Electronic Supplementary Information

Carbon Self Doping Induced High Electronic Conductivity and Photoreactivity of g-C₃N₄

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Theoretical Calculations. The band structures and density of states (DOS) calculations were investigated via the plane-wave-pseudopotential approach based on density functional theory (DFT). Electronic structures were calculated within the generalized gradient approximation from Perdew-Burke-Ernzerhof (GGA-PBE). The cut-off energy was 550 eV, and the Monkhorst-Pack k-point meshes were $5 \times 5 \times 3$ for all structures. In the process of calculations, the convergence tolerances were set as follows: 2.72e-5 eV/ atom for energy, 0.002 eV/ Å for max. force, 0.05 GPa for max. stress, 0.001 Å for max. displacement and 1.36e-4 eV/ atom for SCF.

Synthesis of C-g-C₃N₄ and g-C₃N₄ Photocatalysts. All chemicals used were analytical-grade reagents without further purfication. In a typical synthesis procedure, 1 g of melamine was placed in a 100 mL Teflon-lined autoclave with absolute alcohol up to 80% of the total volume. Then, the autoclave was sealed and heated at 200 °C for 24 h. The resulting colorless transparent material was collected and dried at room temperature and then transferred into a covered crucible to thermal treatment at 520 °C in a muffle furnace for 4 h with a heating rate of 20 °C/min. The final sample was denoted as C-g-C₃N₄. For comparison, pure g-C₃N₄ powders were also prepared by directly calcining melamine at 520 °C for 4 h and denoted as g-C₃N₄.

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Characterization. The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-RB diffractometer with monochromatized Cu K α radiation ($\lambda = 1.5$ Å). Carbon to nitrogen ratio (C/N) of the samples was determined by elemental analysis (EA, Vario ELIII CHNSO). The morphology of the product was determined by a transmission electron microscope (TEM, JEOL JSM-2010) operating at 200 KV. UV–vis diffuse reflectance spectra of samples were obtained using an UV -vis spectrometer (Shimadzu UV-3600). XPS measurements were performed in a VG scientific ESCALAB Mark II spectrometer equipped with two ultra-high vacuum (UHV) chambers. All the binding energies were calibrated to the C 1s peak at 284.6 ev of the surface adventitious carbon. The nitrogen adsorption and desorption isotherms at 77 K were measured using Micrometrics ASAP2020 system after samples were vacuum dried at 180 °C overnight.

Photocatalytic Activity Test. The photocatalytic activities of the products were tested for the removal of RhB and Cr(VI) under visible light irradiation. A 300 W Xenon lamp with a 420 nm cut-off filter was chosen as a visible light source. 0.1 g of photocatalyst was suspended in 100 mL of 5 mg/L RhB or 20 mg/L Cr(VI) aqueous solution in a container with cooling water jacket outside. The suspensions were stirred in the dark to establish an adsorption-desorption equilibrium before the visible light irradiation. During the degradation, 3 mL of the suspension was collected at an interval of 20 min. After being centrifuged, the solution was measured with a Hitachi U-3310 UV-visible spectrophotometer, and the concentration of RhB and Cr(VI) was estimated by measuring the absorption at wavelengths of 553 and 349 nm, respectively.

Photocatalytic H₂ Production Activity. The photocatalytic H₂ production experiments were performed in a 100 mL Pyrex flask at ambient temperature and atmospheric pressure. A 300 W Xe lamp through a UV-cutoff filter ($\lambda > 400$ nm) was used as the light source. In a typical experiment, 50 mg of photocatalyst powder was suspended in 80 mL of aqueous solution containing 25% methanol scavenger in volume. The loading of 1.5 wt% Pt cocatalyst was conducted by directly dissolving H₂PtCl₆ into the above 80 mL mixed solution. Next, the suspensions were stirred and followed by illumination (300 W Xe lamp) for 20 min at room temperature. Before irradiation, suspensions of the cocatalyst were dispersed in an ultrasonic bath and nitrogen was bubbled through the reaction mixture for 40 min to remove the dissolved oxygen and to ensure the anaerobic conditions in the reaction system. A 0.4 mL portion of gas was sampled intermittently through the septum, and hydrogen was analyzed by a gas chromatograph (GC-14C, Shimadzu, Japan, TCD, nitrogen as a carrier gas and 5 Å molecular sieve column).

Analysis of Photocatalysis Mechanism. Triethanolamine (TEOA) was chosen as hole scavengers, potassium dichromate purging with nitrogen was chosen as electrons scavengers.^{1, 2, 3} Typically, the catalyst of 0.1 g with different scavengers were dispersed in RhB aqueous solution (100 mL, 5 mg·L⁻¹) before visible light irradiation. The concentration of RhB during photocatalytic reaction was determined by measuring the absorption of their solution.

Photoelectrochemical experiments. Photoelectrochemical experiments were performed in a conventional three-electrode cell with a platinum plate $(1 \times 1 \text{ cm}^2)$ as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode on a CHI 660C workstation. The photoelectrode (working electrode) was positioned in the middle of a 0.1 M KCl aqueous solution with the glass side facing the incident light. A 300 W Xe lamp with a 420 nm cutoff filter was chosen as a visible light source.

