIS) Nyquist plots of the samples. Generally, the radius of the Nyquist plot was indicative of the charge transfer resistance; a larger arc radius corresponded to higher charge transfer resistance within the material [52]. Notably, there was no significant difference in the radii among DCN, UCN, and CN(10:1), suggesting that their charge transfer rates were comparable. In contrast, V/CN(10:1) displayed an arc with the smallest radius, signifying more efficient electron–hole separation and expedited charge transfer. The result was in good agreement with TPC analysis. These results implied the excellent catalytic performance of the V/CN(10:1) catalyst.

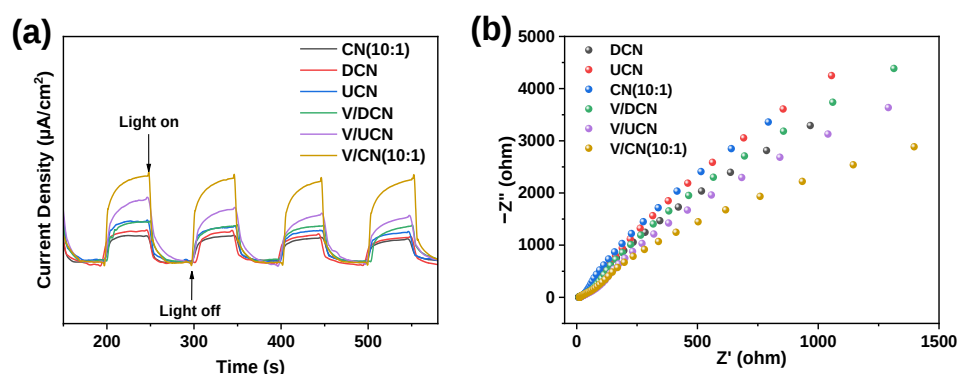


Figure 7. (a) TPC response. (b) EIS Nyquist plots of different carbon nitride and V-doped samples.

2.3. Photocatalytic Performance Evaluation

The photocatalytic degradation of CBZ was employed as a reaction model to investigate the catalytic properties of g-C₃N₄-based materials. Initially, the catalytic performance of V/CN(10:1) catalysts was assessed in different reaction systems. As illustrated in Figure 8a, only 1.3% of CBZ was removed within 30 min using the V/CN(10:1) catalyst in the dark, indicating its low adsorption capacity for CBZ. However, under simulated sunlight conditions, the degradation rate of CBZ increased to 31.7% with the same catalyst over a period of 30 min, demonstrating that V/CN(10:1) exhibited moderate photocatalytic performance. In contrast, when PMS was utilized without any catalyst, the degradation rates of CBZ were recorded at 18.8% and 20.4% after 30 min under dark and light conditions, respectively. These results indicated that only a small amount of CBZ underwent degradation, due to PMS alone, even when coupled with light irradiation. When employing V/CN(10:1) as a catalyst alongside PMS as an oxidant, almost complete degradation of CBZ occurred within 20 min under simulated sunlight irradiation. This finding confirmed that V/CN(10:1) was effective in activating PMS for the photodegradation of CBZ under light irradiation.

