

Enhanced degradation of Rhodamine B through peroxymonosulfate activated by a metal oxide/carbon nitride composite

Text S1 Chemicals and reagents

Rhodamine B (RhB), potassium hydrogen persulfate (PMS), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, urea, methanol (MeOH), isopropanol (IPA), p-benzoquinone (p-BQ), L-Histidine, 5,5-dimethyl-pyrroline-N-oxide (DMPO), 4-Amino-2,2,6,6-tetramethylpiperidine (TEMP), Congo Red (CR), Methylene blue (MB) and Tetracycline (TC) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Both citric acid (CA) and melamine were purchased from Macleans Reagent Co., Ltd. (Shanghai, China). All reagents and drugs were of analytical grade. The solutions in the experiment were all configured with deionized water.

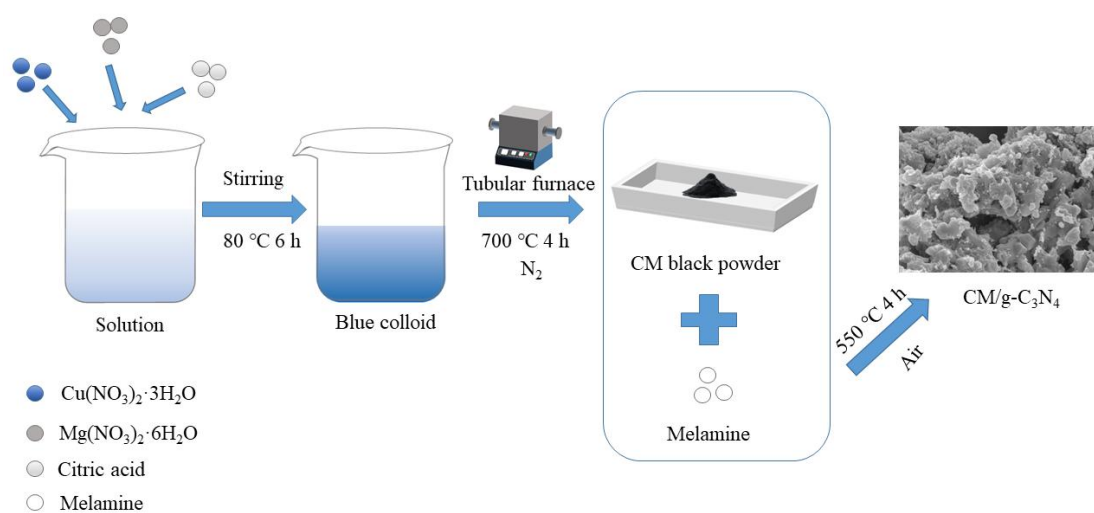
Test S2 Degradation experiment

Generally, the degradation experiment was carried out in a 125 mL glass beaker containing 100.0 mL RhB solution (5.0 mg/L-20.0 mg/L) and catalyst (0.10 g/L-0.60 g/L) at room temperature (25 ± 2 °C). The mixture was stirred mechanically for 10 min. After reaching the adsorption and desorption equilibrium between the RhB and the catalyst, PMS (0.50 mM-3.0 mM) was introduced into the system under constant stirring. At specified time intervals, 2.0 mL of suspension was taken out and immediately filtered through a 0.22- μm syringe filter for analysis. If necessary, the initial pH of reaction was adjusted from 3.0 to 11.0 by adding 0.10 M H_2SO_4 or 0.10 M NaOH. As a control, the adsorption of RhB by CM/g- C_3N_4 and the degradation of RhB by PMS were implemented. The degradation of Congo Red

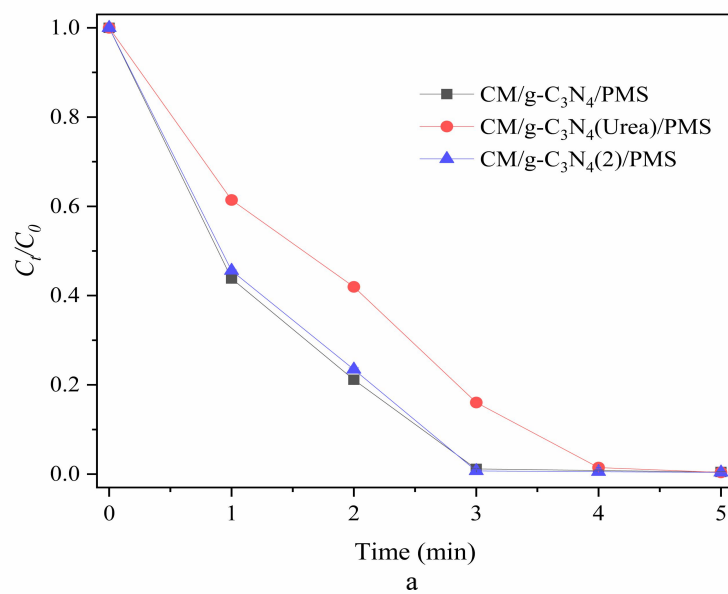
(CR)/Methylene blue (MB)/Tetracycline (TC) and RhB removal in different water matrixes were carried out by the same procedures. The catalyst was recovered after the reaction, washed with ethanol and deionized water, and dried under vacuum at 60 °C, then used in the next reaction under similar experimental conditions to evaluate the reusability of CM/g-C₃N₄. For determining the active substances, in addition to CM/g-C₃N₄, PMS and RhB, quantified scavengers (MeOH, IPA, p-BQ and L-Histidine) were added to the reactor.

