

Visible-Light-Responsive Graphitic Carbon Nitride: Rational Design and Photocatalytic Applications for Water Treatment

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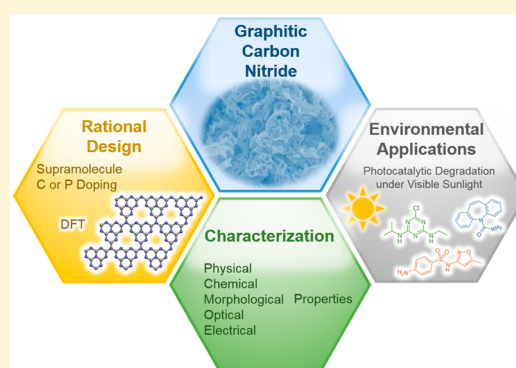
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Supporting Information

ABSTRACT: Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) has recently emerged as a promising visible-light-responsive polymeric photocatalyst; however, a molecular-level understanding of material properties and its application for water purification were underexplored. In this study, we rationally designed nonmetal doped, supramolecule-based $g\text{-C}_3\text{N}_4$ with improved surface area and charge separation. Density functional theory (DFT) simulations indicated that carbon-doped $g\text{-C}_3\text{N}_4$ showed a thermodynamically stable structure, promoted charge separation, and had suitable energy levels of conduction and valence bands for photocatalytic oxidation compared to phosphorus-doped $g\text{-C}_3\text{N}_4$. The optimized carbon-doped, supramolecule-based $g\text{-C}_3\text{N}_4$ showed a reaction rate enhancement of 2.3–10.5-fold for the degradation of phenol and persistent organic micropollutants compared to that of conventional, melamine-based $g\text{-C}_3\text{N}_4$ in a model buffer system under the irradiation of simulated visible sunlight. Carbon-doping but not phosphorus-doping improved reactivity for contaminant degradation in agreement with DFT simulation results. Selective contaminant degradation was observed on $g\text{-C}_3\text{N}_4$, likely due to differences in reactive oxygen species production and/or contaminant-photocatalyst interfacial interactions on different $g\text{-C}_3\text{N}_4$ samples. Moreover, $g\text{-C}_3\text{N}_4$ is a robust photocatalyst for contaminant degradation in raw natural water and (partially) treated water and wastewater. In summary, DFT simulations are a viable tool to predict photocatalyst properties and oxidation performance for contaminant removal, and they guide the rational design, fabrication, and implementation of visible-light-responsive $g\text{-C}_3\text{N}_4$ for efficient, robust, and sustainable water treatment.



INTRODUCTION

A growing number of persistent organic micropollutants such as pharmaceuticals and personal care products (PPCPs), endocrine disrupting compounds (EDCs), pesticides, and herbicides are frequently observed in natural and treated water.^{1,2} These contaminants are recalcitrant to conventional water and wastewater treatment³ and may pose risks to human and ecological systems even at very low concentrations.⁴ Photocatalysis is a promising advanced oxidation process (AOP) for the degradation or mineralization of persistent organic micropollutants because it activates O_2 and/or H_2O at ambient conditions to generate reactive oxygen species (ROS, e.g., $\text{OH}^\cdot$, $\text{O}_2^{\cdot-}$, $\text{HO}_2^\cdot$, H_2O_2 , $^1\text{O}_2$) in situ.^{5,6} Photocatalysis also eliminates the hurdles in the storage, handling, and transportation of oxidants and potentially uses renewable solar energy for water purification.⁷

Visible-light-responsive photocatalysts attract great attention because they can harvest and potentially utilize more sunlight for reactions (visible light constitutes 40% of solar energy) than

conventional photocatalysts (e.g., titanium dioxide, TiO_2) and can be reactive under artificial light. A number of visible-light-responsive photocatalysts were synthesized and used for lab scale water treatment studies, such as metal or nonmetal doped TiO_2 ,⁸ metal doped tungsten trioxide,⁹ silver phosphate,¹⁰ bismuth vanadate,¹¹ bismuth oxyhalides,¹² metal chalcogenides,^{13,14} and upconversion materials.¹⁵ Nevertheless, these materials may suffer from low photocatalytic activity (due to a low surface area or fast charge recombination), limited photostability (e.g., photocorrosion of chalcogenides), release of toxic chemicals (e.g., Cd^{2+} leaching from CdS), and potentially high cost for fabrication (e.g., the use of noble metals). These issues largely limit practical engineering