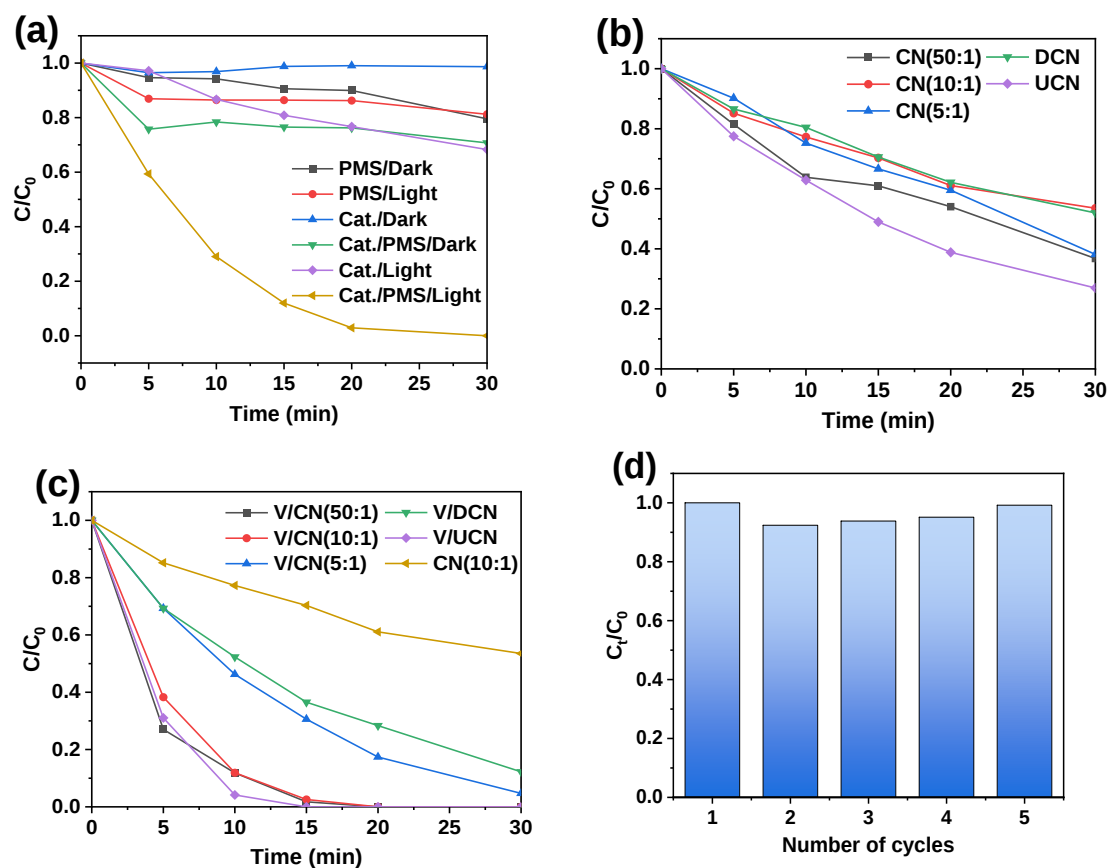
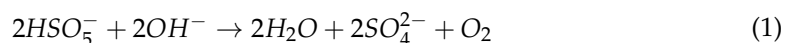


Figure 8. (a) Degradation performance of CBZ by V/CN(10:1) under different reaction conditions. Effects of different proportions of urea and dicyandiamide on (b) the CN/PMS/light system and (c) the V/CN/PMS/light system. (d) Recycling test of V/CN(10:1) for CBZ degradation. Conditions: [CBZ] = 25 μ M; [PMS] = 0.2 mM; [catalyst] = 0.1 g/L; initial [pH] = 7.0; [T] = 25 $^{\circ}$ C.

In order to determine the optimal ratio of urea to dicyandiamide, we investigated the impact of this ratio on the photocatalytic performance of g-C₃N₄ and V-doped samples. As illustrated in Figure 8b, when DCN was employed as a catalyst, approximately 30% of CBZ was converted within 30 min under 0.2 mM PMS and light irradiation. Increasing the mass ratio of urea to dicyandiamide generally enhanced the photocatalytic activity of carbon nitride, with UCN exhibiting the highest level of activity. The modification of vanadium was found to significantly improve the photocatalytic performance of carbon nitride. As shown in Figure 8c, under similar reaction conditions, V/DCN achieved a CBZ degradation rate of 71.6% within 20 min. When the ratio of urea to dicyandiamide increased from 5:1 to 10:1, the degradation rates for V-doped carbon nitride rose dramatically to 82.6%, and 100%, respectively. Notably, further increasing this ratio to either 50:1 or pure urea (1:0) did not yield significant enhancements in photocatalytic efficiency; both samples were able to completely degrade CBZ within 20 min. Although V/UCN demonstrated outstanding photocatalytic activity, its low yield posed challenges for industrial applications. Considering both catalyst yield and photocatalytic performance comprehensively, it was concluded that V/CN(10:1) represented the optimal catalyst for treating CBZ in aqueous environments. Furthermore, we observed that V/CN(10:1) exhibited good catalytic recyclability, as depicted in Figure 8d; there was no noticeable decline in photocatalytic activity throughout five cycles during our experiments.

