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Improvement in Structure and Visible Light Catalytic Performance of g-C₃N₄ Fabricated at a Higher Temperature

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Abstract: A highly-efficient graphitic carbon nitride (g-C₃N₄) photocatalyst for visible light photodegradation of rhodamine B (RhB) and methyl orange (MO) simulating dyeing wastewater was synthesized by the thermal polycondensation of melamine. The photocatalysts were characterized by TG-DTG-DSC, XRD, EA, XPS, FT-IR, SEM, TEM, BET, PL and UV-vis DRS. The results showed that the photocatalytic performance of g-C₃N₄ at a higher calcination temperature was significantly enhanced, and its photocatalytic activities for the photodegradation of RhB and MO were remarkably improved by 64.91% and 41.83%, respectively, which was mainly attributed to the satisfactory crystallinity, stable graphene-like structure, large surface area, and excellent optical properties. It was found that •O₂[−] radicals and •OH radicals were the main active species for the photodegradation process by the free radicals trapping experiments and ESR analysis. The photodegradation mechanism of g-C₃N₄ was proposed predicated using the characterization results.

Keywords: g-C₃N₄; photodegradation; dyeing wastewater; thermal polymerization; crystallinity; active species

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1. Introduction

The world energy demand has primarily depended on gradually depleting fossil fuels such as coal, oil and natural gas [1]. This phenomenon has caused massive energy shortages, in addition to bringing about increasingly severe environmental pollution. Thus, the development and utilization of earth-abundant photocatalysts to convert inexhaustible solar energy into chemical energy are expected to become one of the most promising methods [2–4]. At present, photocatalysts are generally divided into metal oxides/sulfides (TiO₂ [5], ZnS [6], etc.), non-metal semiconductors (g-C₃N₄ [7], P [8], etc.), and precious metal semiconductors (PtSe₂ [9], Ag₃PO₄ [10], etc.).

However, in the former, the wide band gap of metal oxides restricts their use of solar energy [11], and the metal sulfides show poor stability and corrosion resistance during the application [12]; the latter contains precious metals making it much more expensive [13]. Hence, non-metal semiconductors, especially graphitic carbon nitride (g-C₃N₄), have attracted significant attention due to the great visible light response, strong corrosion resistance, good stability, and easy structure adjustment [14–17]. The history of C₃N₄ originated in the early days of 1989 when Liu and Cohen replaced the Si in β-Si₃N₄ with C to obtain a β-C₃N₄ structure with a higher strength than diamond [18]. Until 1996, Teter and Hemley speculated the five structures of C₃N₄, namely α-C₃N₄, β-C₃N₄, cubic-C₃N₄, pseudocubic-C₃N₄ and graphite-C₃N₄, through the first-principles calculations [19]. Compared with the other four high-strength spatial network crystal structures, g-C₃N₄ had a graphitic stacking two-dimensional layered structure and unique energy band characteristics [20], which could harvest visible light and make it at the edge of the appropriate conduction band and valence band for various potential applications.

Until 2009 the research team of Wang and Kazunari first successfully used g-C₃N₄ to catalyze the reduction of water to produce hydrogen under visible light [21]. After that, researchers have conducted various studies on g-C₃N₄ in the photocatalysis field, such as photocatalytic pollutant degradation [22,23], photocatalytic decomposition of water to produce hydrogen and oxygen [24], photocatalytic organic synthesis [25], and photocatalytic oxygen reduction [26,27]. Xue [22] synthesized a MoS₂/g-C₃N₄ photocatalyst by the in situ polycondensation for RhB degradation. It was found that the addition of MoS₂ was beneficial to improving the photocatalytic activity of MoS₂/g-C₃N₄, and its photodegradation rate achieved 97.8%. Zeng [26] prepared the PEI/g-C₃N₄ via grafting cationic polyethyleneimine (PEI) onto g-C₃N₄ to enhance photocatalytic H₂O₂ production. The results showed that the unique electronic interaction in PEI/g-C₃N₄ promoted O₂ reduced to H₂O₂, and its H₂O₂ generation activity was 25 times better than that of the original g-C₃N₄.