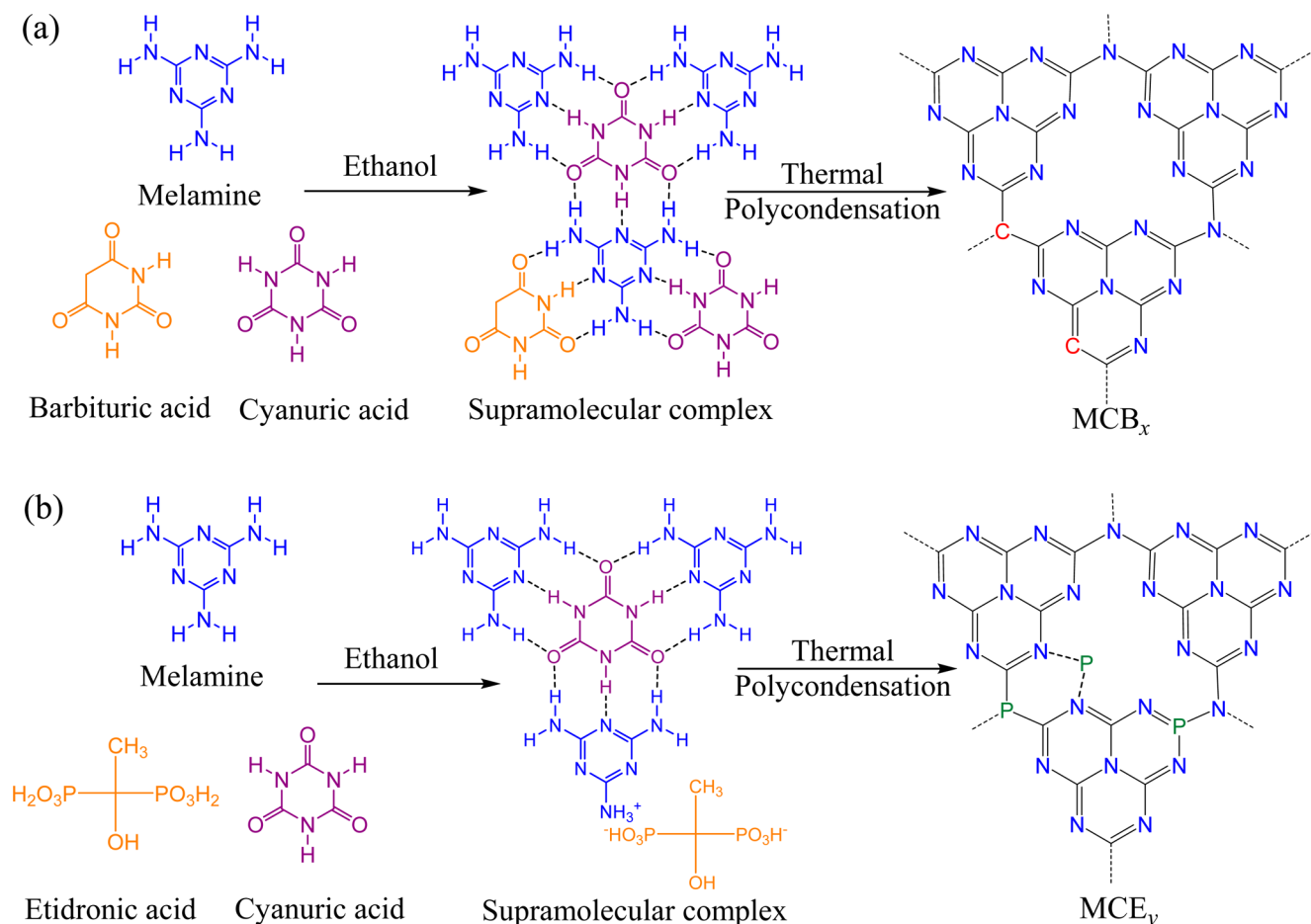
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Scheme 1. Synthesis Schematic of (a) Carbon-Doped and (b) Phosphorus-Doped Supramolecule-Based g-C₃N₄^a