Figure S2 investigates the effects of various reaction parameters, including PMS dosage, catalyst dosage, initial pH, and anionic species, on the catalytic performance of V/CN(10:1). As illustrated in Figure S2a, when the catalyst dosage was increased from 0.1 g/L to

0.3 g/L, a slight enhancement in degradation efficiency was observed; however, CBZ could still be degraded within 20 min with the low catalyst dosage of 0.1 g/L. Considering cost-effectiveness, a catalyst dosage of 0.1 g/L was selected for this study. From Figure S2b, it is evident that increasing the PMS dosage from 0.05 mM to 0.2 mM significantly improved the catalytic activity from 89.8% to nearly 100% within 20 min. This suggested that elevating the PMS concentration enhanced the catalyst activity at a low level of PMS concentration. However, further increases in PMS dosage to 0.3 mM and 0.4 mM did not yield any additional improvement in degradation rate; thus, a PMS concentration of 0.2 mM was chosen for subsequent experiments. Figure S2c demonstrates that the V/CN(10:1) catalyst exhibited excellent catalytic performance across a pH range of 3–7. The degradation efficiency decreased under alkaline conditions, which could be attributed to the following factors: (1) When the pH of the solution exceeded 9.4, PMS dissociated into sulfate radical anions (SO_5^{2-}), which exhibited lower oxidation potential compared with the peroxymonosulfate ion (HSO_5^-). (2) Under alkaline conditions, PMS decomposed into sulfate ions (SO_4^{2-}) according to Equation (1). (3) Excessive OH^- in the system led to a negatively charged catalyst surface, thereby hindering effective interactions between the catalyst and both PMS and CBZ [53,54]. The influence of various anions, such as Cl^- , SO_4^{2-} , and H_2PO_4^- , on photocatalytic activity was also examined. The results are presented in Figure S2d. Notably, no significant decrease in catalytic efficiency was detected within the V/CN(10:1)/PMS/light catalytic system in the presence of these anionic species (Cl^- , SO_4^{2-} and H_2PO_4^-). These findings indicated that the V/CN(10:1) possessed good adaptability under acidic and weakly alkaline conditions, as well as in solutions containing different inorganic salts.



Total organic carbon (TOC) analysis was used as an effective method to assess deep oxidation activity of V-doped catalyst. As illustrated in Figure 9, after 60 min of reaction under the set conditions, the TOC removal rate of CN(10:1) was 27.1%, while the TOC removal rates of V/DCN, V/UCN, and V/CN(10:1) were 45.1%, 59.45%, and 52.9%, respectively. The TOC removal of V/CN(10:1) was increased by 95% compared with pure $\text{g-C}_3\text{N}_4$. The results demonstrated that V doping and porous structure significantly enhanced the mineralization efficiency of carbon nitride, facilitating the conversion of macromolecular organic compounds into CO_2 .

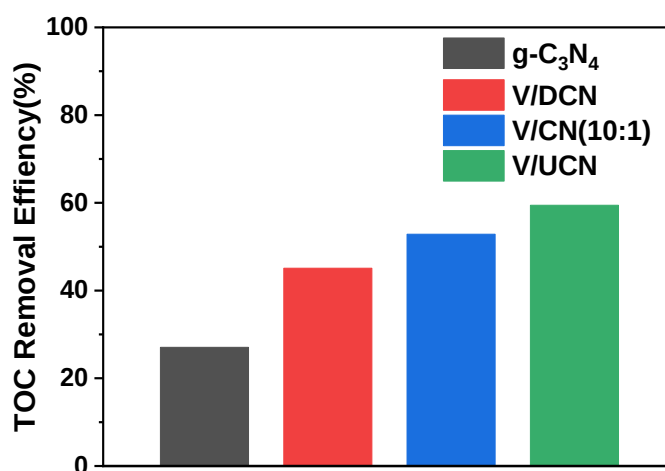


Figure 9. TOC removal rate of the catalyst/PMS/light system after 60 min. Conditions: [CBZ] = 25 μM , [PMS] = 0.2 mM, [catalyst] = 0.1 g/L, initial [pH] = 7.0, T = 40 °C.