Although a variety of studies have been conducted on g-C₃N₄, almost all are aimed at improving its catalytic activity through doped, modified, compounded approaches, and pure g-C₃N₄ was only used as a control group. As known, pure g-C₃N₄ can be universally fabricated via simple thermal polymerization of organic precursors rich in nitrogen, including melamine [28], dicyandiamide [29], and urea [30]. In the previous research, the preparation temperature of pure g-C₃N₄ was selected in the range that did not reach its initial decomposition temperature (<600 °C). Guo [17] used melamine and urea as the raw materials to synthesize the g-C₃N₄ photocatalyst by thermal polycondensation at 550 °C for 3 h. It was found that when the molar ratio of melamine and urea was 1:1, the decolorization rate of the photocatalyst to MB was about 75% after 240 min of light. Yu [31] synthesized the g-C₃N₄ photocatalyst by the thermal polycondensation method using melamine as the raw material at 550 °C for 4 h, and found that the decolorization rates of RhB and MO were 85.9% and 67.4% after 120 min of light, respectively. Whereas there are rare reports on the pure g-C₃N₄ produced at higher calcination temperatures, even near the complete decomposition temperature. Meanwhile, few reports focused on the microstructural transfer of pure g-C₃N₄ during the preparation [17,22,23,25]. More interestingly, in this paper, we found that the microstructure of g-C₃N₄ was markedly changed during the synthesis step, consequently, the photocatalytic activities also varied in the photodegradation test. Based on the above, melamine was used as the precursor to synthesize the g-C₃N₄ photocatalyst by the thermal polymerization method at different higher calcination temperatures, including 700 °C, which was close to the complete decomposition temperature, and then its microstructure transfer was studied. The crystal structure, chemical composition, microstructure, surface area and optical features of the as-prepared photocatalyst were characterized in detail. Subsequently, the photocatalytic activities of g-C₃N₄ were evaluated by measuring the photodegradation removal of rhodamine B (RhB) and methyl orange (MO) simulating dyeing wastewater under visible light. The reusability of the photocatalyst was also studied. Finally, the photodegradation mechanism of g-C₃N₄ was proposed based upon the characterization.

2. Results and Discussion

2.1. Characterization of Photocatalysts

2.1.1. Morphology and Thermal Analysis

The yields and colors of all samples are shown in Table 1. It can be found that the yield of the sample decreased as the calcination temperature increased. When the temperature rose to 750 °C, the CN-750 sample volatilized completely and no product was collected. The phenomenon was caused by the continuous deamination and polycondensation of melamine during the heating process [31]. Moreover, the chemical bonds of the generated g-C₃N₄ were continuously destroyed at higher temperatures, which promoted its decomposition to generate nitrogen and cyano fragments, leading to a reduction of product yield. The yield changes in production can be confirmed by the thermal analysis (Figure 1). It was observed from Figure 1a that melamine began to decompose at 250 °C

and completely decomposed at 350 °C. There was a robust endothermic peak when the mass significantly reduced, which was ascribed to the thermal condensation deamination of melamine. Melamine underwent structural reorganization in the thermal polycondensation reaction, continuously released NH_3 , and finally polymerized into a stable $\text{g-C}_3\text{N}_4$ system. Compared with melamine, the thermal stability of CN-700 (Figure 1b) was greatly improved. CN-700 began to decompose when the temperature was over 580 °C, and when the temperature rose to 750 °C, CN-700 was completely decomposed into gases, such as ammonia and hydrogen cyanide, resulting in no product being acquired at 750 °C.

Additionally, from the photograph of all products with the same mass of 0.50 g in Table 1, the CN-X color became darker as the calcination temperature increased. The polycondensation degree of the sample was enhanced when the temperature increased, which changed its photoelectric properties and made a darker color of the product. Moreover, the stacked state of the product gradually loosened with the temperature increasing. Clearly, the CN-700 sample presented the loosest stacked state than the others, indicating that it had the maximum volume and its internal structure was more loose and porous, which led to an improvement in surface area and pore volume. The increased surface area and pore volume can be verified by subsequent N_2 adsorption–desorption analysis.

Table 1. Yield and color comparison of all samples.

Samples	CN-450	CN-500	CN-550	CN-600	CN-650	CN-700	CN-750
Yield (wt%)	60.0	58.3	56.2	49.5	45.0	33.8	—

Figure 1. TG-DTG-DSC curve of (a) melamine and (b) CN-700.