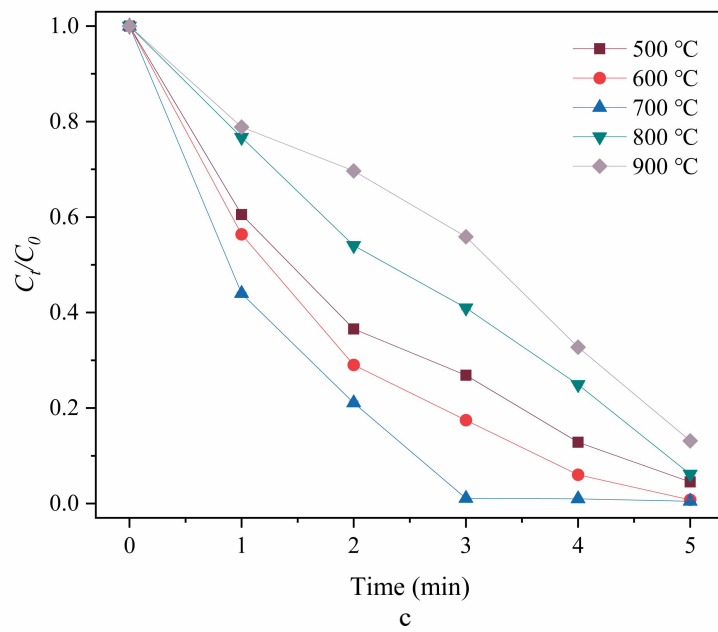
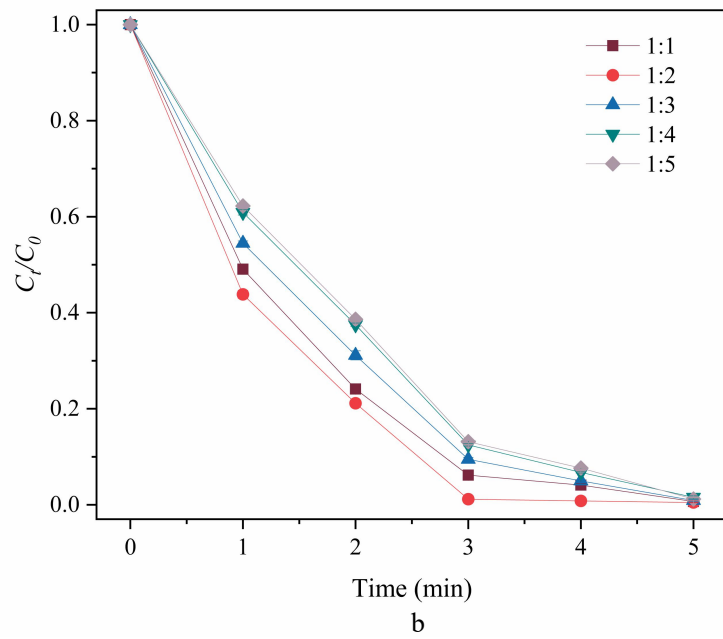
Text S3 Characterizations

The microstructural of catalyst was revealed by scanning electron microscopy (SEM, ZEISS Gemini 300) equipped with an energy dispersive spectrometer (EDS) detector system and high-resolution transmission electron microscope (HRTEM, JEOL JEM-2100). X-ray powder diffraction (XRD) patterns of the catalysts were measured on a Bruker D8 X-ray diffractometer using Cu K α radiation (λ = 0.1542 nm). The specific surface areas and pore characteristics of the catalysts were investigated using the Brunauer-Emmett-Teller (BET) N₂ adsorption-desorption method with a Micromeritics ASAP 2460 instrument. The surface components of CM/g-C₃N₄ before and after the degradation were determined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). The functional groups of catalyst were characterized by Fourier transform infrared spectroscopy (FTIR, Vertex 70).



Scheme S1 Preparation of CM/g- C_3N_4 .