^aIn addition to MCB_x and MCE_y, MC was also synthesized via the supramolecular approach by thermal polycondensation of melamine and cyanuric acid. Details of g-C₃N₄ synthesis are included in the [Experimental Section](#). C or P represents the possible sites for carbon or phosphorus doping based on DFT simulations.

applications of visible-light-responsive photocatalysts for water purification.^{8,10,14–16}

Recently, graphitic carbon nitride (g-C₃N₄) has emerged as an innovative photocatalyst with tunable band gaps of 1.8–2.7 eV that allow the harvesting of visible light up to 460–698 nm (potentially utilizing 13–49% of solar energy, though photocatalytic activity may be reduced at a longer wavelength).^{17–19} This material is made from earth-abundant, inexpensive C and N containing precursors (e.g., urea and melamine), is biocompatible with no reported toxicity, is resistant to photocorrosion, and remains chemically stable in harsh environments.^{20–23} However, the application of g-C₃N₄ in environmental remediation is at its nascent stage. A few studies reported that g-C₃N₄ held promise for the oxidation of organic dyes and the inactivation of microorganisms,^{24–33} but all of them were focused on the degradation of model contaminants in simple water chemistry that has limited environmental relevance. There are no reports about the degradation of persistent organic micropollutants on g-C₃N₄ in complex water matrices that are representative of treatment operations in practice. Photocatalytic performance on g-C₃N₄ may also be challenged by a low surface area, fast recombination of charge carriers (i.e., electrons and holes), and limited visible-light utilization,^{24–27} which demands more work to tailor the photocatalyst properties for effective water purification.

Supramolecular preassembly of triazine precursors has become an attractive approach to tailor the properties and reactivity of g-C₃N₄.^{26,34–42} The supramolecular approach is more environmentally benign and sustainable compared to widely used hard-templating with nanosilica because no toxic or corrosive chemicals are involved (e.g., HF or NH₄HF₂ for the postremoval of silica and pore generation).^{40,41} Cyanuric acid was widely applied with melamine because they can interact with each other by forming hydrogen bonds, producing a highly stable aggregate as the precursor of g-C₃N₄.^{26,34–39} Cyanuric acid is less thermally stable than melamine and decomposed into gases at an elevated temperature, which may create a porous structure of g-C₃N₄ with an increased surface area and charge separation.^{43,44} The molecular structure of g-C₃N₄ has also been tailored with metal dopants,^{45–47} nonmetal dopants,^{48–51} or nanoparticles^{52–54} to improve charge separation and visible-light utilization. We selected earth-abundant, low-cost, nontoxic dopants, i.e., carbon and phosphorus, because metal dopants or nanoparticles are more expensive (e.g., noble metal loading)^{52–54} and may leach or be deactivated in complex aquatic chemistries (e.g., metals fouled by natural organic matter, NOM, or sulfide).^{55,56} Barbituric acid or etidronic acid was used for carbon or phosphorus doping because it can be incorporated into the supramolecular complex