2.1.2. Structure and Composition Analysis

The XRD patterns of the CN-X samples were assayed in Figure 2. The CN-450 and CN-500 products had incomplete polymerization, and were crystal structures with different phases including melam and melem, resulting in some characteristic peaks of nitrogen oxide compounds existing. When the temperature rose to above 550 °C, the CN-550, CN-600, CN-650, CN-700 samples displayed similar characteristic diffraction peaks near 13.0° and 27.3° , which was in line with the typical graphene-like hexagonal phase of $\text{g-C}_3\text{N}_4$ (JCPDS 87-1526) [32], meaning that graphene-like $\text{g-C}_3\text{N}_4$ was generated. The diffraction peak around 13.0° ascribed to the (100) plane was the distance of the repeating unit in the plane of the conjugate layer, corresponding to the macrocyclic structure between the tri-s-triazine units. The typical dominant peak near 27.3° designated to the (002) plane was a

typical graphite-layered structure, corresponding to the interlayer stacking of aromatics [33]. When the calcination temperature rose from 550 °C to 700 °C, it was observed that the diffraction peak shape of the (002) plane became sharper, and the diffraction angle 2θ shifted to a larger angle direction, from 27.357° for CN-550 to 27.743° for CN-700. This fact indicated that the sample formed at the higher temperature had a higher polymerization degree and better crystallinity, resulting in a greater force between the layers, and was more conducive to the progress of the condensation reaction. Moreover, the lattice spacing of CN-X gradually reduced to 0.321 nm as the calcination temperature rose, which was less than the ideal crystalline g-C₃N₄ ($d = 0.340$ nm). This compact structure was due to the electronic localization and strong interlayer force. The above results confirmed that CN-700 had a more substantial polymerization degree and better crystallinity than other samples, which was advantageous to enhance its photocatalytic activity [32].

Figure 2. XRD patterns of samples.

The CN-700 was analyzed by XPS to reveal its composition and chemical valence (Figure 3). It was clear that C, N and O elements were detected in the XPS survey in Figure 3a. The O1s peak might be elicited from the surface adsorbed oxygen species. Obviously, the peaks of N1s located at 398.50, 400.10, 401.20, and 404.10 eV were ascribed to the C=N, C-N, the free amino group, and π excitations [17,32], respectively (Figure 3b). The peaks of C1s in Figure 3c at 284.60 eV and 288.00 eV belonged to the C-C bond and the sp^2 -hybridized C atom in g-C₃N₄, respectively [34]. Meanwhile, it was found in the FT-IR spectra of the CN-X samples (Figure 4) that the strong bands in the range of 1700–1200 cm^{−1} belonged to the structural characteristic peaks of C=N and C-N [23]. The characteristic band at about 801 cm^{−1} was the stretching vibration peak caused by the triazine structure in g-C₃N₄ [33]. The above supported the results of XRD and XPS, which further proved that the products calcined at over 550 °C were graphene-like g-C₃N₄. Furthermore, it was found that the broad band of 3500–3000 cm^{−1} (Figure 4) corresponded to the stretching vibration of N-H, indicating that some amino groups remained in CN-X. With the increase in temperature, the distribution range of absorption peaks within this range became narrow, indicating that the internal structural order of CN-X was positively improved, which was also consistent with the crystallinity trend in XRD.

Figure 3. XPS spectra of CN-700 sample: (a) XPS survey; (b) N1s spectra; (c) C1s spectra.

Figure 4. FT-IR spectra of CN-450, CN-500, CN-550, CN-600, CN-650, and CN-700.

The EA of different samples is shown in Table 2. As the calcination temperature increased, the N, H contents of CN-X gradually decreased, while the C content showed an opposite tendency. This was attributed to the escape of H atoms and part of the N atoms in the form of NH_3 during the heating process, leaving C atoms and part of the N atoms.

It was observed that when the calcination temperature rose to 550 °C, the contents of the H and N atoms declined seriously, while at higher temperatures of 600, 650 and 700 °C, they were released comparably. The above showed that the CN-550, CN-600, CN-650, CN-700 products displayed a complete graphene-like layered g-C₃N₄ formation, greatly improving the stability of the product. Hence, the remaining H and N atoms of products, in this case, were not easy to lose. Moreover, the $n(\text{N/C})$ value in the CN-X gradually decreased with the increase in calcination temperature, tending to the theoretical value of g-C₃N₄ ($n(\text{N/C}) = 1.33$), which further verified the above-mentioned XRD and FT-IR; the high temperature was conducive to the enhancement of the polymerization degree and crystallinity of CN-X.

