Effect of pH on the Catalytic Degradation of Rhodamine B by Synthesized CDs/g-C₃N₄/CuₓO Composites

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ABSTRACT: The narrow pH range of Fenton oxidation restricts its applicability in water pollution treatment. In this work, a CDs/g-C₃N₄/CuₓO composite was synthesized via a stepwise thermal polymerization method using melamine, citric acid, and Cu₂O. Adding H₂O₂ to form a heterogeneous Fenton system can degrade Rhodamine B (Rh B) under dark conditions. The synthesized composite was characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and N₂ adsorption/desorption isotherms. The results showed that CDs, Cu₂O, and CuO were successfully loaded on the surface of g-C₃N₄. By evaluating the catalytic activity on Rh B degradation in the presence of H₂O₂, the optimal contents of citric acid and Cu₂O were 3 and 2.8%, respectively. In contrast to a typical Fenton reaction, which is favored in acidic conditions, the catalytic degradation of Rh B showed a strong pH-dependent relation when the pH is raised from 3 to 11, with the removal from 45 to 96%. Moreover, the recyclability of the composite was evaluated by the removal ratio of Rhodamine B (Rh B) after each cycle. Interestingly, recyclability is also favored in alkaline conditions and shows the best performance at pH 10, with the removal ratio of Rh B kept at 95% even after eight cycles. Through free radical trapping experiments and electron spin resonance (ESR) analysis, the hydroxyl radical (•OH) and the superoxide radical (•O₂⁻) were identified as the main reactive species. Overall, a mechanism is proposed, explaining that the higher catalytic performance in the basic solution is due to the dominating surface reaction and favored in alkaline conditions.

1. INTRODUCTION

Organic pollutants produced by the dye industry are harmful to the environment and human beings due to their high toxicity, persistence, and poor biodegradability. The key to advanced oxidation processes (AOPs) is the in situ-produced hydroxyl radical (•OH) with relatively high reactivity and nonselectivity for different organic pollutants. As one of the most efficient treatments for such organic pollutants, an AOP can mineralize almost all organic pollutants, which can be completely degraded into water, carbon dioxide, and some easily degradable inorganic ions in wastewater without causing secondary pollution. Like a typical AOP, a Fenton reaction can produce more number of •OH when the ferrous ions react with hydrogen peroxide (H₂O₂). Some disadvantages of the Fenton reaction are a narrow pH range (pH < 4), the formation of iron sludge, and the high cost of catalyst recovery.

Graphitic carbon nitride (g-C₃N₄), a nonmetallic semiconductor, has a wide range of applications due to the narrow band gap (2.7 eV), low cost, nontoxicity, good chemical stability, and superior resistance to acids and alkalis. However, some shortcomings, such as a high photoexciting electron−hole recombination, low specific surface area, and low utilization rate, limit the application of g-C₃N₄ in the field of photocatalysts. Therefore, many strategies, such as changing the morphology, nonmetal or metal and metal oxide loading, construction of heterojunctions, etc., have been employed to improve its photocatalytic performance. Among these strategies, the use of carbon nanodots (CDs) to modify g-C₃N₄ not only increased the specific surface area of pure g-C₃N₄ but also improved its photocatalytic activity and promoted photocatalytic H₂ production.

On this basis, several studies have been conducted by introducing a third compound (e.g., TiO₂, Ag₃PO₄, Ag nanoparticles, etc.) into CDs/g-C₃N₄ to further improve the photocatalytic performance on H₂ production or pollutant degradation. Besides improving the photocatalytic performance, the CDs/g-C₃N₄ composite may also act as a Fenton-like catalyst and catalyze the decomposition of H₂O₂ to form •OH in the light-shielding condition according to its intrinsic...
property, which has been used to remove organic pollutants.\textsuperscript{26} Recent studies have shown that in some pollutants, the introduction of a metal oxide into the CDs/g-C\textsubscript{3}N\textsubscript{4} matrix may improve the degradation efficiency, such as loading ZnO on the surface of CDs/g-C\textsubscript{3}N\textsubscript{4} to prepare a CDs/g-C\textsubscript{3}N\textsubscript{4}/ZnO nanocomposite for tetracycline total degradation.\textsuperscript{27}

Similar to the redox properties of iron, copper can undergo a Fenton-like system with H\textsubscript{2}O\textsubscript{2} to achieve mutual conversion between Cu\textsuperscript{+} and Cu\textsuperscript{2+} and produce \textbullet OH, as shown in eqs 1 and 2.\textsuperscript{28,29} It should be noted that eq 2 is a rate-limiting step and Cu\textsuperscript{2+} can be from a copper complex [Cu(H\textsubscript{2}O\textsubscript{6})\textsuperscript{2+}] at a neutral pH, which can be used in the Cu\textsuperscript{2+}/Cu\textsuperscript{+}/H\textsubscript{2}O\textsubscript{2} Fenton-like system.\textsuperscript{30} Cu\textsuperscript{+}/Cu\textsuperscript{2+} has limited applicability due to the narrow range of pH and the extreme volatility of Cu\textsuperscript{+}. Therefore, to expand the application of CDs/g-C\textsubscript{3}N\textsubscript{4} and overcome some limitations of the Fenton system and the Cu\textsuperscript{+}/Cu\textsuperscript{2+} Fenton-like system, this study chose to load Cu\textsubscript{2}O on CDs/g-C\textsubscript{3}N\textsubscript{4} and form a Fenton-like system for the degradation of Rh B in the reaction.

\[
\text{Cu}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{2+} + \cdot\text{OH} + \text{OH}^- \quad (1)
\]

\[
\text{Cu}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^+ + \cdot\text{O}_2\text{H} + \text{OH}^- \\
k = 4.6 \times 10^5 \text{M}^{-1} \text{s}^{-1} \quad (2)
\]