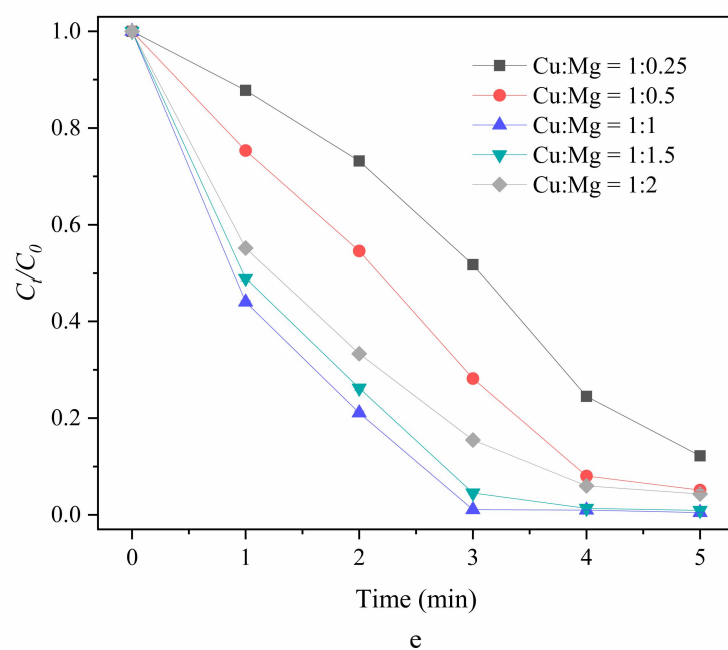
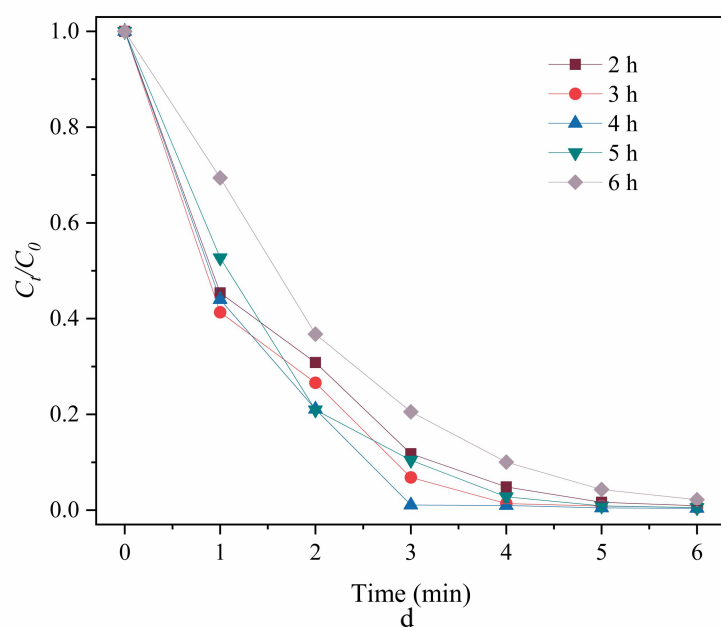
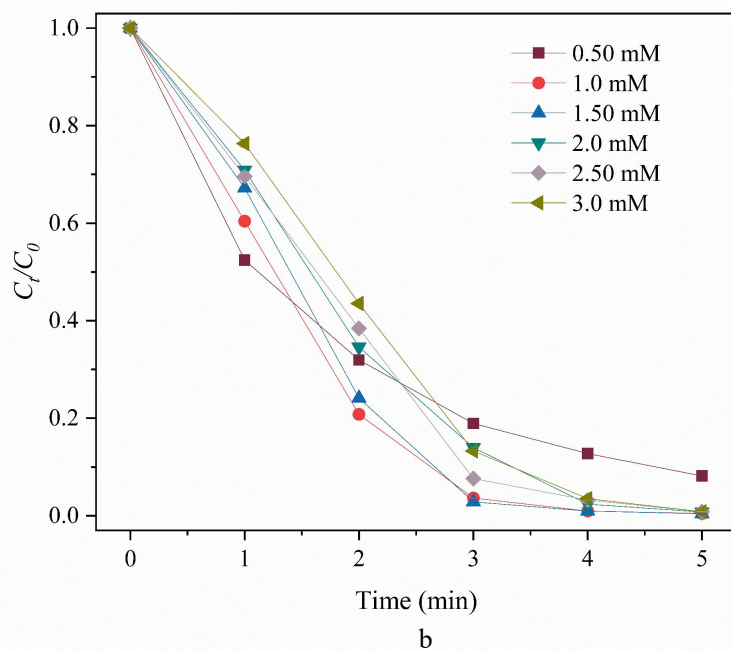
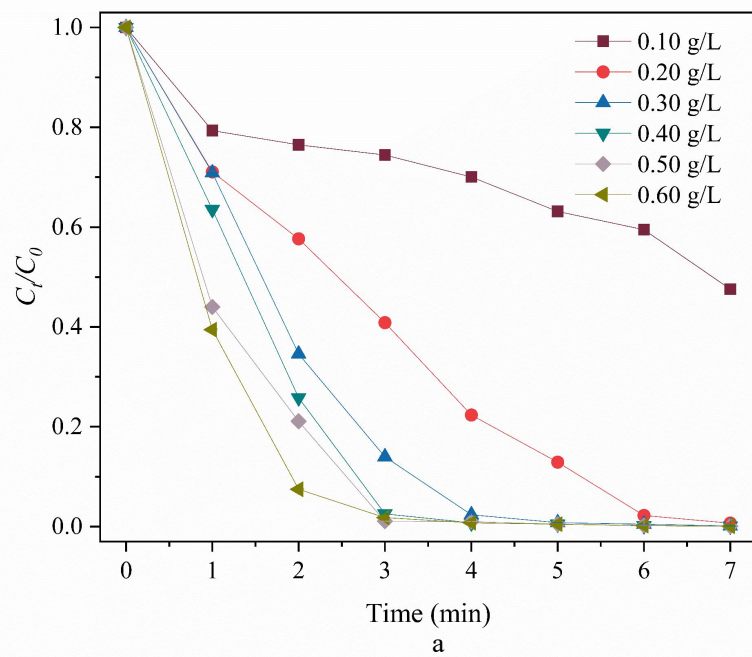