Table 2. EA results of the samples.

Samples	N (wt%)	C (wt%)	H (wt%)	$n(\text{N})/n(\text{C})$
CN-450	64.46	32.84	2.36	1.68
CN-500	64.20	33.27	2.13	1.65
CN-550	62.62	34.82	1.43	1.54
CN-600	62.47	35.11	1.29	1.52
CN-650	62.34	35.79	1.11	1.49
CN-700	62.24	35.85	0.98	1.48

2.1.3. Microstructure Analysis

The SEM images of the CN-X sample are shown in Figure 5. The TEM image of the CN-700 was assayed in Figure 6. As seen, the sample presented a massive accumulation state when the calcination temperature increased (Figure 5). The increase in temperature was beneficial to the formation of debris structures. Remarkably, CN-700 was observed to have a large number of fragmented structures. In addition, it can be seen from Figure 7 that the N₂ adsorption–desorption curves of all samples presented typical IV adsorption curves and H3-type hysteresis loops, which were consistent with the phenomenon that the samples in Figure 5 were stacked with a lamellar structure. With the increase in the calcination temperature, the surface area of the samples was also increased from 3.133 m²/g of $S_{\text{BET}}(\text{CN-450})$ to 42.465 m²/g of $S_{\text{BET}}(\text{CN-700})$ (Table 3). A larger surface area can provide more active sites, leading the sample to be more efficient for photocatalysis. Furthermore, the pore volume of the samples in Table 3 showed a trend of increasing with increasing temperatures. CN-700 had the most enormous pore volume of 0.225 cm³/g, indicating it showed the loosest stack state, further confirming the observation in Table 1. In conjunction with the TG-DTG-DSC (Figure 1), it was found that the higher temperature was conducive to the further deamination and polymerization of the sample. The process tended to produce a thinner g-C₃N₄ sample, consistent with the phenomenon that CN-700 had a graphene-like flake structure and was composed of thin nanosheets with slightly curved edges in the TEM image (Figure 6). The attained graphene-like structure can greatly promote the progress of the photocatalytic reaction because the photogenerated electrons can be conveniently transferred to absorb light energy [35].

Table 3. S_{BET} and V_{pore} of samples.

Samples	CN-450	CN-500	CN-550	CN-600	CN-650	CN-700
$S_{\text{BET}}(\text{m}^2/\text{g})$	3.133	4.325	7.291	14.060	21.114	42.465
$V_{\text{pore}}(\text{cm}^3/\text{g})$	0.005	0.007	0.022	0.047	0.072	0.225

Figure 5. SEM images of CN-450 (a,d), CN-500 (b,e), CN-550 (c,f), CN-600 (g,j), CN-650 (h,k) and CN-700 (i,l).

Figure 6. TEM image of CN-700.

Figure 7. N₂ adsorption–desorption isotherms.

2.1.4. Optical Performance Analysis

Commonly, the optical features of photocatalysts were studied through PL and UV-vis DRS. It was examined from the PL spectra (Figure 8) that as the calcination temperature increased, the PL peak intensity decreased dramatically. PL represents the effective migration and separation ability of photogenerated carriers during the photocatalytic reaction. It was universally believed that the lower the PL peak intensity, the faster the carrier migration, resulting in higher photocatalytic activity. Therefore, CN-650 and CN-700 had higher photocatalytic activity than other samples. However, compared with CN-650, the CN-700 sample showed slightly higher PL intensity. The reason was that when the calcination temperature rose to 700 °C, the crystallinity of CN-700 improved owing to the formation of more perfect tris-s-triazine structural units, and the number of structural defects was reduced during the decomposition, the recombination probability of photogenerated electron-hole pairs was increased [36], so the PL intensity was slightly enhanced. Moreover, the transitions of electrons or holes to defects belonged to the harmful radiationless transitions, and the reduction in the number of defects in CN-700 reduced the harmful non-radiative transitions [32], which made both the PL intensity and photocatalytic activity enhanced.