2.4. Reaction Mechanism

Various trapping agents were introduced into the system to investigate the impact of reactive oxygen species (ROS) on the degradation process of CBZ. Different trapping agents, including potassium iodide (KI), tert-butanol (TBA), p-benzoquinone (p-BQ), ethanol (EtOH), and histidine (L-His), were added into the V/CN(10:1)/PMS/light system [26,55], with the experimental results illustrated in Figure 10a. It is known that TBA serves as the primary trapping agent for $\bullet\text{OH}$, while EtOH functions as the main trapping agent for both $\text{SO}_4\bullet^-$ and $\bullet\text{OH}$ radicals. The degradation rate of CBZ was partially inhibited by TBA, indicating that $\bullet\text{OH}$ was one of the principal active species involved in the photocatalytic process. This inhibitory effect was further intensified with the addition of an equivalent concentration of EtOH to the reaction system, suggesting that $\text{SO}_4\bullet^-$ also played a role in the photocatalytic reaction. It is important to note that neither TBA nor EtOH completely suppressed CBZ degradation; thus, other active species were likely generated within the photocatalytic system. The degradation rate of CBZ also decreased significantly upon the addition of KI, indicating that h^+ was one of the primary active species involved in the photocatalytic process. Similarly, adding L-His and p-BQ led to notable reductions in degradation rates, suggesting that singlet oxygen ($^1\text{O}_2$) and superoxide radicals ($\text{O}_2\bullet^-$) also played critical roles in this photocatalytic mechanism. Therefore, within the V/CN(10:1)/PMS/light system, $\text{SO}_4\bullet^-$, $\bullet\text{OH}$, h^+ , $^1\text{O}_2$, and $\text{O}_2\bullet^-$ emerged as major contributors to CBZ degradation processes.

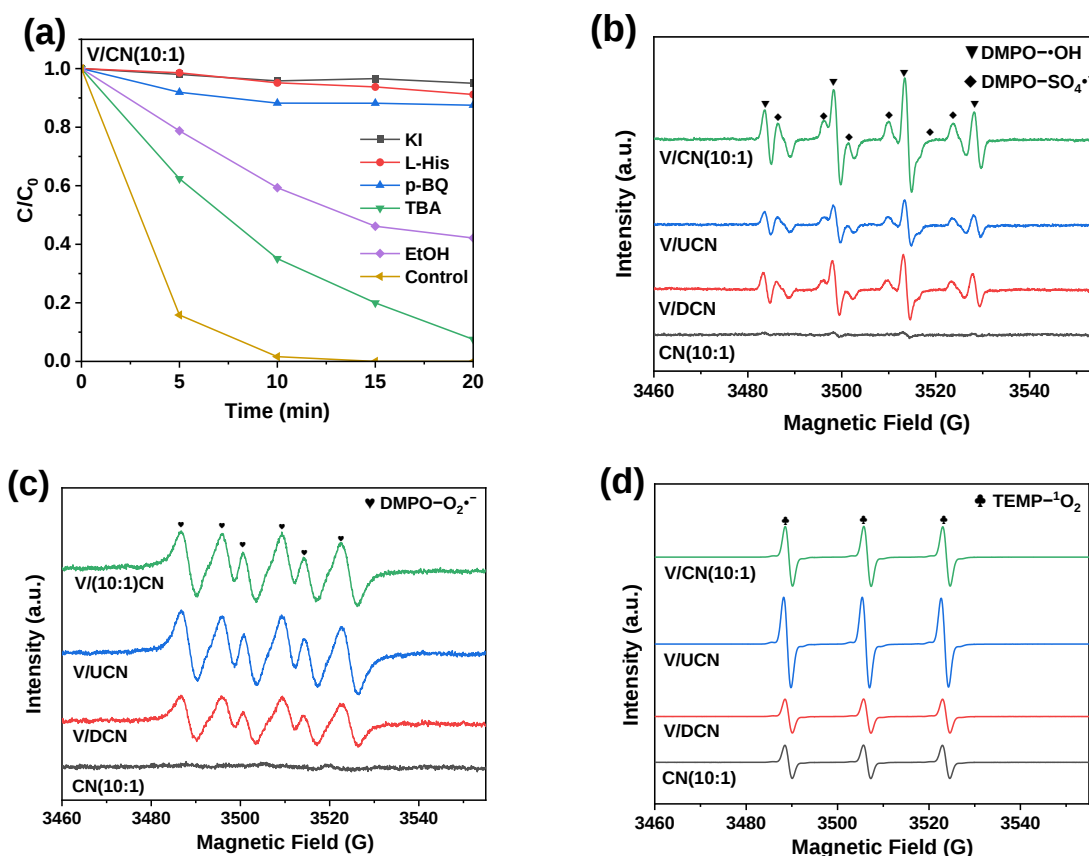
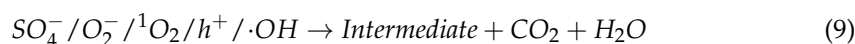
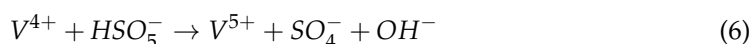
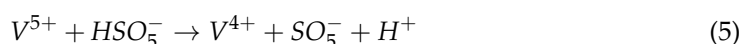
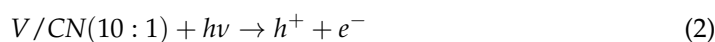
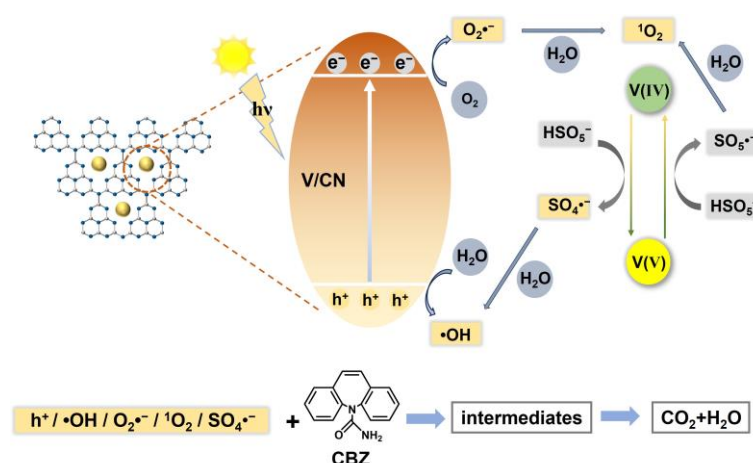