Figure S1 Effects of different g-C₃N₄ precursors (a), mass ratios of copper-magnesium oxide to melamine (b), pyrolysis temperatures (c), pyrolysis times (d) and molar ratios of copper to magnesium precursor (e) on the catalytic performance of material. Reaction conditions: [PMS] = 2.0 mM, [catalyst] = 0.50 g/L, [RhB] = 10.0 mg/L, 25 °C.



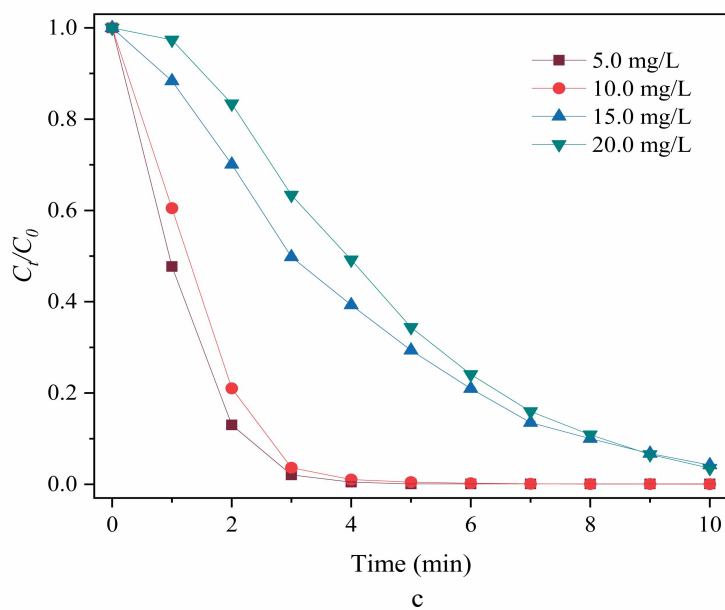


Figure S2 Effects of catalyst dosage (a), PMS concentration (b) and RhB concentration (c) for RhB degradation. Reaction conditions: [PMS] = 0.50-3.0 mM, [CM/g-C₃N₄] = 0.10-0.60 g/L, [RhB] = 5.0-20.0 mg/L, 25 °C.

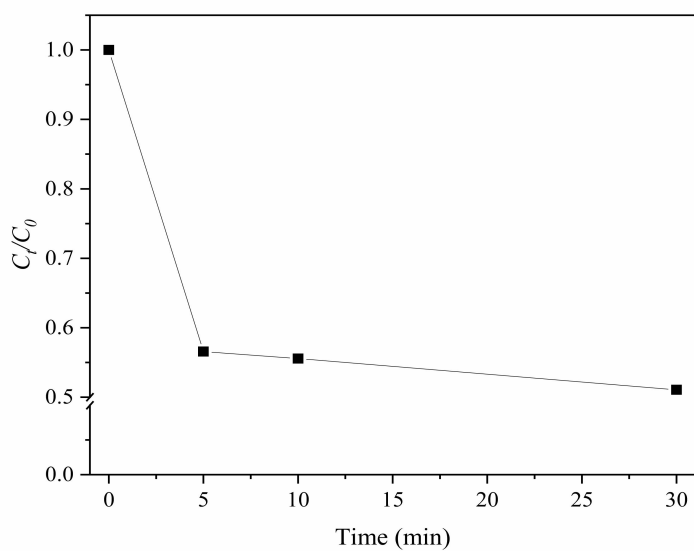


Figure S3 Mineralization efficiency of CM/g-C₃N₄/PMS system. Reaction conditions: [PMS] = 1.0 mM, [CM/g-C₃N₄] = 0.30 g/L, [RhB] = 10.0 mg/L, 25 °C.