Furthermore, the PL peak of the sample had a red shift phenomenon as the calcination temperature increased. When the calcination temperature was lower, the polymerization degree of the products such as CN-450, CN-500 was subsequently lower, and there was a phenomenon that low-grade polymers coexisted, so the short PL emission wavelength made it red-shifted. Moreover, if the temperature further increased, the low-grade polymer continuously polymerized to form a flaky polymer, and the Π conjugated system also expanded, causing the band gap in the system to gradually decrease, thereby resulting in a red shift of the corresponding PL peak [20].

Figure 8. PL spectra of CN-450, CN-500, CN-550, CN-600, CN-650, and CN-700.

The UV-vis DRS spectrum in Figure 9a shows that similar absorption edges of all the samples appeared in the visible light region. Figure 9b shows the corresponding band gaps of samples; its calculation method is referred to in the literature [37]. It was interesting to find that when the calcination temperature increased, the maximum absorption wavelength of the CN-X sample had a red shift. Its band gap gradually decreased ($E_{g\text{CN-450}} = 2.81$ eV, $E_{g\text{CN-500}} = 2.75$ eV, $E_{g\text{CN-550}} = 2.72$ eV, $E_{g\text{CN-600}} = 2.61$ eV), the visible light absorption range correspondingly extended, which made the sample easier to be excited by visible light. While as the temperature was further increased, the flaky structure in the CN became smaller due to the high-temperature decomposition of the sample, and the subsequent quantum confinement effect made the fluorescence emission wavelength blue shifted [38], leading to a slight increase in the band gap ($E_{g\text{CN-650}} = 2.66$ eV, $E_{g\text{CN-700}} = 2.69$ eV).

Figure 9. (a) UV-vis DRS spectra, and (b) the corresponding banding energy gap of samples.

2.2. Photocatalytic Activity Studies

To assess the potential capabilities of the samples for wastewater treatment, RhB and MO solutions were utilized as target pollutants to conduct photodegradation experiments. Before each photodegradation experiment, the reaction system was stirred for 2 h in darkness, and the adsorption kinetics were regression fitted based on the experimental results. The results are shown in Figure 10. It was observed from Figure 10a,b that the whole experiment of adsorbing organic dyes reached the adsorption–desorption equilibrium after 2 h in darkness. CN-700 showed the highest adsorption efficiency, and its adsorption rates for RhB and MO were only 14.08% and 6.01% in darkness for 2 h, meaning that the decreasing of concentration of RhB and MO throughout the degradation process was mainly caused by the subsequent photocatalytic reaction. Furthermore, it can be seen from the adsorption kinetic curves (Figure 10c–f) that compared with the quasi-first-order kinetic model, the quasi-second-order kinetic model, in this case, could better describe the adsorption process of RhB and MO by CN-X, indicating that chemical adsorption was the main step for CN-X adsorbed RhB and MO dyes. After the whole reaction was in the adsorption–desorption equilibrium, the light source was turned on to carry out the photodegradation experiment. The results are shown in Figure 11a,b. It was found that the decolorization rate of RhB (Figure 11a) or MO (Figure 11b) was nearly zero without a catalyst after prolonged irradiation, indicating that the photodegradation of RhB and MO itself was negligible. In contrast, when the photocatalysts were added, the degradation of RhB and MO was notably improved. It was worth noticing that CN-450 displayed the worst visible light photocatalytic activity, which showed a decolorization rate of 92.89% after 90 min of RhB solution and only 59.00% after 4 h of MO solution. The phenomenon was due to many intermediate products such as melam and melem that were not completely converted into $g\text{-C}_3\text{N}_4$ in the CN-450 sample, reducing the actual number of active sites that participated in the photocatalytic reaction.