Figure 10. (a) Degradation performance of V/CN(10:1) with different capture agents (KI, TBA, p-BQ, EtOH, and L-His) under simulated sunlight irradiation; (b) DMPO spin-trapping ESR spectra in aqueous solution; (c) DMPO spin-trapping ESR spectra in methanol solution; and (d) TEMP spin-trapping ESR spectra in aqueous solution in the presence of V/CN(10:1), V/UCN, V/DCN, and CN(10:1) under simulated sunlight irradiation. Conditions: [CBZ] = 25 μM , [catalyst] = 0.1 g/L, [PMS] = 0.2 mM, [KI] = 0.1 mM, [EtOH] = [TBA] = 10 mM, [p-BQ] = [L-His] = 1 mM.

The generation of reactive radicals during the catalytic process in the V/CN/PMS/light system was further investigated using electron spin resonance (ESR) techniques. 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was employed to detect $\bullet\text{OH}$ and $\text{SO}_4\bullet^-$ radicals in aqueous solutions, as well as $\text{O}_2\bullet^-$ radicals in methanol solutions. Additionally, $^1\text{O}_2$ was detected using 2,2,6,6-tetramethyl-4-piperidinol (TEMP) in aqueous solutions [56]. As illustrated in Figure 10b, the V-doped samples exhibited quadruple state peaks for DMPO- $\bullet\text{OH}$ with an intensity ratio of 1:2:2:1 and six characteristic peaks for DMPO- $\text{SO}_4\bullet^-$ with a signal intensity ratio of 1:1:1:1:1:1. The signal intensity of V/CN(10:1) was significantly higher than that observed for V/UCN and V/DCN. In contrast, CN(10:1) displayed weak signals for both $\bullet\text{OH}$ and $\text{SO}_4\bullet^-$. These results indicated that V/CN(10:1) effectively promoted the activation of PMS to generate $\text{SO}_4\bullet^-$ and $\bullet\text{OH}$ radicals during photocatalysis. The characteristic signal peaks of DMPO- $\text{O}_2\bullet^-$ can be seen in the g- C_3N_4 -based samples shown in Figure 10c. Notably, the detectable signal intensity for CN(10:1) was very weak; however, the $\text{O}_2\bullet^-$ radical signals generated by V/CN(10:1) and V/UCN were considerably stronger than those from CN(10:1). As depicted in Figure 10d, all samples exhibited characteristic triple signal peaks for TEMP- $^1\text{O}_2$ with a signal intensity ratio of 1:1:1. The intensity of the $^1\text{O}_2$ peaks for V/CN(10:1) was slightly weaker than that for V/UCN but was 1.78 times as much as that for CN(10:1). Combining the findings from the ESR techniques and the trapping agent experiments revealed that $\text{SO}_4\bullet^-$, $\bullet\text{OH}$, $^1\text{O}_2$, $\text{O}_2\bullet^-$, and h^+ collectively contributed to the remarkable catalytic activity of V/CN(10:1) for CBZ degradation. Moreover, compared with CN(10:1) and V/DCN, V/CN(10:1) demonstrated enhanced activation capability toward PMS, resulting in increased production of $\text{SO}_4\bullet^-$, $\bullet\text{OH}$, $^1\text{O}_2$, and $\text{O}_2\bullet^-$ radicals, thereby leading to its superior photocatalytic performance.