In this study, a more promising strategy is proposed to fix Cu\textsubscript{2}O on CDs/g-C\textsubscript{3}N\textsubscript{4} by thermal polymerization, in which CDs/g-C\textsubscript{3}N\textsubscript{4}/Cu\textsubscript{x}O composites are obtained that can initiate a Fenton-like reaction in the presence of H\textsubscript{2}O\textsubscript{2} to generate active free radicals that are used for the degradation of organic pollution. The prepared composites were characterized by FT-IR, XRD, TEM, XPS, and BET techniques. The optimal synthesis and experiment conditions, including CDs content, Cu\textsubscript{x}O content, H\textsubscript{2}O\textsubscript{2} concentration, solution ion reaction, and influence of different pH values, were explored. Also, to further explore the reasons for the differences in the changes at different pH conditions, the changes in the dissolved oxygen, total copper content, and the stability of composites at different pH values were studied. Besides, reactive oxygen species (ROS) were investigated by ESR analysis and free radical capture experiments. Based on the above results, the degradation mechanism of Rh B was outlined in the presence of H\textsubscript{2}O\textsubscript{2} with the CDs/g-C\textsubscript{3}N\textsubscript{4}/Cu\textsubscript{x}O composite in a wide range of pH conditions.

**Figure 1.** TEM and HRTEM images of CD\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} (a–c) and CD\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4}/Cu\textsubscript{x}O (d–f).
2. RESULTS AND DISCUSSION

2.1. Characterization of Catalysts

2.1.1. FT-IR. The as-prepared composites, labeled as g-C₃N₄, CD₃/g-C₃N₄, and CDs/g-C₃N₄/CuₓO, were investigated to distinguish the functional groups via the FT-IR spectrum. As presented in Figure S1, the characteristic peaks of g-C₃N₄ were observed at 1200−1645 cm⁻¹, corresponding to the stretching vibration modes of CN-bond heterocycles (C=N and C−N groups). The appearance of the absorption peak at 810 cm⁻¹ was allocated to the normal vibration of the tris(3′,5′-dimethylpyrazol-1-yl)-s-triazine structure. The aforementioned absorption peaks could be characterized as g-C₃N₄, similar to a previous study. Further, a broadband emerged approximately at 3200 cm⁻¹, which can be allocated to the stretching vibration modes of NH and NH₂ group. For CD₃/g-C₃N₄ and CDs/g-C₃N₄/CuₓO, similar peaks were present, showing that the skeletal structure of g-C₃N₄ was not damaged in these composites. With Cu₂O doped into CDs/g-C₃N₄/CuₓO, the corresponding peak of the stretching vibration of the Cu−O bond of Cu₂O and CuO was not detected in FT-IR, implying that the corresponding copper-based functional groups were not formed by thermal polymerization of the synthesized composites.

2.1.2. XRD. The crystal structures of Cu₂O, g-C₃N₄, CD₃/g-C₃N₄, and CDs/g-C₃N₄/CuₓO were acquired via XRD patterns, as shown in Figure S2. For g-C₃N₄, the weak peak close to 13.0° can be indexed to the (100) diffraction planes, corresponding to the in-planar structural packing motif of tri-s-triazine units. In addition, the strong diffraction peak at 27.5° corresponding to the typical (002) plane was due to the interlayer accumulation of the conjugated aromatic system. Besides the characteristic peaks of g-C₃N₄, with the loading of CDs, the sharp peak of CDs could be detected at 25.2°. After doping with Cu₂O, the characteristic peaks of g-C₃N₄ appeared similar, but three diffraction peaks were observed at 36°, 38°, and 61.5° in CDs/g-C₃N₄/CuₓO composite, which were in good agreement with the crystalline structure of CuO indexed with the standard (111) plane, the (111) plane, and corresponding to the (220) plane of the Cu₂O phase, respectively. However, compared to g-C₃N₄ and CD₃/g-C₃N₄, the (100) plane of the diffraction peaks weakened noticeably, the peak corresponding to the (002) plane shifted slightly, and no diffraction peak arose from the CDs in the CDs/g-C₃N₄/CuₓO composite as Cu₂O addition may affect the thermal condensation of melamine, resulting in lower crystallinity of the (100) and (002) crystal planes. Moreover, the invisible diffraction peak of CDs may be due to the relatively low diffraction intensity in the composite. Therefore, the XRD spectral patterns revealed the coexistence of CuO and Cu₂O in the CDs/g-C₃N₄/CuₓO composite.

2.1.3. TEM. The morphology and microstructures of CD₃/g-C₃N₄ and CDs/g-C₃N₄/CuₓO samples were observed by TEM and HRTEM. As shown by the corresponding HRTEM image in Figure 1e, lattice fringes with interlayer distance were measured to be 0.245 and 0.232 nm, which correspond to the (111) plane of CuO and the (111) plane of Cu₂O. XRD results showed Cu₂O and CuO in the CDs/g-C₃N₄/CuₓO composite.

Figure 2. High-resolution (a) C 1s, (b) N 1s, (c) Cu 2p, and (d) Cu LMM spectra of the CDs/g-C₃N₄/CuₓO composite.
found on the surface of the CDs/g-C3N4/CuO composite with the same diameter as CDs in CD3/g-C3N4 (Figure 1c,d). A comparison between the TEM and HRTEM of CDs/g-C3N4 and CDs/g-C3N4/CuO established that CDs and CuO are successfully loaded on the CDs/g-C3N4/CuO surface.