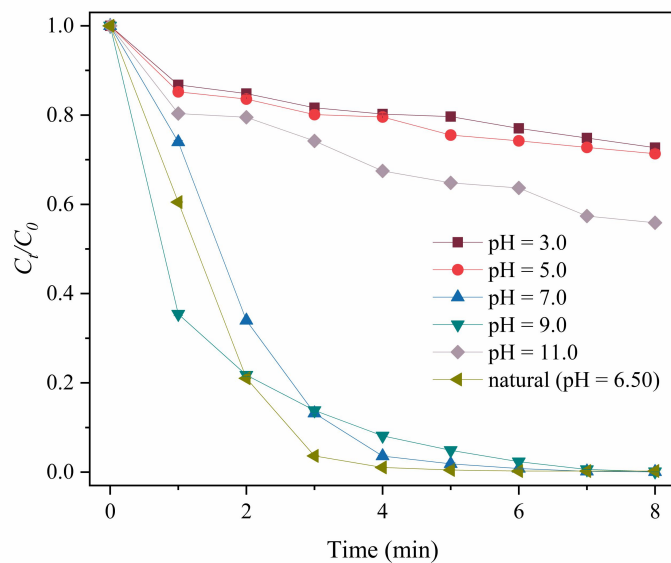


Figure S4 Effect of initial pH for RhB degradation in the CM/g-C₃N₄/PMS system. Reaction conditions: [PMS] = 1.0 mM, [CM/g-C₃N₄] = 0.30 g/L, [RhB] = 10.0 mg/L, 25 °C.