Based on the results of the above analysis, a possible mechanism for the degradation of CBZ in the V/CN(10:1)/PMS/light system was proposed. The schematic is shown in Scheme 2. When V/CN(10:1) was irradiated by light, the electrons were excited to conduction band, and a pair of charge carriers were generated on the surface of the catalyst (Equation (2)). The photogenerated e^- reacted with dissolved oxygen in water to produce $\text{O}_2\bullet^-$ (Equation (3)). The hole h^+ oxidized H_2O to form $\bullet\text{OH}$, which directly participated in the degradation of CBZ (Equation (4)), wherein HSO_5^- could be oxidized by V(V) to form $\text{SO}_5\bullet^-$, which was reduced to V(IV) (Equation (5)). In addition, V(IV) further reduced HSO_5^- to form $\text{SO}_4\bullet^-$, which was oxidized to V(V) (Equation (6)). The cyclic redox reaction of V(V) and V(IV) within the V/CN(10:1) ensured the generation of massive $\text{SO}_5\bullet^-$ and $\text{SO}_4\bullet^-$ during the photocatalytic reaction. Furthermore, the $\text{SO}_5\bullet^-$ reacted with water to produce $^1\text{O}_2$ (Equation (8)). The $\bullet\text{OH}$ were also generated through the reaction of $\text{SO}_4\bullet^-$ with water (Equation (7)). The reactive radicals generated by the V/CN(10:1) ultimately oxidized CBZ to CO_2 and H_2O (Equation (9)) [25].





Scheme 2. Proposed mechanism of the V/CN(10:1)/PMS/light system on CBZ degradation.

2.5. CBZ Degradation Pathway

To elucidate the oxidation pathway of CBZ, ultra-performance liquid chromatography coupled with high-definition mass spectrometry (UPLC/HDMS) in positive ion mode was employed to detect the intermediates generated during the CBZ degradation by V/CN(10:1) in the presence of PMS. Table S2 summarizes the molecular formulas, retention times, and relative molecular masses of potential intermediates. The plausible degradation pathways are illustrated in Figure 11. Initially, PMS was activated by V/CN(10:1) under light conditions, leading to the generation of abundant ROS. The olefinic double bonds of CBZ underwent oxidation by ROS, resulting in the formation of P1 ($m/z = 252.1$). Subsequently, P1 could be hydrolyzed to yield both P2 ($m/z = 270.1$) and P3 ($m/z = 270.1$). Additionally, P1 may also transform into P4 ($m/z = 252.1$) through ring opening and further oxidation by ROS. P2 experienced a series of transformations including oxidation, rearrangement, and deamidation of its amide group ($-\text{CONH}_2$), ultimately producing P5 ($m/z = 180.1$). Ultimately, compounds P3, P4, and P5 were further degraded into smaller organic molecules that were subsequently mineralized into carbon dioxide and water.