2.1.4. XPS. The elemental and surface chemical states of the CDs/g-C3N4/CuO composite were investigated via XPS spectral analysis. Only C, N, O, and Cu were present in the composite, and the atomic content ratios were 41.64, 52.28, 3.98, and 2.1%, respectively (Figure S3). Compared with the standard XPS binding energy table, the binding energy peaks of the four elements get slightly shifted toward the higher values. The results are shown in Figure 2 and Table S1. Figure 2a shows the high-resolution XPS spectrum of C 1s with peaks at 284.94 and 288.31 eV allocated to C−C and N−C==N, respectively. The peak at 287.90 eV was identified as C−OH, indicating the successful loading of CDs on the CDs/g-C3N4/CuO composite. The N 1s spectrum displayed in Figure S4 contains three peaks, corresponding to 398.53, 399.05, and 400.73 eV, which are located at the triazine rings (C−N==C), the sp3-hybridized nitrogen (N−C3), and amino groups (C−N−H), respectively. This indicates that the structure of g-C3N4 is not completely altered by the addition of CDs and Cu2O. For the O 1s spectrum, it contains three peaks, corresponding to 530.57 eV (O−C=), 532.04 eV (C−OH), and 533.21 eV (adsorbed water). Figure 2c displays that there are six characteristic peaks in Cu 2p; the binding energies at 933.10 and 952.95 eV were assigned to Cu 2p3/2 and Cu 2p1/2 of Cu2+, and those at 935.02 and 955.13 eV were identified as Cu2p1/2 and Cu 2p3/2 of Cu2+. The deconvoluted peaks at 943.09 and 963.11 eV derived from the satellite peaks of Cu2+, established the existence of Cu2+ in the composite. Since the binding energies of Cu2+ and Cu2+ are very close, they are hard to distinguish unless the Cu LMM peak is observed (Figure 3d). The Cu LMM peaks of the composite were completely altered by the addition of CDs and Cu2O. For the O composite, the highest ratio of Rh B was removed in 60 min with pure g-C3N4, although the removal rate increased dramatically by raising the content of CDs, reaching its maximum when the CD content was 3. The increase in the removal rate could be ascribed to the fact that the higher amount of CDs might aggregate to form clusters and affect the progress of surface reactions. Therefore, the content of optimal CDs was confirmed as γ = 3, and CD3/g-C3N4 was selected as the typical composite for further synthesis of CDs/g-C3N4/CuO composites.

2.2.2. Effect of CuO Content. The effect of CuO content was studied by evaluating the removal rates of Rh B with CD3/g-C3N4/CuO composites marked as C1−C6 in the presence of H2O2. The removal of Rh B was remarkably improved by adding CuO before and after the injection of H2O2 (Figure 4a), suggesting that the addition of CuO improves both the adsorption and catalytic performance of the composite. However, the final removal ratio of Rh B was not linearly related to the content of CuO. To be specific, the highest ratio for the adsorption phase and the catalytic degradation phase, during the whole process, responded to C1 and C2, respectively. The H2O2 concentration was also monitored (Figure 4b). The results showed that the decomposition of H2O2 was also enhanced by raising the amount of CuO, reaching the highest rate at C4. Notably, at C2, Rh B was degraded completely, with only 73.3% of H2O2 consumed and exhibited the highest utilization rate of Rh B, as shown by eq 4. Therefore, the C2 composite was selected for further exploration in subsequent experiments. (C2 was taken as the optimal catalyst for property study. The CDs/g-C3N4/CuO composite in the following text refers to C2 unless otherwise stated.)

2.2.3. Effect of H2O2 concentration. H2O2, as a precursor of *OH, was employed to induce Rh B degradation in the presence of the CDs/g-C3N4/CuO composite after the system reached the adsorption/desorption equilibrium. To evaluate the effect of H2O2, different concentrations of H2O2 were added. When the H2O2 concentration increased from 1 to 10 mM, the degradation rate of Rh B also increased (Figure S6). The degradation rate and utilization of Rh B (calculated from eq 4) with different concentrations of H2O2 are compared in Table S2 (t = 60 min). The higher concentrations of H2O2 induced a higher degradation ratio of Rh B. However, the general trend of the utilization rate of H2O2 decreased with an increase in the
concentration as a very high H₂O₂ concentration was more prone to H₂O₂ decomposition, suggesting that more H₂O₂ concentration could lead to higher production of •OH and that in the side reaction H₂O₂ could be consumed by the formed •OH.⁴⁹,⁵⁰ Thus, the H₂O₂ at 5 mM utilization rate was relatively high, and the degradation rate of Rh B was also in the middle. Therefore, considering its degradation rate and utilization together, the optimal concentration of H₂O₂ was selected as 5 mM in other experiments.

2.2.4. Effect of Solution Reaction. To verify the potential homogeneous reaction in the system, a similar experiment was conducted by taking several samples at selected time points, filtering separately, and placing them together to observe the time-resolved concentration of Rh B in the filtrate.⁵¹ The results are summarized in Figure S7a. In contrast to the original heterogeneous reaction, only a slight decrease was observed in all filtrates, indicating a weaker solution reaction as compared to the surface reaction. The concentrations of Rh B and H₂O₂ in the filtrates were monitored from 1 min to several days. Figure S7b shows that Rh B was decomposed completely although at a much lower rate than that of the original heterogeneous system. Therefore, considering its degradation rate and utilization together, the optimal concentration of H₂O₂ was selected as 5 mM in other experiments.

2.2.5. Effect of pH. 2.2.5.1. Degradation of Rh B and Decomposition of H₂O₂ under Different pH Conditions. The strict pH limitation (pH < 4) is a major disadvantage of various homogeneous Fenton reactions, preventing its application in neutral and alkaline conditions. Therefore, the study of the pH effect in the present system is very important. In the current study, several experiments were conducted by varying the solution pH from 3 to 11 to evaluate the pH effect on the degradation of Rh B and decomposition of H₂O₂. Initially, the Rh B solution was adjusted to different pH conditions and was scanned with an ultraviolet-visible spectrophotometer (Figure S8) to nullify the effect of pH on the maximum absorption peak. It was observed that the maximum absorption peak of Rh B can be maintained at 555 nm with the given pH ranges.