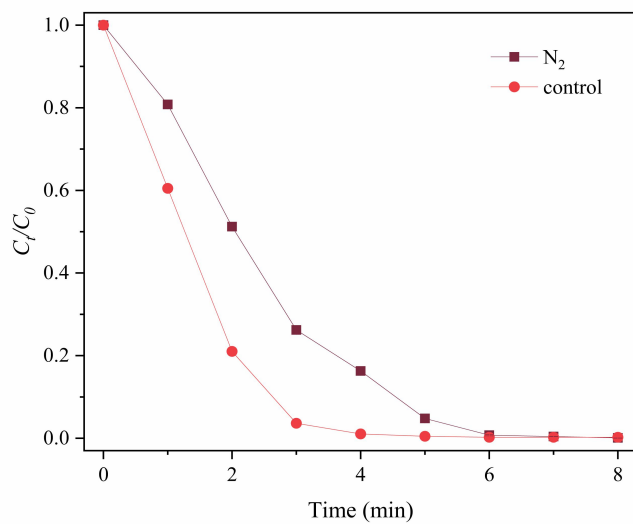
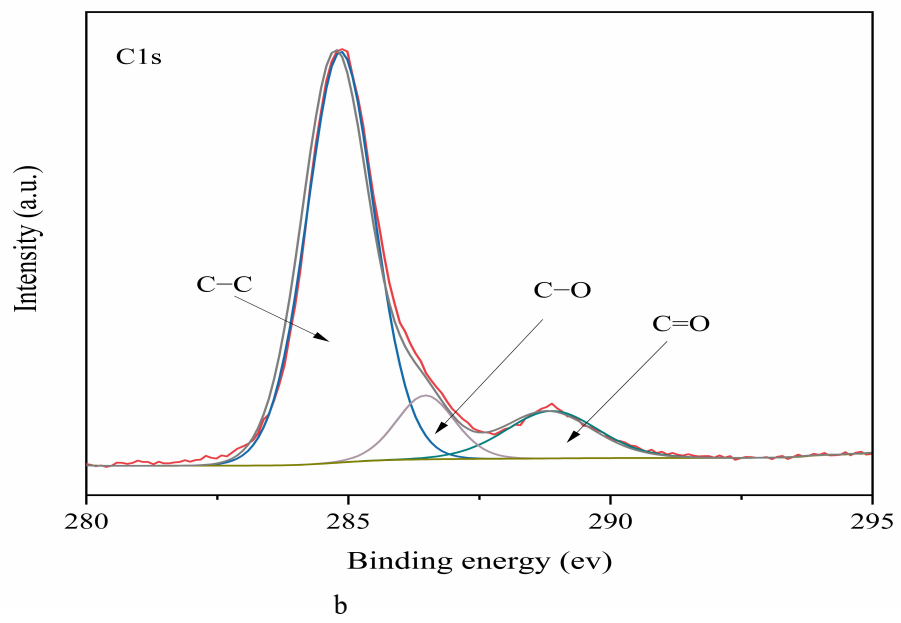
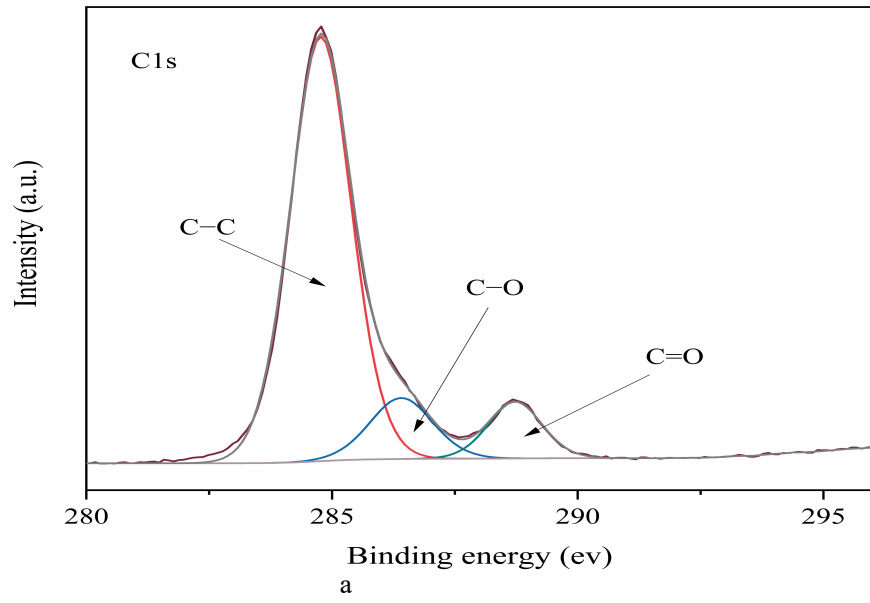
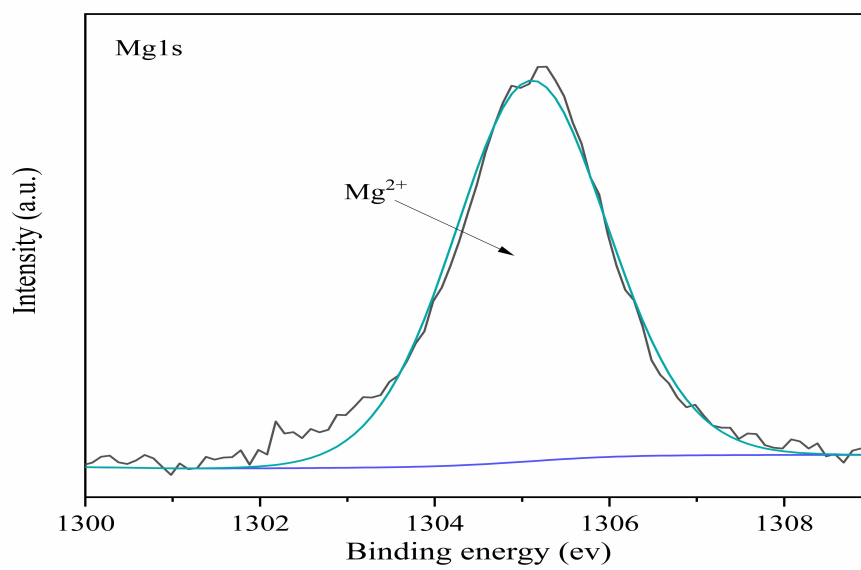
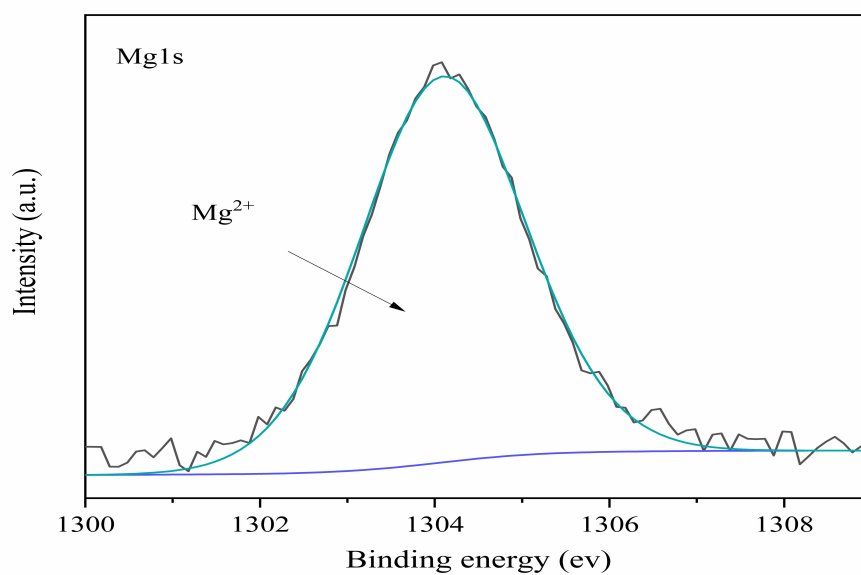