With an increase in the calcination temperature, the activity of the as-prepared photocatalyst was accordingly enhanced. When the calcination temperature reached 700 °C, the CN-700 sample showed the best photocatalytic activity for RhB and MO solutions: the decolorization rate of CN-700 to RhB solution was up to 99.11% after only 30 min of visible light, which was 64.91% higher than that of CN-550; the decolorization rate of CN-700 to MO solution reached 98.81% after 4 h of visible light, which was 41.83% higher than that of CN-550. CN-700 exhibited the highest photocatalytic activity due to its high crystallinity, stable graphene-like structure, large surface area, and excellent optical performances. The enhanced crystallinity accelerated the transfer of photoelectrons to the surface of the photocatalyst, thereby inhibiting the recombination of photo-induced electron-hole pairs. The stable graphene-like structure also facilitated the transfer of photogenerated electrons to absorb light energy and promoted photocatalytic progress. In addition, a large surface area was conducive to the adsorption of pollutants. On the one hand, it provided more reactive sites. On the other hand, it was also advantageous to the migration of photogenerated electron-hole pairs on the surface of the samples to improve the separation ability of photogenerated electrons and holes. The slightly higher PL intensity in CN-700 reduced the harmful radiationless transitions, despite improving the recombination rate of electron-hole pairs, which enhanced the photocatalytic activity [32]. Additionally, the reduced band gap of CN-700 indicated that it expanded the absorption range of visible light, which was favorable to the enhancement of photocatalytic activity.

The kinetic degradation curves of RhB and MO in the presence of various samples were further analyzed, as shown in Figure 11c,d. The corresponding kinetic rate constants are presented in Table 4. It was evidently seen that in the photocatalytic degradation of RhB and MO studies, the kinetic degradation curves of all samples basically conformed to the quasi-first-order reaction kinetic. The quasi-first-order kinetic rate constant of CN-X gradually increased when the calcination temperature increased, meaning that the photodegradation rate was accelerated. The rate constants of CN-700 for photodegradation of RhB and MO were the largest of 0.10643 min^{-1} and 0.72071 h^{-1} , meaning that CN-700 displayed the

best photocatalytic activity. The above further corroborated the characterization results in Figure 11a,b.

The recycle stability of photocatalysts is a critical evaluation index in industrial applications. Figure 11e,f show the six photocatalytic consecutive runs of the CN-700 for the degradation of RhB and MO. It was observed that the decolorization rates of RhB and MO only slightly decreased and kept over 93% after six runs. Consequently, the as-prepared CN-700 sample showed excellent recycling stability and was a promising photocatalyst in wastewater treatment.

Additionally, the photodegradation ability of CN-700 was compared with other previously reported catalysts, and the results are summarized in Table 5. It can be clearly observed that, compared with the low-concentration RhB or MO solution used in the previous reports, the CN-700 photocatalyst used in this work displayed a higher removal efficiency of high-concentration dyes in a shorter time. Therefore, CN-700 was a very potential photocatalyst and was extremely attractive for actual dyeing wastewater treatment.

Figure 10. Adsorption efficiencies of RhB (a) and MO (b) in the dark condition; corresponding adsorption kinetic curves for RhB (c,e) and MO (d,f) for all samples.

Figure 11. Photocatalytic activities of RhB (a) and MO (b) under visible light; corresponding kinetic curves of RhB (c) and MO (d) for all samples; recycling runs in the photodegradation of RhB (e) and MO (f).

Table 4. Kinetic rate constants of samples.

Samples	k_{RhB} (min^{-1})	R^2 (RhB)	k_{MO} (h^{-1})	R^2 (MO)
CN-450	0.02243	0.98505	0.22073	0.98289
CN-500	0.02454	0.99019	0.24660	0.97966
CN-550	0.02961	0.99783	0.29348	0.98178
CN-600	0.04734	0.99971	0.34919	0.99164
CN-650	0.05832	0.99703	0.44543	0.98943
CN-700	0.10643	0.98062	0.72071	0.99338

Table 5. Comparison of different catalysts for dyes removal under visible light.

Catalyst	Catalyst Dosage (mg)	Irradiation Time (min)	Dye Solution	Removal Efficiency (%)	Refs
Ag ₃ PO ₄ /p-g-C ₃ N ₄	50	60	RhB (10 mg/L)	99	Jiang, et al. [39]
CuO–Cu ₂ O	40	240	MO (5 mg/L)	60	Joorabi, et al. [40]
MCN	50	40	RhB (2 mg/L)	100	Yu, et al. [31]
			MO (2 mg/L)	94.2	
g-C ₃ N ₄	15	100	RhB (10 mg/L)	97	Wang, et al. [32]
g-C ₃ N ₄ /CNTs-1	20	60	RhB (10 mg/L)	98.1	Liu, et al. [34]
CNAgP0.3	60	500	MO (10 mg/L)	99	Liu, et al. [41]
MCNS-4	100	210	MO (10 mg/L)	82.7	Jourshabani, et al. [42]
			RhB		
CN-700	100	30	(100 mg/L)	99.11	This work
		240	MO (20 mg/L)	98.81	