To further explore the effect of pH on the Fenton-like reaction and to compare the catalytic degradation of Rh B with CDs/g-C₃N₄/CuₓO composites, several different pH conditions were selected. The pH change showed a negligible effect on the adsorption phase (Figure 5a), while during the catalytic degradation phase, the degradation rate of Rh B exhibited a highly basic-favored trend. At pH 10 and 11, the removal rate was significantly higher than that at pH 3. H₂O₂ concentration in the catalytic degradation phase was also monitored (Figure 5b). Despite the similar degradation rate of Rh B at pH 10 and 11 (Figure 5a), the decomposition rate of H₂O₂ was much lower at pH 10 than that at pH 11. As discussed in the previous section, pH 10 showed better utilization efficiency. Therefore, the CDs/g-C₃N₄/CuₓO composite can be widely used in the application range of pH.

2.2.5.2. Dissolved Oxygen Changes in Solution. To further understand how the decomposition of H₂O₂ is affected by the change in pH since the decomposition of H₂O₂ results in H₂O and O₂, the dissolved oxygen could be used as a probe to study the effect of pH.⁵² Figure 6 depicts a similar trend in the concentration of Dissolved Oxygen (DO), reaches a maximum

![Figure 4](image1.png)

Figure 4. (a) [Rh B]/[Rh B]₀ and (b) [H₂O₂]/[H₂O₂]₀ as a function of time in the presence of 2 g/L from C1 to C6 with an initial concentration of [H₂O₂]₀ = 5 mM, [Rh B]₀ = 0.064 mM, and V = 100 mL.

![Figure 5](image2.png)

Figure 5. (a) [Rh B]/[Rh B]₀ as a function of time in the presence of 2 g/L CDs/g-C₃N₄/CuₓO composite at different pH values with the initial concentration of [H₂O₂]₀ = 5 mM, [Rh B]₀ = 0.064 mM, and V = 100 mL. (b) Amount of H₂O₂ consumed by the catalysts in the degradation of Rh B at different pH values.
and then decreases. The maximum was obtained earlier with higher pH. The reason can be explained as follows: the experiment was carried out in the air, and according to Henry’s law, the initial concentration of dissolved oxygen is 8 mg/L, and the observed increase in dissolved oxygen concentration is attributed to oxygen formation in the solution being faster than the equilibration with the surrounding gas phase. As the reaction \( \text{H}_2\text{O}_2 \rightarrow 1/2\text{O}_2 + \text{H}_2\text{O} \) continues, the formation rate of \( \text{O}_2 \) increases sharply and is dependent on the pH.\(^{53}\) With the consumption of \( \text{H}_2\text{O}_2 \), the formation of \( \text{O}_2 \) also slows down; thus, the peak appears. Such a trend and pH dependence are in line with the results in Figure 5.

### 2.2.5.3. Ion Leaching under Different pH Conditions

According to several studies, the leaching of copper ions from the present heterogeneous system may be affected by pH.\(^{54,55}\) The concentration of dissolved Cu species was measured by inductively coupled plasma (ICP) spectrometry in the presence of a typical heterogeneous system (Figure 7). It can be seen that higher pH inhibits Cu leaching; the maximum concentration at pH 3 was about 60 times that at pH 11. According to the Eh-pH diagram of Cu-\( \text{H}_2\text{O}_2 \), it mainly exists in the form of \( \text{Cu}^{2+} \) or \( \text{Cu}^{+} \), and \( \text{Cu}_2\text{O} \) and \( \text{Cu(OH)}_2 \) under acidic and alkali conditions, respectively. It was observed that the leaching of copper ions on the catalyst surface was promoted under acidic conditions; it had a certain inhibitory effect on the leaching of ions on the catalyst surface under alkaline conditions, thereby indicating that the surface reaction of the composite was dominant in the reaction.

#### 2.2.5.4. Recycling Experiment

To verify the recyclability and stability of the prepared CDs/g-C\(_3\)N\(_4\)/Cu\(_2\)O composite, three sets of recycling experiments were explored. In the wet cycle, the number of composites remains unchanged, and Rh B and \( \text{H}_2\text{O}_2 \) were directly added after the reaction. In the dry cycle, a series of centrifugation, washing, and drying treatments were used on the composites after the reaction for the next cycle reaction. The composites were recycled via a wet or dry process, and the pH was fixed at 11, 4.6, and 10.

##### 2.2.5.4.1 Recycling via the Wet Process at pH 11

The first set was performed at pH 11 via a wet recycling process since the original degradation rate of Rh B is relatively high. The concentrations of both \( \text{H}_2\text{O}_2 \) and Rh B against reaction time were investigated during each cycle (Figure S9). The decomposition rate of \( \text{H}_2\text{O}_2 \) slightly declined after 12 continuous cycles, while the degradation ratio of Rh B declined dramatically from 88.8 to 67.5\% (Figure S9a). Then, Rh B was cyclically degraded under the same conditions (Figure S9b). The time interval was 30 min, and Rh B and \( \text{H}_2\text{O}_2 \) were added at the end of each cycle. It was noticed that although Rh B can be efficiently degraded by the CDs/g-C\(_3\)N\(_4\)/Cu\(_2\)O composites, the degradation efficiency is reduced after 10 cycles with incomplete degradation. The \( \text{H}_2\text{O}_2 \) concentration was adjusted from 5 to 10 mM under pH 11, and \( \text{H}_2\text{O}_2 \) showed rapid decomposition completely (Figure S10). In addition to the influence of method error and the side reaction at pH 11, it was observed that the degradation residues cover the surface of the composites for the wet cycle, thereby affecting the progress of the reaction.

##### 2.2.5.4.2. Recycling via the Dry Process at pH 4.6 (Unadjusted pH)

To reduce the impact of pH adjustment, under unadjusted pH (as the catalytic degradation performance is not lower than that under some pH conditions), a dry method was used to evaluate the circulation performance of CDs/g-C\(_3\)N\(_4\)/Cu\(_2\)O. As shown in Figure S11, the degradation of Rh B and the consumption of \( \text{H}_2\text{O}_2 \) are significantly affected by the number of cycles, and both experience a significant decrease. This indicates that the dry process has a greater impact on the CDs/g-C\(_3\)N\(_4\)/Cu\(_2\)O composite. At pH 4.6, the copper on the surface of the CDs/g-C\(_3\)N\(_4\)/Cu\(_2\)O composite mainly exists in the form of ions on the solution and causes loss of copper on the surface of the composite during the dry process.