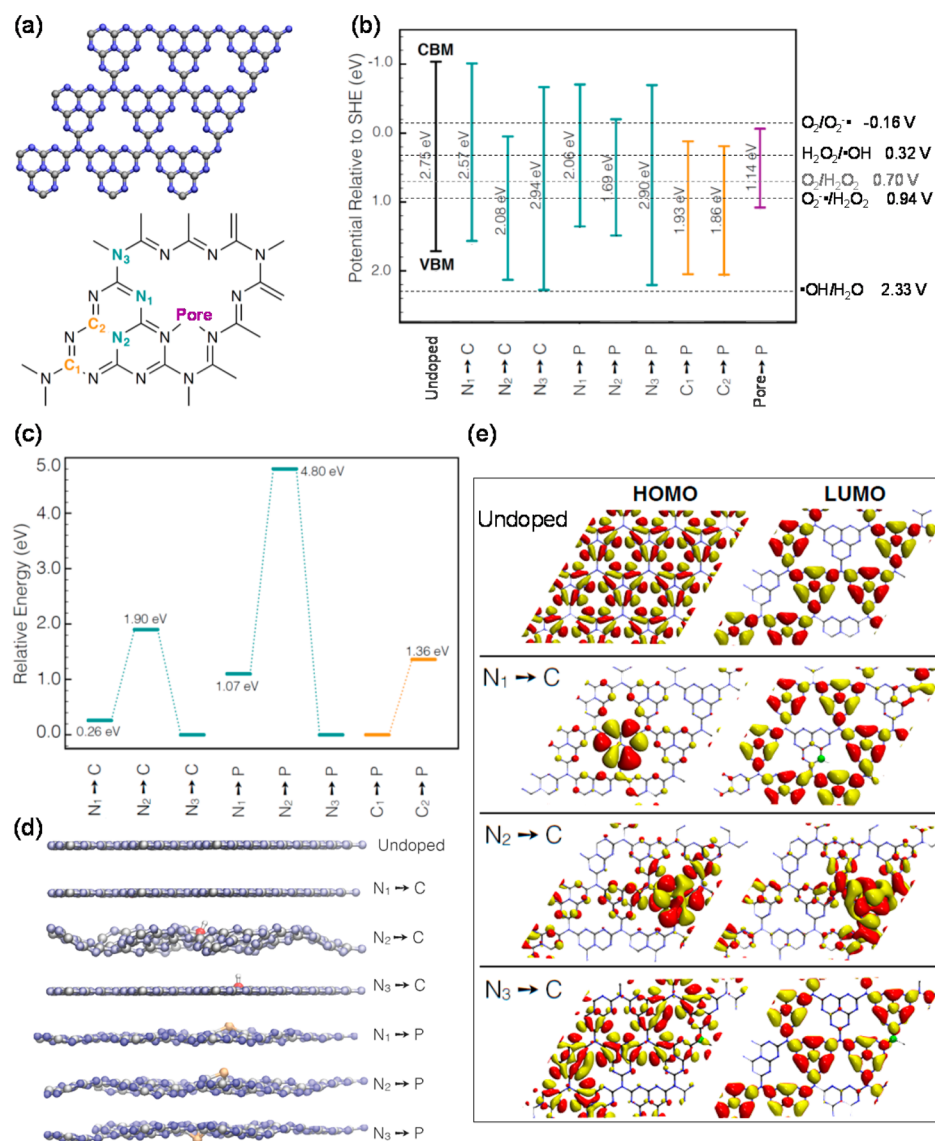


Figure 1. (a) Undoped g-C₃N₄ sheet employed in electronic structure calculations and designated sites for doping (i.e., N₁, N₂, N₃, C₁, C₂, and Pore). (b) Band gap, VBM, and CBM of undoped and doped g-C₃N₄, determined with respect to the SHE. Redox potentials of ROS production are also included for comparison. (c) Relative stability of doped g-C₃N₄ with respect to the most stable member of each family (i.e., carbon-doped g-C₃N₄, phosphorus-doped g-C₃N₄ for carbon sites, and phosphorus-doped g-C₃N₄ for nitrogen sites). The stability is compared only within each dopant family, as the zero energy reference point differs for each doping pattern. (d) Optimized geometry of undoped and doped g-C₃N₄; the dopant atom is highlighted in red or yellow. (e) HOMO and LUMO of undoped and carbon-doped g-C₃N₄.

of melamine and cyanuric acid via hydrogen bonding or electrostatic interactions to promote efficient doping.^{35,38,57,58}

In this work, instead of trial-and-error material development by an Edisonian approach, we applied density functional theory (DFT) simulations as a guide to rationally design the doped supramolecule-based g-C₃N₄ with an improved photocatalytic activity for the degradation of persistent organic micro-pollutants. First, the molecular structure, band gap, band energy levels, and charge separation of carbon- and phosphorus-doped g-C₃N₄ were evaluated by DFT simulations, which provide the mechanistic understanding of photocatalyst properties and the prediction of photocatalytic activity for contaminant removal. In contrast to the previous DFT simulations which only investigate the effect of carbon or phosphorus doping on limited possible positions of g-C₃N₄ structure,^{51,59,60} we evaluated g-C₃N₄ properties and stability of any possible doped structure (see [Results and Discussion](#)) and