2.3. Possible Mechanism

A suite of active species trapping experiments was carried out to probe the photodegradation mechanism of RhB and MO (Figure 12a,b). It was found that the decolorization rate of RhB and MO was up to 99.11% and 98.81%, respectively, without scavenger. The dyes' photodegradation efficiencies declined slightly when the EDTA-2Na and DMSO were added. However, when p-BQ and IPA were also added to the solution, the decolorization rate of photodegraded RhB and MO was greatly reduced, especially when p-BQ was added, the RhB and MO decolorization rates were decreased dramatically to 39.28% and 48.04%, respectively. The observation indicated that $\bullet\text{O}_2^-$ played a major role in the degradation of RhB and MO, while $\bullet\text{OH}$ radicals played a minor role. This phenomenon was caused by the band gap of the CN-700 photocatalyst of 2.69 eV ($E_{\text{CB}} = -1.12$ eV, $E_{\text{VB}} = +1.57$ eV). In this work, the electron was excited from the valence band (VB) to the conduction band (CB), and the hole was generated in the VB simultaneously. $\bullet\text{O}_2^-$ could easily be produced because of a more negative reduction potential of the CB position of CN-700 than that of $\text{O}_2/\bullet\text{O}_2^-$ (-0.33 eV/NHE) by the electron. Moreover, since the reduction potential of $\text{O}_2/\text{H}_2\text{O}_2$ was 0.695 eV [43], electrons could generate $\bullet\text{OH}$ through the reaction of O_2 and H^+ , of which the equations are as follows: $\text{O}_2 + 2\text{e}^- + 2\text{H}^+ = \text{H}_2\text{O}_2$, $\text{H}_2\text{O}_2 + \text{e}^- = \bullet\text{OH} + \text{OH}^-$. However, compared with the potential of $\bullet\text{OH}/\text{OH}^-$ ($+1.99$ eV/NHE), the CN-700 ($E_{\text{VB}} = +1.57$ eV) was not positive enough, so the h^+ in the VB cannot oxidize the OH^- in the water to form $\bullet\text{OH}$. It just reacted with organic dyes immediately.

Figure 12. Photodegradation performance of RhB and MO using different radical scavengers over CN-700 under visible light (a,b), DMPO- $\bullet O_2^-$ and DMPO- $\bullet OH$ spin-trapping ESR spectra (c).

Figure 12c shows the spin capture ESR spectra of DMPO- $\bullet O_2^-$ and DMPO- $\bullet OH$ for the CN-700 sample. It can be seen that no ESR signal was generated under dark conditions. While when the light was turned on, six strong characteristic signals of DMPO- $\bullet O_2^-$ adduct and four weak characteristic peaks of DMPO- $\bullet OH$ with an intensity of 1:2:2:1 were observed on CN-700, indicating the $\bullet O_2^-$ and $\bullet OH$ radicals were generated in the entire reaction system, and $\bullet O_2^-$ was the main oxidation specie of CN-700 for the photodegradation of organic pollutants. This further confirmed the trapping results of Figure 12a,b. Based on the above analysis, Scheme 1 presents a schematic diagram of the possible mechanism of the CN-700 degradation of RhB and MO.

Scheme 1. The possible photocatalytic mechanism schematic.

3. Conclusions

In summary, a series of g-C₃N₄ photocatalysts at different calcination temperatures were prepared using melamine as the precursor. The results showed that the photocatalytic activities of photocatalysts for the photodegradation of RhB and MO were remarkably improved, which was mainly attributed to the satisfactory crystallinity, stable graphene-like structure, large surface area, and excellent migration ability of the photogenerated electrons of the catalysts. It was found that CN-700 displayed the highest photocatalytic activity of 99.11% and 98.81% for the degradation of RhB and MO, respectively. Furthermore, the photodegradation of RhB and MO stayed at over 93% after six runs, indicating that the CN-700 sample had excellent reusability and was a promising photocatalyst for the actual dyeing of wastewater treatment. Finally, •O₂[−] radicals and •OH radicals were the main active species in the photodegradation of organic dyes and were discovered through free radicals trapping experiments and ESR analysis. The photodegradation mechanism of CN-700 was also proposed based on the characterization.