##### 2.2.5.4.3. Recycling via the Dry Process at pH 10 Conditions

After optimizing the conditions, combined with the influence of pH 10, the CDs/g-C\(_3\)N\(_4\)/Cu\(_2\)O composite has a higher degradation efficiency for Rh B, so the dry method is also used to study the circulation performance of CDs/g-C\(_3\)N\(_4\)/Cu\(_2\)O. After eight cycles, the degradation efficiency of the composite on Rh B could be reduced by 4\%, and the degradation ratio reached more than 95\% in each cycle (Figure 8b). At the same time, the \( \text{H}_2\text{O}_2 \) consumed in each cycle was tested, and it almost completely decomposed after eight cycles, as shown in Figure 8a. This is because at pH 10, the copper on the surface of the composite mainly exists in the form of \( \text{Cu}_2\text{O} \) and \( \text{Cu(OH)}_2 \), and the loss of copper ions during the dry process can be overlooked. This observation agrees with the previous results regarding the ion leaching shown in Figure 7.

Therefore, it can be concluded that the CDs/g-C\(_3\)N\(_4\)/Cu\(_2\)O composite has good stability and strong catalytic performance at pH 10. To further establish the stability of the material, the XRD
and FT-IR spectral patterns of the CDs/g-C$_3$N$_4$/Cu$_x$O composite were studied before and after the 8th reaction cycle (Figure 8c,d). No noticeable changes were seen after the reaction in the structure and elemental groups of CDs/g-C$_3$N$_4$/Cu$_x$O.

A comparison with the previous studies was made in terms of cycle stability and pH range to validate the catalytic performance of the prepared CDs/g-C$_3$N$_4$/Cu$_x$O composite. Better cycle stability and a wider range of pH applications were observed for the prepared composites (Table S3). Therefore, the above findings show outstanding activity and reusability of the as-prepared CDs/g-C$_3$N$_4$/Cu$_x$O.

2.2.6. Degradation Mechanism. To determine the mechanism of Rh B degradation by the CDs/g-C$_3$N$_4$/Cu$_x$O composite at different pH conditions, radical trapping experiments and ESR analyses were designed and the main active species generated by Rh B degradation were identified.

2.2.6.1. Radical Trapping. Several studies have shown that P-benzoquinone (BQ) and isopropanol (IPA) are often used as scavengers for •OH and •O$_2$ because they can quickly trap free radicals (Table S4) and have a high reaction rate constant. In particular, p-benzoquinone (BQ) was used as a scavenger for superoxide (•O$_2$) and hydroxyl radicals (•OH); isopropanol (IPA) may react with only •OH. Additionally, pure N$_2$ purging was employed to investigate the effect of dissolved oxygen in the reaction. The degradation rate of Rh B retarded after the addition of IPA (10 mM) and BQ (10 mM), but it got suppressed more significantly with the addition of BQ since BQ

Figure 8. (a) Cyclic degradation of Rh B consumed and the change of H$_2$O$_2$ with 2 g/L CDs/g-C$_3$N$_4$/Cu$_x$O composite in the presence of 10 mM H$_2$O$_2$ at pH 10. (b) Cycling runs for the catalytic degradation of Rh B (0.064 mM) with 2 g/L CDs/g-C$_3$N$_4$/Cu$_x$O composite in the presence of 10 mM H$_2$O$_2$ at pH 10. (c) XRD patterns and (d) FT-IR spectra of the CDs/g-C$_3$N$_4$/Cu$_x$O sample before and after the cycling catalytic experiments.

Figure 9. (a) DMPO spin-trapping EPR spectra of DMPO-•O$_2$ in methanol dispersion in the Rh B degradation experiment and (b) DMPO-•OH in aqueous dispersion in the Rh B degradation experiment with the CDs/g-C$_3$N$_4$/Cu$_x$O composite.
can trap both *\( \cdot \)OH and *\( \cdot \)O\(_2\)\(^-\), while IPA only traps *\( \cdot \)OH (Figure S12a). Moreover, the inhibition effect of IPA increases as its concentration increases. By comparing the results with and without N\(_2\), it was observed that Rh B degradation is affected by the presence of O\(_2\).

To determine the inhibition effect of the scavengers more clearly, the reaction parameters were fitted to a pseudo-first-order kinetic model, and the corresponding parameters are shown in Figure S12c (where \( k \) represents the reaction rate). It can be seen that the reaction is significantly inhibited after adding the scavengers and introducing N\(_2\), and the fitting results are consistent with the results shown in Figure S12a. The results indicate that *\( \cdot \)OH and *\( \cdot \)O\(_2\)\(^-\) are the main oxidation species in the reaction process,\(^{62,63}\) and O\(_2\) has a certain positive effect on the reaction. However, neither scavenger nor O\(_2\) affected the H\(_2\)O\(_2\) decomposition (Figure S12b).

To further determine the effect of pH on the generation of free radicals, free radical capture experiments were carried out under the conditions of pH 4.6 and 10 (Figure S12d). As can be seen, BQ shows a better inhibition effect than that of IPA at a given pH, which means that *\( \cdot \)O\(_2\)\(^-\) is more significant than *\( \cdot \)OH on the degradation of Rh B or the production of *\( \cdot \)O\(_2\)\(^-\) is higher than *\( \cdot \)OH. Moreover, by comparing the data after the addition of IPA or BQ with the blank at a certain pH, it is clear that the inhibition effect is also basic-favored.