compared the calculated band energy with ROS redox potentials to determine the thermodynamic feasibility of photocatalytic reactions on the doped g-C₃N₄. Next, we synthesized doped supramolecule-based g-C₃N₄ by the thermal polymerization of melamine–cyanuric acid–barbituric acid (or etidronic acid) complexes ([Scheme 1](#)).^{26,38,44} As indicated in a comprehensive review,⁴² similar carbon or phosphorus doping was also reported for supramolecule-based g-C₃N₄, but different solvents (water vs ethanol), precursors for doping (inorganic phosphoric acid vs organic etidronic acid), or experimental procedures for synthesizing the supramolecular complexes resulted in g-C₃N₄ with distinct structures in contrast to our study (see [Results and Discussion](#)).^{35,57} To the best of our knowledge, this is the first work that systematically applies DFT simulations as a guide to rationally design the doped g-C₃N₄ with improved performance for the environmental application.

The photocatalytic performance of supramolecule-based $g\text{-C}_3\text{N}_4$ and conventional $g\text{-C}_3\text{N}_4$ fabricated from only melamine or urea was evaluated in batch suspensions under the irradiation of simulated visible sunlight ($\lambda > 400$ nm), and the degradation kinetics of a model organic contaminant (i.e., phenol) and persistent organic micropollutants (i.e., atrazine, carbamazepine, and sulfamethoxazole) across a variety of water chemistries representative of drinking water and wastewater treatment was explored. Our study aims to identify the most influential properties of $g\text{-C}_3\text{N}_4$ for the photocatalytic degradation of persistent organic micropollutants by the synergy of simulation and experimental approaches and evaluate the viability of $g\text{-C}_3\text{N}_4$ for engineering applications in water treatment. The outcome of this work provides first insights into the guideline of photocatalytic $g\text{-C}_3\text{N}_4$ design and lays the groundwork for the application of $g\text{-C}_3\text{N}_4$ as an efficient, stable, low-cost visible-light-responsive photocatalyst toward more sustainable treatment of impaired water supplies.

EXPERIMENTAL SECTION

DFT Simulations. Electronic structure calculations were conducted using DFT^{61,62} as implemented in the CP2K suite.⁶³

Synthesis and Characterization of $g\text{-C}_3\text{N}_4$. Conventional $g\text{-C}_3\text{N}_4$ samples, M and U, were prepared from the thermal polycondensation of melamine or urea, respectively. Under the same thermal treatment, the supramolecule-based $g\text{-C}_3\text{N}_4$ sample without nonmetal doping, MC, was synthesized from melamine and cyanuric acid. Carbon- or phosphorus-doped supramolecule-based $g\text{-C}_3\text{N}_4$ samples, MCB_x or MCE_y , were synthesized from various mass ratios of melamine, cyanuric acid, and barbituric acid or etidronic acid, and x or y represents the mass of barbituric acid or etidronic acid, respectively. The physical, chemical, morphological, optical, and electronic properties of $g\text{-C}_3\text{N}_4$ were characterized.

Photocatalytic Degradation of Contaminants. Photocatalytic experiments were conducted in batch reactors under a 1000 W xenon lamp equipped with a water optical filter to remove infrared light and a 400 nm long-pass optical filter ($\lambda > 400$ nm) to simulate the visible light in solar irradiation. The spectral irradiance and photon fluence of the xenon lamp were recorded by a spectroradiometer (Figure S1). Reactivity studies were conducted in a jacketed beaker with the presence of a contaminant (initial concentrations of 20 or 100 μM), a phosphate buffer (pH 7.3, 1 mM), and a catalyst (1 g L^{-1}) at 25 $^\circ\text{C}$ under magnetic stirring at 500 rpm. Any mass transfer limitations were eliminated under this well-mixed condition (details in the Supporting Information), and the observed reaction kinetics represents the intrinsic activity of $g\text{-C}_3\text{N}_4$. MCB_x and MCE_y synthesis was optimized using phenol and/or atrazine degradation as a performance indicator, and the doped $g\text{-C}_3\text{N}_4$ with the highest reactivity (i.e., $\text{MCB}_{0.07}$) was selected for the degradation of persistent organic micropollutants, including atrazine, carbamazepine, and sulfamethoxazole, which are known to be recalcitrant to traditional water and wastewater treatment.³ The concentration of contaminants collected at regular time intervals was analyzed by high performance liquid chromatography (HPLC). To explore the influence of water matrixes representative of water treatment systems, the reactivity of $\text{MCB}_{0.07}$ for atrazine degradation under xenon lamp irradiation ($\lambda > 400$ nm) was explored in simulated water samples with complex constituents and in real water samples collected from the Griffith Water Treatment Plant (GWP) and the Broad Run Wastewater Reclamation Facility (BRWRF) in