4. Materials and Methods

4.1. Materials

All chemicals used in the experiments were analytically pure. Melamine (99.0%), isopropanol (IPA, 99.7%), p-benzoquinone (p-BQ, 99.0%), dimethyl sulfoxide (DMSO, 99.5%) and disodium edetate (EDTA-2Na, 99.0%) were purchased from Sinopharm Chemical Reagent Co. Ltd., China. RhB (98%) and MO (99%) were procured from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China).

4.2. Photocatalyst Synthesis

The g-C₃N₄ photocatalyst was synthesized through the thermal polycondensation of melamine. In brief, 10 g melamine was poured into a covered ceramic crucible, and then calcined in a muffle furnace with a heating rate of 5 °C/min to different final temperatures

and kept for 4 h. After the thermal process finished, the final g-C₃N₄ powder was obtained after grinding. Particularly, the obtained g-C₃N₄ samples calcined at 450, 500, 550, 600, 650, 700, 750 °C were named as CN-X (X = 450, 500, 550, 600, 650, 700, 750), respectively.

4.3. Characterization

Thermogravimetry, differential thermogravimetry and differential scanning calorimetry (TG-DTG-DSC) (STA449 F3, Netzsch, Germany) was used to characterize the thermal stability of photocatalysts. In order to analyze the composition and structure of photocatalysts, X-ray diffraction (XRD) (D8 Advance, Bruker, Germany), X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi, Thermo Fischer, USA), Fourier transform infrared spectra (FT-IR) (Vertex 70, Bruker, Germany), N₂ adsorption–desorption curves (determined by Brunauer–Emmett–Teller (BET) method, Quadrasorb SI, Kantar, USA) and elemental analysis (EA) (Vario EL, Elementar, Germany) were performed. Scanning electron microscopy (SEM) (XL-30, Philips, Holland) and transmission electron microscope (TEM) (100CX-2, JEOL, Japan) were used to observe the morphology of photocatalysts. The optical performances of photocatalysts were determined by photoluminescence spectrum (PL) (FLS1000, Edinburgh, UK), ultraviolet-visible diffuse reflection spectra (UV-vis DRS) (UV-2700, Shimadzu, Japan) and electron spin resonance (ESR) (EMXplus, Bruker, Germany).

4.4. Photocatalytic Experiments

The photocatalytic performance of samples in this work was measured by the photodegradation of RhB and MO. The degradation experiments were performed in a 30 mL reactor under visible irradiation ($\lambda > 420$ nm) by a 1000 W xenon lamp. The distance between the lamp and the catalyst was constant for each experiment. The schematic of the photocatalytic reactor is shown in Figure 13. During the whole reaction, the temperature was kept at 25 °C. Typically, 100 mg of CN-X was poured into the reactor, then 20 mL of RhB solution (100 mg/L) or MO solution (20 mg/L) was added and stirred for 2 h in darkness to reach adsorption–desorption equilibrium. Subsequently, 5 mL solution sample was taken out at regular intervals after exposure to visible light irradiation. The sample taken out each time was separated from the solution by a high-speed centrifuge at 8000 rpm, and then the supernatant was taken and analyzed immediately on a UV-vis spectrophotometer under the maximum absorption wavelength ($\lambda_{\text{RhB}} = 553$ nm, $\lambda_{\text{MO}} = 463$ nm). The photodegradation of RhB and MO without the addition of the photocatalyst was also conducted as the blank experiments under the same experimental conditions as described above. Each reaction finished, the photocatalyst was centrifuged, washed, dried, and collected, and then the photocatalyst was used for its recycle stability assessment of degradation experiments.

4.5. Trapping Experiments of Radicals

The trapping experimental procedures were similar to the photocatalytic tests, except that the 10 mM scavengers were added to the suspension before visible light irradiation, to detect the active species in the visible light photocatalytic process of RhB and MO dyes decomposition. IPA, p-BQ, DMSO and EDTA-2Na were also used as scavengers for •OH radicals, •O₂[−] radicals, electrons and holes.

Figure 13. Photocatalytic reaction device diagram.

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Sample Availability: Samples of the compounds CN-X are available from the authors.

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