The EPR experiment was conducted to further identify the existence of *\( \cdot \)OH and *\( \cdot \)O\(_2\)\(^-\), radicals formed during the reaction of the CDs/g-C\(_3\)N\(_4\)/Cu\(_2\)O composite. The spin-trapping DMPO (5,5-dimethyl-1-pyrroline-N-oxide) (100 mM) is a persistent radical scavenger to trap other radicals, such as DMPO-*\( \cdot \)O\(_2\)\(^-\) or DMPO-*\( \cdot \)OH, which are spin adducts with characteristic EPR signals. The EPR signal was not clearly observed without the H\(_2\)O\(_2\) condition (Figure 9a), whereas it clearly revealed a four-line spectrum with the relative intensities of 1:1:1:1 with H\(_2\)O\(_2\), a characteristic signal of the DMPO-*\( \cdot \)O\(_2\)\(^-\) adduct.\(^{65}\) Besides, the EPR spectra featuring the characteristic 1:2:2:1 quartet indicated successful trapping of *\( \cdot \)OH by DMPO with H\(_2\)O\(_2\) in the Rh B degradation experiment as depicted in Figure 9b.\(^{32}\) Further, no EPR signal of spin adduct DMPO-*\( \cdot \)OH was observed without H\(_2\)O\(_2\). The results are consistent with those of the trapping experiments. Hence, we further verified the dominant role of *\( \cdot \)OH and *\( \cdot \)O\(_2\)\(^-\) active species.

2.2.6.2. Mechanism. Based on the above-mentioned results, a mechanism was proposed (see Scheme 1). In the heterogeneous system containing the CDs/g-C\(_3\)N\(_4\)/Cu\(_2\)O composite, H\(_2\)O\(_2\), and Rh B, there are acidic-favored solution reactions, basic-favored surface reactions, and pH-independent surface reactions, while the surface reactions dominate the degradation of Rh B.

**Scheme 1. Mechanism of Various Radical Generations over CDs/g-C\(_3\)N\(_4\)/Cu\(_2\)O in a Catalytic System**

It can be said that under acidic conditions, dissolved Cu(I) is mainly generated in the reaction system and undergoes a homogenous Fenton-like reaction with H\(_2\)O\(_2\) to produce *\( \cdot \)OH and *\( \cdot \)O\(_2\)\(^-\) in solution; the related process is presented in (i) and (ii) and denoted reaction (I).\(^{30}\) However, under basic conditions, Cu\(_2\)O, Cu(OH)\(_2\), and the complex mainly exist in the reaction system, which can react with H\(_2\)O\(_2\) to produce *\( \cdot \)OH and *\( \cdot \)O\(_2\)\(^-\) radicals through surface reactions, mostly catalytic decomposition of H\(_2\)O\(_2\), and the related reaction III is shown as (Vii).\(^{64,65}\) Besides, H\(_2\)O\(_2\) can be catalytically decomposed on the surface of CDs, g-C\(_3\)N\(_4\), and the matrix of the CDs/g-C\(_3\)N\(_4\)/Cu\(_2\)O composite, generating *\( \cdot \)OH and *\( \cdot \)O\(_2\)\(^-\) (as per the related process presented as (iii), (iv), and (v)) (i.e., reaction II).\(^{30,66,67}\) Since reaction (II) did not involve light exposure, it was relatively slow in this work, and the reactions are pH-independent.\(^{7}\) Therefore, the major reactions in the heterogeneous system are reactions (I) and (II) in the acidic solution and reactions (II) and (III) in the basic solution. The role of reaction (I) is more significant under the acidic condition as compared to the basic condition (Figures 5 and S7). However, the major reactions in the heterogeneous system are the surface reactions (II) and (III) irrespective of the solution pH.

As compared to the acidic conditions, under basic conditions, the CDs/g-C\(_3\)N\(_4\)/Cu\(_2\)O composite exhibited stronger catalytic activity and stability, which can continuously decompose H\(_2\)O\(_2\) to generate *\( \cdot \)OH and *\( \cdot \)O\(_2\)\(^-\) so as to induce Rh B degradation (Figures 5 and S9). Also, the curve of degradation of Rh B follows the decomposition trend of H\(_2\)O\(_2\) with the same pH, thereby indicating that pH primarily affects the decomposition of H\(_2\)O\(_2\) and thus the degradation of Rh B (Figure 5).

The *\( \cdot \)OH and *\( \cdot \)O\(_2\)\(^-\) produced in this reaction are used for the degradation of Rh B, and the related process is shown in (vii).\(^{66}\) For the analysis of Rh B products, the degradation products after the reaction could be analyzed by LC/MS.\(^{68}\) Generally, the decomposition of Rh B undergoes a three-step process: N-deethylation, chromophore cleavage with subsequent triazine ring-opening, and mineralization.\(^{69}\) The active free radicals produced by the reaction destroy the structure of Rh B, degrading it into less harmful compounds.

**3. CONCLUSIONS**

In this work, a catalyst CDs/g-C\(_3\)N\(_4\)/Cu\(_2\)O was synthesized by a simple homogeneous method of thermal polymerization with stepwise modification of g-C\(_3\)N\(_4\) with CDs and Cu\(_2\)O, the catalytic performance of which is strongly pH-dependent. The major findings are enumerated as follows.

- In the applied pH range (3–11), the catalytic performance is increased by raising the solution pH (45–96%). The optimal pH was confirmed to be 10 due to the relatively high degradation ratio of Rh B, lower consumption of H\(_2\)O\(_2\), and better recyclability.
- The dry method in the recycling experiments shows better recyclability than using the wet method. The degradation ratio of Rh B, in the dry method at pH 10, remains 95% even after eight cycles.
- The major reactive species leading to the Rh B degradation in the present system are confirmed to be *\( \cdot \)OH and *\( \cdot \)O\(_2\)\(^-\).
- In the proposed mechanism, the major reactions in the heterogeneous system are reactions (I) and (II) in the acidic solution, and the role of reaction (I) is more significant, while the major reactions are reactions (II) and (III) in the basic solution.
and (III) in the basic solution, which are mainly the surface reactions in the heterogeneous system.

Overall, in this study, we developed a promising Fenton-like catalyst that exhibits a wider working pH and good recyclability and overcomes the narrow workable pH of the Fenton reaction.