Virginia. To understand the mechanism of the photocatalytic degradation on $g\text{-C}_3\text{N}_4$, we conducted phenol degradation on U with the presence of radical or hole scavengers under xenon lamp irradiation ($\lambda > 400$ nm). *tert*-Butyl alcohol, superoxide dismutase, catalase, ammonium oxalate, and L-histidine were used to quench the reactions involved with the hydroxyl radical ($\cdot\text{OH}$), superoxide anion radical ($\text{O}_2^{\cdot-}$), H_2O_2 , hole, and $^1\text{O}_2$. Scavenger concentration was optimized to completely quench the reaction between the target radical and phenol/atrazine.

The pseudo-first-order rate constant for contaminant photocatalytic degradation was obtained by performing a linear regression of natural log of contaminant concentrations vs time. The reaction rate constants (with 95% confidence intervals) were reported with respect to the photon fluence, i.e., the pseudo-first-order rate constant divided by the photon fluence. Details of the experimental procedures are included in the Supporting Information.

RESULTS AND DISCUSSION

DFT Simulations Predict Photocatalytic Performance of Carbon or Phosphorus Doped $g\text{-C}_3\text{N}_4$. Our preliminary studies were performed on an undoped, HSE06-optimized (3×3) $g\text{-C}_3\text{N}_4$ supercell (Figure 1a), revealing a planar geometry (Figure 1d) and a bandgap of 2.75 eV (Figure 1b). The conduction and valence band edges (-1.03 and 1.71 eV), measured with respect to the absolute potential of the standard hydrogen electrode (SHE; 4.44 eV), likewise lie near the experimentally determined values of -0.83 and 1.83 eV.⁶⁴ Encouraged by the robust nature of these results, particularly with respect to prior theoretical studies,^{60,65–68} we explored carbon and phosphorus doping at three inequivalent nitrogen sites (N_1 , N_2 , and N_3), phosphorus substitution at inequivalent carbon atoms (C_1 and C_2), and the incorporation of phosphorus within the $g\text{-C}_3\text{N}_4$ pore (i.e., interstitial doping), all with one dopant introduced to one doping site (Figure 1a). The doped materials are labeled as A $\rightarrow$ B doped $g\text{-C}_3\text{N}_4$ for further discussion (A is the doping site of N_1 , N_2 , N_3 , C_1 , C_2 , and Pore, and B is the doping element of C or P).

To determine the thermodynamic ability of these materials to generate ROS and holes, we quantified their valence band maximum (VBM) and conduction band minimum (CBM) in conduction with an implicit solvation model, represented by the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies, respectively. As shown in Figure 1b (details in the Supporting Information), only $\text{N}_{1,3} \rightarrow \text{C}$ and $\text{N}_{1-3} \rightarrow \text{P}$ doped $g\text{-C}_3\text{N}_4$ can produce $\text{O}_2^{\cdot-}$ via one-electron reduction of O_2 because their CBM is more negative than the redox potential of $\text{O}_2/\text{O}_2^{\cdot-}$ ($E^0(\text{O}_2/\text{O}_2^{\cdot-}) = -0.16$ V vs SHE). All doped materials are able to produce H_2O_2 and $\cdot\text{OH}$ from the one-electron reduction of $\text{O}_2^{\cdot-}$ and H_2O_2 , respectively ($E^0(\text{O}_2^{\cdot-}/\text{H}_2\text{O}_2) = 0.94$ V and $E^0(\text{H}_2\text{O}_2/\cdot\text{OH}) = 0.32$ V vs SHE). However, O_2 reduction for $\text{O}_2^{\cdot-}$ formation is the first step for ROS production on the conduction band (i.e., sequential reduction of $\text{O}_2 \rightarrow \text{O}_2^{\cdot-} \rightarrow \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH}$), and those doped $g\text{-C}_3\text{N}_4$ that cannot reduce O_2 may not produce sufficient ROS and thus result in low photocatalytic activity for contaminant degradation. Multi-electron reduction could facilitate ROS production on the conduction band because it is more thermodynamically favorable than one-electron reduction ($E^0(\text{O}_2/\text{H}_2\text{O}_2) = 0.70$ V vs SHE), but the loading of cocatalysts (e.g., Pt, Au, and Cu(II)) is always required.^{69,70} Recent studies have shown that $g\text{-C}_3\text{N}_4$ in the form of nanosheets⁷¹ or containing electron-