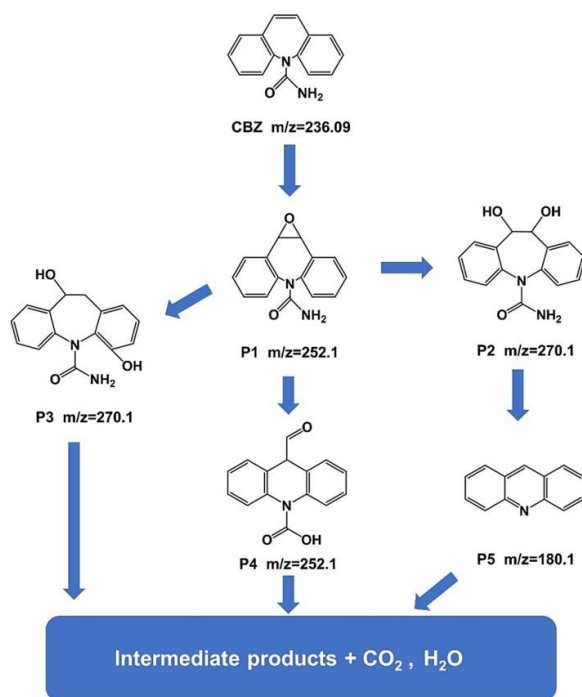


Figure 11. A proposed degradation pathway of CBZ in the V/CN(10:1)/PMS/light system.

3. Experimental Section

3.1. Materials

Dicyandiamide ($C_2H_4N_4$) and 5,5-dimethyl-1-pyrroline N-oxide (DMPO, $C_6H_{11}NO$) was purchased from Beijing J&K Technology Co., Ltd., Beijing, China. Carbamazepine (CBZ, $C_{15}H_{12}N_2O$), ammonium metavanadate (NH_4VO_3), sodium chloride (NaCl), sodium sulphate (Na_2SO_4), sodium carbonate (Na_2CO_3), sodium dihydrogen phosphate (NaH_2PO_4), sodium hydroxide (NaOH), sodium chloroacetate ($ClCH_2COONa$), p-Benzoquinone (p-BQ, $C_6H_4O_2$), L-Histidine (L-His, $C_6H_9N_3O_2$), potassium iodide (KI), and 2,2,6,6-Tetramethylpiperidine (TEMP, $C_9H_{20}N_2$) were purchased from Aladdin Biochemical Technology Co., Ltd., Shanghai, China. Urea ($CO(NH_2)_2$), tert-butanol (TBA, $C_4H_{10}O$), and ethanol (EtOH, C_2H_6O) were purchased from Maclean's Biochemical Technology Co., Ltd., Shanghai, China.

3.2. Synthesis of V-Doped g- C_3N_4 Catalyst

Briefly, 10 g of urea, a specified amount of dicyandiamide, and NH_4VO_3 were dissolved in 15 mL of deionized water. The solution was then stirred at 80 °C for 12 h to ensure complete removal of water. Subsequently, the mixture was transferred to a covered ceramic crucible and heated in a muffle furnace at 550 °C for 2 h. The resulting product was designated as V/CN(x:y), where x:y denotes the mass ratio of urea to dicyandiamide. The products synthesized solely from urea and dicyandiamide were referred to as UCN and DCN, respectively. Following doping with V atoms, the products were named V/UCN and V/DCN accordingly. The mass fraction of the initial mass of V relative to the total mass of the V-doped carbon nitride catalyst is approximately 3%.

3.3. Characterization

The chemical structures of the synthesized g- C_3N_4 -based catalysts were characterized using Fourier transform infrared spectroscopy (FT-IR; Nicolet is50, Thermo Fisher Scientific, Waltham, MA, USA), X-ray diffraction (XRD; D8 Discover, Bruker, Karlsruhe, Germany), and X-ray photoelectron spectroscopy (XPS; Thermo Scientific K-Alpha, Thermo Fisher Scientific, Waltham, MA, USA). The morphology of the catalysts was analyzed via field emission scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS; Gemini-500, Carl Zeiss AG, Oberkochen, Germany) and transmission electron microscopy (TEM; JEM-2100, JEOL, Tokyo, Japan). The Brunauer–Emmett–Teller (BET) surface area and pore volume of the prepared catalysts were determined from nitrogen adsorption isotherms at 77 K using a surface area and porosity analyzer (BET; APSP 2460, Micromeritics, Norcross, GA, USA). The optical absorption spectra of the as-prepared samples were obtained through UV-Vis diffuse reflectance spectroscopy (DRS; Lambda 950, PerkinElmer, Waltham, MA, USA). Ultra-performance liquid chromatography/high-definition mass spectrometry (UPLC/HDMS) in positive ion mode was employed to detect intermediates generated within the photocatalytic system. Additionally, electron paramagnetic resonance spectroscopy (EPR, A300, Bruker, Karlsruhe, Germany) was utilized to identify various reactive radical species such as $SO_4^{\bullet-}$, $\bullet OH$, $O_2^{\bullet-}$, and 1O_2 captured by DMPO or TEMP in the photocatalytic system.