4. EXPERIMENTAL SECTION

4.1. Reagents. Reagents used in this study included melamine (CP, C₃H₆N₆, ≥99.0%), citric acid monohydrate (AR, C₆H₈O₇·H₂O, ≥99.5%), cuprous oxide (AR, Cu₂O, ≥97.0%), hydrogen peroxide (CP, H₂O₂, 30.0%), acetic acid (AR, CH₃COOH, ≥99.5%), sodium acetate (AR, CH₃COONa·3H₂O, ≥99.5%), potassium iodide (AR, KI, ≥99.0%), ammonium molybdate (CP, H₃MoN₂O₄, 99.7%), hydrochloric acid (AR, HCl, 36%), sodium hydroxide (AR, NaOH, ≥98.0%), hydrogen peroxide (CP, H₂O₂, 30%), acetic acid (AR, CH₃COOH, ≥99.5%), acetyl acetone (AR, C₆H₈O₇·H₂O, ≥98.0%), ethylene glycol (AR, C₂H₆O·H₂O, 98.0%), hydrogen peroxide (CP, H₂O₂, 30.0%), acetic acid (AR, CH₃COOH, ≥99.5%), ethanol (AR, C₂H₅OH, 99.7%), hydrochloric acid (AR, HCl, 36%), sodium hydroxide (AR, NaOH, ≥98.0%), isopropanol (AR, IPA, ≥99.7%), p-benzoquinone (CP, BQ, ≥98.0%), rhodamine B (AR, C₂₂H₁₈ClN₂O₃, ≥99.0%), 5,5-dimethyl-1-pyrroline-N-oxide (AR, DMPO, ≥97.0%), and nitrogen (CP, N₂, ≥99.0%) stored in gas cylinders. All solutions were prepared with deionized water, and all chemicals were supplied by the manufacturer (Sinopharm Chemical Reagent co. Ltd., Shanghai, China) and used as received without further purification.

4.2. Preparation of CDs/g-C₃N₄/CuxO Composites.

4.2.1. CDs/g-C₃N₄. CDs/g-C₃N₄ composites were prepared by thermal polymerization, using citric acid monohydrate as the precursor of CDs as previously reported. Typically, 0.6 g of citric acid and 20 g of melamine were placed in an aluminum crucible, mixed well, and calcined at 600 °C for 3 h at the ramping rate of 2 °C min⁻¹ in a muffle furnace. After naturally cooling down at room temperature (RT), the CdS/g-C₃N₄ composite was obtained. Furthermore, several CdS/g-C₃N₄ composites (y = 1–6) that included different amounts of CDs were prepared, where y represents the initial mass ratio of citric acid monohydrate to melamine.

4.2.2. CDs/g-C₃N₄/CuxO Composite. The cuprous oxide (Cu₂O)-modified CDs/g-C₃N₄ composite was prepared by a similar thermal polymerization pathway as previously reported. Typically, 5 g of CDs/g-C₃N₄ composite material and 0.14 g of Cu₂O were added to 10 mL of ethanol solution with stirring for 0.5 h. The mixed material/solution was placed in an aluminum crucible, heated at a ramp of 1 °C min⁻¹ to 520 °C for 3 h, and cooled to RT in a muffle furnace. The derived powder was stored and labeled as C2. Additionally, CDs/g-C₃N₄/CuxO composites that included different amounts of Cu₂O were prepared (Table S5).

4.3. Material Characterization. Fourier transform infrared spectroscopy ( Nicolet iS FT-IR spectrometer, Thermo Fisher Scientific) was used to investigate the samples of infrared absorption spectra using the standard potassium bromide (KBr) disk method in the wavenumber range from 400 to 4000 cm⁻¹. The structural properties of the composite were detected by powder X-ray diffraction (XRD, D/max- III A, Bruker Corporation, Germany) measurements, which used Cu Kα radiation (λ = 1.54 A; angle of 2θ, 10–70°). The morphology and microstructure of the synthesized composites were characterized by transmission electron microscopy (TEM) (TEM JEM-2100 model, JEOL Ltd., Japan) and high-resolution TEM (HRTEM).

An investigation of the surface component elemental state of the resultant catalyst was done using X-ray photoelectron spectroscopy (XPS, via an ESCALAB 250XI, Thermo Fisher Scientific, Inc.), and the C 1s signal at 284.60 eV was used as the internal standard to calibrate binding energies.

The specific surface and pore volume were analyzed by the Brunauer–Emmett–Teller (BET) (TriStar II 3020, Micromeritics Instrument Corporation, Georgia) via isothermal desorption and adsorption with high-purity nitrogen.

The absorbance of the studied reagents, i.e., H₂O₂ and Rh B, was measured by a V-5600 spectrophotometer (Shanghai Metash Instruments Co. Ltd., China) and a UV-5500 PC (Shanghai Metash Instruments Co. Ltd., China) spectrophotometer in the wavelength range of 200–800 nm.

The pH of the solutions was measured using the ST2100 pH meter (China) with an accuracy of ±0.01 pH units and a working temperature from 5 to 40 °C.

The prepared samples were weighed to ±10⁻⁴ g in an ME104E microbalance (Mettler Toledo, China). The dissolved oxygen (DO) of the solution was analyzed by the portable dissolved oxygen meter (JPB-607A, China).

An inductively coupled plasma optical emission spectrometer (ICP-OES) Prodigy 7 (Teledyne instrument Labs, Mason, OH) was used to measure the total copper ion concentration of the solution.

The ROS were detected by electron paramagnetic resonance (EPR) using an A300 spectrometer (Bruker Instrument, Germany) and spin-trapping agents such as 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, 100 mM) aqueous solution (Bruker Instrument, Germany).

4.4. Catalytic Activity Experiment. Rh B was used as the target dye for evaluating the catalytic properties of the synthesized composites. All catalytic degradation experiments were conducted in the dark with magnetic stirring at RT.