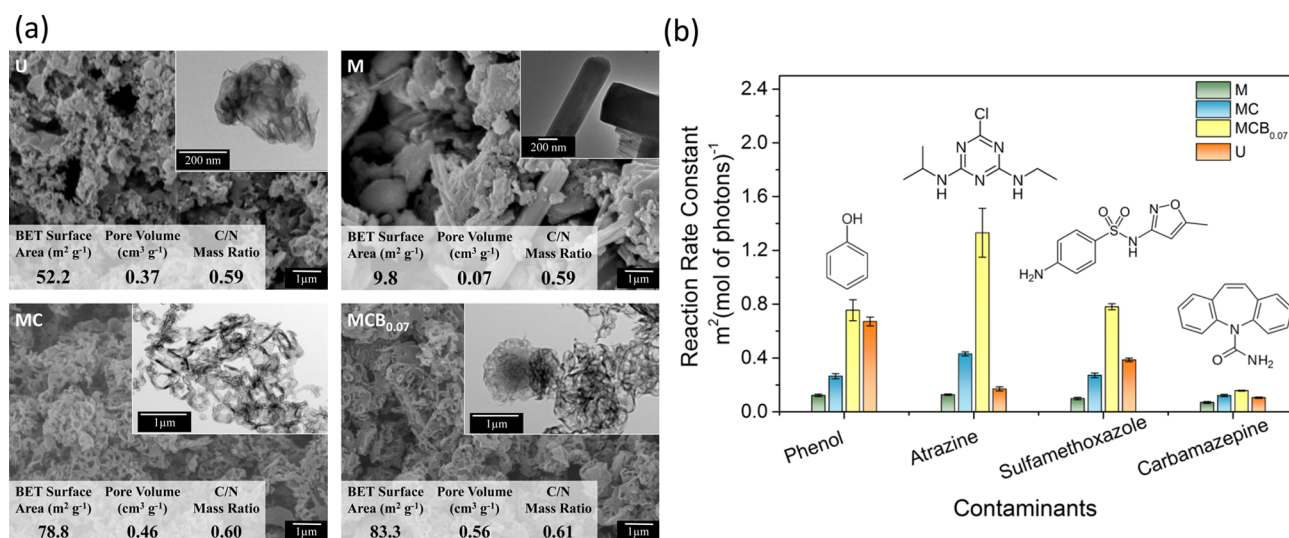


Figure 2. (a) SEM and TEM (insets) images of g-C₃N₄ samples U, M, MC, and MCB_{0.07}. Inset tables show the surface area, pore volume, and bulk carbon to nitrogen (C/N) mass ratio of each sample. (b) Photocatalytic degradation rate constants of phenol, atrazine, sulfamethoxazole, and carbamazepine on g-C₃N₄ (U, M, MC, and MCB_{0.07}) under simulated visible sunlight irradiation ($\lambda > 400$ nm, xenon lamp). The initial contaminant concentration was 100 μ M, and the reactions were conducted in a phosphate buffer (pH 7.3, 1 mM). Photocatalyst loading was 1 g L⁻¹. Error bars represent 95% confidence intervals of replicates.