Figure S5 Effect of nitrogen on the degradation of RhB in the CM/g-C₃N₄/PMS system. Reaction conditions: [PMS] = 1.0 mM, [CM/g-C₃N₄] = 0.30 g/L, [RhB] = 10.0 mg/L, N₂ = 100.0 mL/min, 25 °C.





c



d

Figure S6 X-ray photoelectron spectroscopy spectra of C1s (a, b) and Mg 1s (c, d) in the CM/g- C_3N_4 before (a, c) and after (b, d) the reaction.

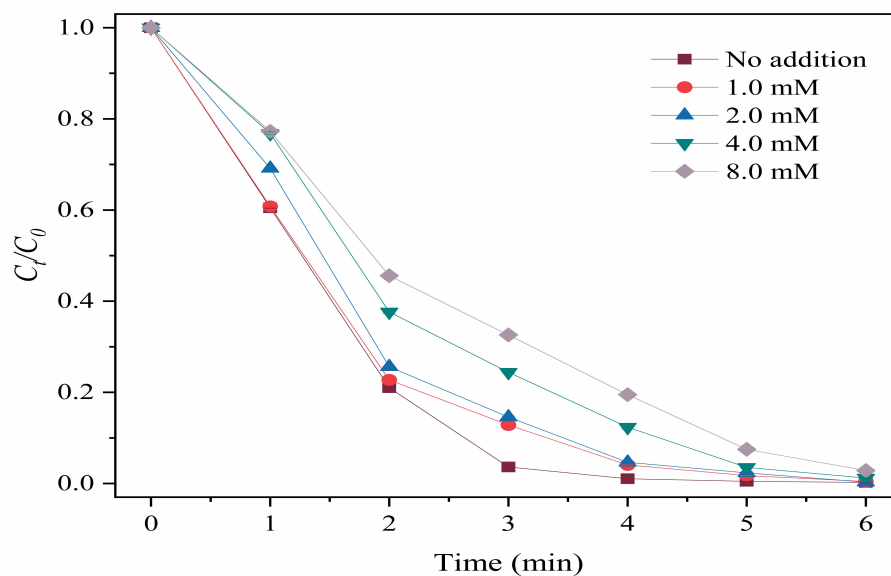


Figure S7 Effect of H_2PO_4^- on the degradation of RhB in the CM/g- C_3N_4 /PMS system.

Reaction conditions: [PMS] = 1.0 mM, [CM/g- C_3N_4] = 0.30 g/L, [RhB] = 10.0 mg/L, 25 °C.

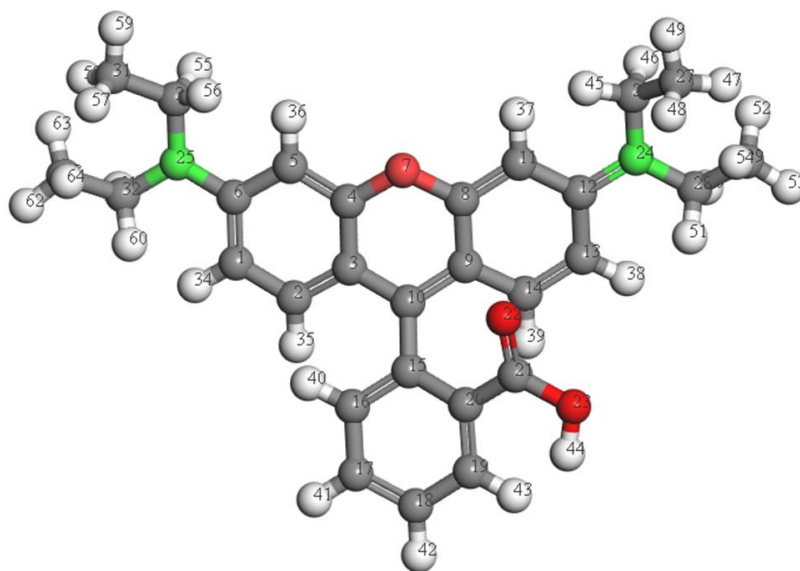


Figure S8 The molecular structure of the optimized RhB (a) (oxygen, red; carbon, gray; nitrogen, green; hydrogen, white).