In a typical experiment, a certain amount of synthesized composite was added to the Rh B solution and stirred for 40 min to achieve adsorption/desorption equilibrium before the addition of H₂O₂, which triggered the catalysis. At fixed time points, 4 mL of suspension was taken and filtered using a 0.22 μm membrane filter. The absorbance was measured so as to obtain the time-resolved concentrations of H₂O₂ and Rh B. In some cases, the concentrations of H₂O₂, Rh B, and dissolved copper species in the filtered samples were also monitored to evaluate the potential reaction in the homogeneous system.

The concentration of Rh B was determined by measuring the absorbance at 555 nm using an ultraviolet–visible (UV–vis) spectrophotometer. The H₂O₂ concentration was detected by the Ghormley triiodide method, which states that I⁻ could be oxidized to triiodide (I₃⁻) by H₂O₂ in the presence of acetic acid and the catalyst ammonium molybdate (AMO). The absorbance of I₃⁻ can be measured by a spectrophotometer at 350 nm. The intermediate products produced in the experiment may interfere with the measurements, but the experimental error was less than 2% for the concentrations of Rh B and H₂O₂ determined.

The specific free radical scavengers, including benzoquinone (BQ) and isopropanol (IPA), were separately added into the suspension after the adsorption–desorption equilibrium before the addition of H₂O₂, scavenging ·OH and ·O₂, respectively. Additionally, the suspension was purged with N₂ to remove O₂ in the whole reaction process.

The degree of degradation was expressed by degradation ratios and utilization, which are defined in eqs 3 and 4, where [Rh B]₀ or [H₂O₂]₀ is the initial concentration of Rh B and H₂O₂, and [Rh B]ᵣ or [H₂O₂]ᵣ is the concentration of Rh B (mM) or H₂O₂ at time t (t = 60 min), respectively. All of these
experiments were carried out in beakers in the dark to avoid dye sensitization.

\[
\text{degradation ratios } \% \text{RhB } \frac{[\text{RhB}]_0 - [\text{RhB}]}{[\text{RhB}]} \times 100\% \\
\text{utilization } \% \frac{[\text{RhB}]_0 - [\text{RhB}]}{[\text{H}_2\text{O}_2]_0 - [\text{H}_2\text{O}_2]} \times 100\%
\]  

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsomega.0c05915.

FT-IR spectra of g-C₃N₄, CD₃/g-C₃N₄, and CD₃/g-C₃N₄/CuO composites (Figure S1); XRD patterns of CuO, g-C₃N₄, CD₃/g-C₃N₄, and CD₃/g-C₃N₄/CuO composites (Figure S2); XPS spectra of the CDs/g-C₃N₄/CuO composite (Figure S3); high-resolution XPS spectra of O 1s (Figure S4); N₂ adsorption/desorption isotherm and the pore-size distribution of g-C₃N₄, CD₃/g-C₃N₄, and CD₃/g-C₃N₄/CuO (Figure S5); [Rh B]/[Rh B]₀ as a function of time with different H₂O₂ concentrations in the presence of 2 g/L CD₃/g-C₃N₄/CuO composite with the initial concentration of [Rh B]₀ = 0.064 mM and V = 100 mL (Figure S6); [Rh B]/[Rh B]₀ as a function of time in stock CD₃/g-C₃N₄/CuO (2 g/L) suspensions and filtrates obtained at selected time intervals with the initial concentration of [Rh B]₀ = 0.064 mM, [H₂O₂]₀ = 5 mM, and V = 100 mL; degradation of Rh B in heterogeneous catalytic reaction and filtered solution in 1 min reacting over a longer period of time (Figure S7); variation of the Rh B wavelength at different pH values (Figure S8); recycling performance for 5 mM H₂O₂ decomposition in the presence of the 2 g/L CD₃/g-C₃N₄/CuO composite at pH 11 at 25 min per cycle and V = 100 mL; recycling performance of the 2 g/L CD₃/g-C₃N₄/CuO composite for Rh B (0.064 mM) degradation in the presence of 5 mM H₂O₂ at pH 11 at 30 min per cycle (Figure S9); [Rh B]/[Rh B]₀ as a function of time in the presence of the 2 g/L CD₃/g-C₃N₄/CuO composite for Rh B (0.064 mM) degradation in the presence of 10 mM H₂O₂ at pH 11 (Figure S10); H₂O₂ consumed in cycling reactions by the 2 g/L CD₃/g-C₃N₄/CuO composite for Rh B (0.064 mM) degradation in the presence of 5 mM H₂O₂ at pH 4.6 (unadjusted pH; V = 100 mL); recycling degradation of the Rh B (0.064 mM) was conducted by the 2 g/L CD₃/g-C₃N₄/CuO composite in the presence of 5 mM H₂O₂ at pH 4.6 (unadjusted pH; V = 100 mL) (Figure S11); [Rh B]/[Rh B]₀ and [H₂O₂]/[H₂O₂]₀ as a function of time in the presence of different quenchers by the 2 g/L CD₃/g-C₃N₄/CuO composite for Rh B (0.064 mM) degradation in the presence of 5 mM H₂O₂; parameters of the pseudo-first-order kinetic models of different quenchers by the 2 g/L CD₃/g-C₃N₄/CuO composite for Rh B (0.064 mM) degradation in the presence of 5 mM H₂O₂; [Rh B]/[Rh B]₀ as a function of time in the presence of different quenchers by the 2 g/L CD₃/g-C₃N₄/CuO composite for Rh B (0.064 mM) degradation in the presence of 5 mM H₂O₂ at different pH values (Figure S12); XPS results of the CD₃/g-C₃N₄/CuO composite (Table S1); efficiency of Rh B at different H₂O₂ concentrations (Table S2); comparison of the catalytic performance of CD₃/g-C₃N₄/CuO and several reported relative studies (Table S3); reaction formulas and reaction rate constants of possible reactions in radical trapping (Table S4); and the initial mass ratio of CuO to CD₃/g-C₃N₄ for CD₃/g-C₃N₄/CuO composites (Table S5).
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