3.4. Photocatalytic Tests

The catalytic activity of the catalyst was investigated through the degradation of carbamazepine (CBZ). All reactions were conducted in 40 mL glass vials. Following the addition of 2 mg of catalyst powder to 20 mL of a CBZ solution (25 μM), the mixture was sonicated for 10 min to achieve adsorption equilibrium. Subsequently, PMS was introduced, and the vials were placed on a shaker within a solar simulation device (Q-SUN Xe-1, Q-Lab,

Cleveland, OH, USA) for photocatalytic reaction. The concentration of CBZ at various reaction times was analyzed using ultra-high-performance liquid chromatography (HPLC, Waters, Milford, MA, USA). An acetonitrile-water eluent with a volume ratio of 40:60 and a flow rate of 0.30 mL min^{-1} served as the mobile phase. The photo-degradation efficiency was evaluated by calculating C/C_0 , where C_0 represents the initial concentration of CBZ and C denotes the remaining concentration at specific time intervals. In both acidic and alkaline systems, pH adjustments were made prior to irradiation by adding either $0.1 \text{ M H}_2\text{SO}_4$ or NaOH . The mineralization rate was determined using a total organic carbon analyzer (TOC-LCPH; Shimadzu, Kyoto, Japan).

4. Conclusions

In this study, vanadium-doped carbon nitride was synthesized through a one-step thermal polymerization process, utilizing urea and dicyandiamide as precursors for carbon nitride and NH_4VO_3 as the vanadium source. The effects of the urea-to-dicyandiamide ratio and vanadium doping on the catalyst yield, structure, and photocatalytic performance were systematically investigated. The findings indicated that when the urea-to-dicyandiamide ratio was set at 10:1, the yield of the V-doped sample was doubled compared with that of V/UCN. This sample maintained a nanosheet and hollow tubular structures with a high surface area. It was likely that vanadium was incorporated into the carbon nitride framework in the form of V-N_x bonds within V/CN(10:1). Consequently, V/CN(10:1) exhibited superior photocatalytic activity for CBZ degradation, compared with both CN(10:1) and V/DCN; its performance was comparable to that of V/UCN. Furthermore, this catalyst had good catalytic reusability, in which the degradation efficiency remained above 95% after five reaction cycles. During the photocatalytic process, key active species such as $\text{SO}_4^{\bullet-}$, $\bullet\text{OH}$, $^1\text{O}_2$, $\text{O}_2^{\bullet-}$, and h^+ played pivotal roles in CBZ degradation. Compared with CN(10:1) and V/DCN, more $\text{SO}_4^{\bullet-}$, $\bullet\text{OH}$, $^1\text{O}_2$, and $\text{O}_2^{\bullet-}$ radicals could be produced by the activation of PMS by V/CN(10:1), thereby contributing to its excellent photocatalytic performance. The degradation pathway within the V/CN/PMS/light system was elucidated through the detection of intermediates produced during catalytic reactions using UPLC-MS. This study established a foundation for the development of efficient photocatalysts aimed at treating pharmaceutical pollutants in water.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/catal15030206/s1>, Figure S1: EDS spectrum of V/CN(10:1). Figure S2: The photocatalytic activity of V/CN(10:1) under (a) different catalyst concentrations, (b) different concentrations of PMS, (c) different pH conditions, and (d) different inorganic salt ions. Table S1: Catalyst yield based on precursors and BET surface area and total pore volume of various samples. Table S2: Main information on intermediates in degradation systems.

Author Contributions: Original draft preparation, investigation, and validation. Y.H., R.P. and S.S.; Review, editing, and funding acquisition, X.C.; Data curation and validation, F.C. and W.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Baima Lake Laboratory Joint Funds of the Zhejiang Provincial Natural Science Foundation of China (LBMHY24E060003), the Scientific Research Foundation of Zhejiang Sci-Tech University (19212450-Y), and the Fundamental Research Funds of Zhejiang Sci-Tech University (23212112-Y).

Data Availability Statement: The authors can confirm that all relevant data are included in the article.

Conflicts of Interest: The authors do not have any financial or non-financial interests that are directly or indirectly related to the work submitted for publication.

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