The photoelectrodes were prepared as described in Zhang's paper.⁴ Typically, the spreading aqueous slurries of g-C₃N₄ and carbon self-doped g-C₃N₄ on ITO glass substrate with a glass rod, using adhesive tapes as spaces. The suspension was prepared by grinding 20 mg of pure g-C₃N₄ or carbon self-doped g-C₃N₄, 40 µL of PEDOT-PSS (Sigma-Aldrich, 1.3-1.7%) aqueous solution and 200 µL of water, and the film was dried in air and annealed at 150 °C for 10 min.

Reference

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Figure S1. XPS spectra of the resulting samples. (a) C1s and (b) N1s of the sample $g-C_3N_4$ and $C-g-C_3N_4$.



Figure S2. Comparison of photocatalytic RhB degradation in different photocatalysis systems under visible light irradiation ($\lambda > 420$ nm). (a) g-C₃N₄, (b) C-g-C₃N₄. TEOA was chosen as the hole scavenger; N₂ was used to remove molecular oxygen to probe the reaction between molecular oxygen with photogenerated electrons; the addition of potassium dichromate plus purging with nitrogen was chosen as electrons scavengers where dichromate ions would trap the photogenerated electrons.

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Figure S3. Diffuse reflectance spectra of $g-C_3N_4$ and $C-g-C_3N_4$. The inset is the UV-vis absorbance spectra of $g-C_3N_4$ and $C-g-C_3N_4$.

Figure S4. TEM images of $g-C_3N_4$ (a) and $C-g-C_3N_4$ (b) samples.



Figure S5. Current-time curves of $g-C_3N_4$ and $C-g-C_3N_4$ photoelectrodes in 0.1 M aqueous KC1 under visible light ($\lambda > 420$ nm, 300 W Xe lamp) (a). PL spectra of $g-C_3N_4$ and $C-g-C_3N_4$ (b).



Figure S6. Mott-Schottky plots (a), band gap structures of $g-C_3N_4$ and $C-g-C_3N_4$ (b).



Figure S7. DMPO spin-trapping electron spin resonance spectra of $g-C_3N_4$ and $C-g-C_3N_4$ in methanol dispersion for DMPO- $\cdot O_2^-$.

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Figure S8. N₂ adsorption-desorption isotherms of g-C₃N₄ and C-g-C₃N₄ samples.

We explored recycling test and XRD measurement to check the stability of C-g-C₃N₄ during photocatalytic reaction (Figure S9 and Figure S10, ESI) and did not find significant change in the photocatalytic activity and crystalline structure after four cycles, indicating the carbon self-doped g- C_3N_4 were very stable during photocatalysis.



Figure S9. Recycling test for the photooxidation of RhB on C-g-C₃N₄.



Figure S10. XRD patterns of the C-g-C₃N₄ before and after photocatalytic reaction.

We utilized ESR technique to check the formation of \cdot OH, but did not find any \cdot OH signals (Figure S11). We also found that the addition of tert-butyl alcohol (10 mM, \cdot OH scavenger) could not change the RhB photooxidation rates over either g-C₃N₄ or C-g-C₃N₄ (Figure S12). These experimental results suggest no formation of hydroxyl radicals. While the addition of H₂O₂ (1 mg L⁻¹) could not result in photooxidation RhB under visible light in the absence of photocatalyst (Figure S12), suggesting that H₂O₂ would not contribute to the photooxidation of RhB. These experimental results confirm that direct hole oxidation is mainly responsible for the photodegradation of RhB over the two samples in this study.



Figure S11. DMPO spin-trapping electron spin resonance spectra of $g-C_3N_4$ and $C-g-C_3N_4$ in methanol dispersion for the detection of DMPO-·OH.



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Figure S12. Comparison of photocatalytic RhB degradation in different photocatalysis systems under

visible light irradiation ($\lambda > 420$ nm). (a) g-C₃N₄, (b) C-g-C₃N₄.

TABLE S1. Summary of surface areas and the photocatalytic activities of various photocatalysts as well as the photocatalytic activity enhancement times induced by carbon self doping.

Sample	$\begin{array}{c} A_{BET}{}^{[a]}\\ (m^2 \! / g) \end{array}$	K(RhB) ^[b] (min ⁻¹)	$K'(RhB)^{[c]}$ $(g \cdot min^{-1} \cdot m^{-2}, \times 10^{-3})$	$\frac{K(Cr(VI))^{[d]}}{(h^{-1})}$	$\frac{\text{K'(Cr(VI))}^{[e]}}{(g \cdot h^{-1} \cdot m^{-2}, \times 10^{-3})}$
g-C ₃ N ₄	8	0.0081	1.0	0.06025	7.5
C-g-C ₃ N ₄	34	0.0362	1.1	0.10126	3.0
Enhancement	4 25	A 47	11	1 68	0.40
times	т.23	- -/	1,1	1.00	0.40

[a] The specific surface area. [b, d] The reaction kinetics of RhB photooxidation and the Cr(VI) photoreduction at initial stage were analyzed with the pseudo-first-order model as expressed by $\ln(C/C_0)$ = -kt. [c, e] The k' values were k values normalized with the surface areas, respectively.