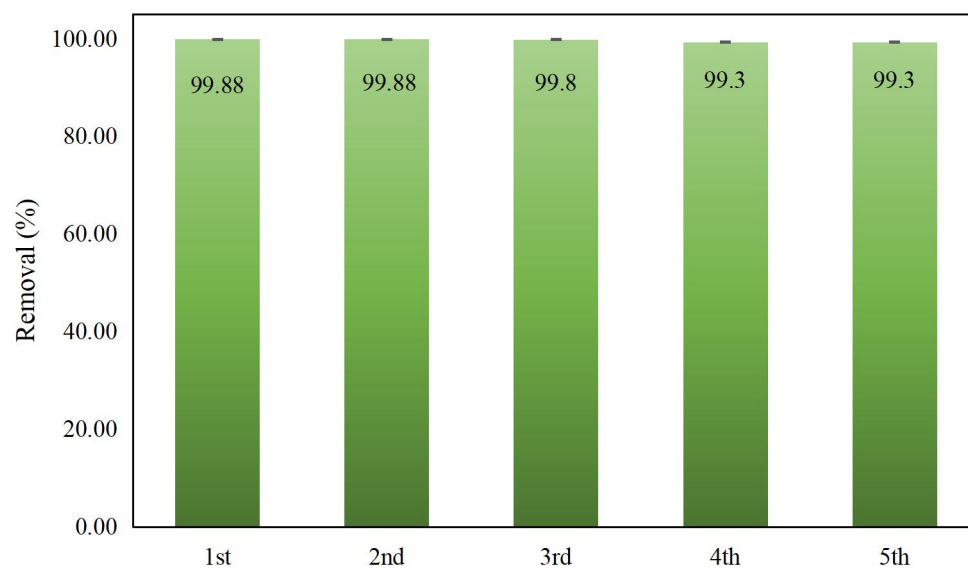


Figure S9 Degradation of RhB with the recycled CM/g-C₃N₄. Reaction conditions: [PMS] = 1.0 mM, [CM/g-C₃N₄] = 0.30 g/L, [RhB] = 10.0 mg/L, 25 °C.

Table S1 *k* value of CM/g-C₃N₄/PMS system in different conditions.

Catalyst	PMS	RhB	
dosage	concentration	concentration	<i>k</i> value
(g/L)	(mM)	(mg/L)	(min ⁻¹)
0.10	2.0	10.0	0.0867
0.20	2.0	10.0	0.3550
0.30	2.0	10.0	1.0107
0.40	2.0	10.0	1.1119
0.50	2.0	10.0	1.1759
0.60	2.0	10.0	1.2916
0.30	0.50	10.0	0.4939
0.30	1.0	10.0	1.1703
0.30	1.50	10.0	1.1596
0.30	2.0	10.0	1.0107
0.30	2.50	10.0	0.9911
0.30	3.0	10.0	0.8455
0.30	1.0	5.0	1.4365
0.30	1.0	10.0	1.1703
0.30	1.0	15.0	0.2543
0.30	1.0	20.0	0.2187

Table S2 RhB degradation in different system.

	Catalyst dosage (g/L)	PMS concentration (mM)	RhB concentration (mg/L)	Reaction time (min)	<i>k</i> value (min ⁻¹)	Removal efficiency	Ref.
Fe ₃ O ₄ /Co ₃ S ₄	0.05	1.0	200.0	20	0.302	100.00%	[1]
5%-T/LDOs	0.50	5.0	10.0	10	0.4537	95.80%	[2]
Co-G	0.02	0.16	50.0	10	0.9438	100.00%	[3]
Co _{1+x} Fe _{2-x} O ₄	0.20	0.65	40.0	30	0.260	91.20%	[4]
CM/g-C ₃ N ₄	0.30	1.0	10.0	5	1.1703	99.88%	This work

Table S3 Atomic area ratios of different compositions in the CM/g-C₃N₄ before and after the reaction.

Composition	Before reaction (%)	After reaction (%)
C-C	79.00	77.42
C-O	11.68	10.40
C=O	9.32	12.18
O ²⁻	9.58	25.14
-OH	43.27	45.79
adsorbed oxygen	41.99	13.78
C=N-C	86.45	40.03
C-N	13.55	59.97
Cu ⁺	42.59	51.14
Cu ²⁺	57.41	48.86

Table S4 Partial Fukui indexes of RhB molecule.

Atom	f^0	Atom	f^0
C1	0.025	C18	0.040
C4	0.023	C19	0.028
C8	0.028	C20	0.023
C10	0.055	C21	0.035
C11	0.027	O22	0.039
C12	0.023	O23	0.031
C15	0.031	N24	0.023
C16	0.029	N25	0.020
C17	0.034		

References

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