deficient aromatic diimide (as a cocatalyst)⁷² can promote the multielectron photocatalytic reduction of O₂ for H₂O₂. None of the undoped or doped g-C₃N₄ derivatives are able to oxidize water and produce $\cdot$ OH on the valence band because the VBM is smaller than E⁰($\cdot$ OH/H₂O) (2.33 V vs SHE). This suggests that g-C₃N₄ oxidizes contaminants through a surface-localized hole that is generated from the valence band. N_{1,2} $\rightarrow$ P and Pore $\rightarrow$ P doped g-C₃N₄ have a lower-lying VBM and are expected to show low reactivity in photocatalytic oxidation. The band gap of N₃ $\rightarrow$ C and N₃ $\rightarrow$ P doped g-C₃N₄ is larger than that of undoped g-C₃N₄ (2.94 and 2.90 vs 2.75 eV), and these doped materials will only harvest and potentially utilize light with wavelengths shorter than 422 and 428 nm, respectively, resulting in low photocatalytic activity. The stability of doped g-C₃N₄ derivatives was also evaluated; N_{1,3} $\rightarrow$ C, N₃ $\rightarrow$ P, and C₁ $\rightarrow$ P doped g-C₃N₄ were found to possess the most viable structure (with the lowest relative energy, Figure 1c). Our results are in agreement with previous experimental measurements, e.g., the structure of N₁ $\rightarrow$ C and C₁ $\rightarrow$ P doped g-C₃N₄ were confirmed by solid-state nuclear magnetic resonance spectroscopy.^{48,73} Previous simulations also suggested that interstitial doping by phosphorus (i.e., Pore $\rightarrow$ P) might be thermodynamically stable;⁶⁰ however, the calculated redox properties of this material are expected to render it catalytically incompetent. Taken together, our DFT simulations predict that carbon-doped g-C₃N₄ (N₁ $\rightarrow$ C) will outperform phosphorus-doped g-C₃N₄ for photocatalytic degradation of contaminants, as its band energy levels promote contaminant oxidation by both ROS and holes, a reduced band gap improves visible light utilization, and a thermodynamically stable structure is possessed.

As shown in Figure 1d, both N₁ $\rightarrow$ C and N₃ $\rightarrow$ C doped g-C₃N₄ exhibit a planar geometry similar to that of undoped g-C₃N₄. Conversely, N₂ $\rightarrow$ C doped g-C₃N₄ is characterized by a significant out-of-plane deformation. The N₁₋₃ $\rightarrow$ P geometries are collectively more distorted, each exhibiting some degree of undulation due to the bulky phosphorus substituent, and are presumably less thermodynamically stable than their carbon-

doped counterparts due to strain. Following these observations, we determined the hole distribution in the valence band (HOMO) and electron distribution of the conduction band (LUMO) of these materials, as shown in Figure 1e. While the HOMO of undoped g-C₃N₄ is relatively delocalized, the LUMO exhibits a staggered distribution on alternating trimers. The same trend is observed for the LUMO of carbon-doped systems, though N₂ $\rightarrow$ C doped g-C₃N₄ exhibits a higher degree of localization due to a pronounced "tenting" of the g-C₃N₄ sheet. The HOMO of carbon-doped g-C₃N₄ is markedly different from the undoped material and is distributed around the dopant site. While the orbital structure will undergo remodeling subsequent to exciton formation and charge migration, it is reasonable to speculate that the impurity-localized valence electrons provide the primary sites for localized hole formation within the valence band of doped g-C₃N₄. Prior theoretical investigations have indicated that charge migration between adjacent tri-s-triazine units is unlikely, underscoring this supposition.⁶⁰ In any event, our results indicate that DFT calculations can provide fundamental insights into the mechanism by which doping can improve redox and reactivity characteristics of g-C₃N₄.

The effect of nonmetal doping on the photocatalytic performance of g-C₃N₄ was evaluated by testing MCB_x or MCE_y for phenol and/or atrazine degradation under simulated visible sunlight irradiation ($\lambda > 400$ nm, xenon lamp) and comparing the activity with MC. As shown in Figure S3, the synthesized MCB_x exhibited significantly enhanced photocatalytic activity, especially at the low barbituric acid content (i.e., $x = 0.01$ – 0.07). MCB_{0.07} had the highest reaction rate constant, and its reactivity was enhanced by 2.8-fold compared to that of MC (0.8 ± 0.08 vs 0.3 ± 0.02 m² (mol of photons)⁻¹). The photocatalytic activity of MCB_x significantly decreased at higher barbituric acid mass loadings ($x > 0.1$), likely due to excessive carbon doping promoting charge recombination.⁴⁸ An optimum dopant level is necessary to improve charge separation and photocatalytic activity. However, phosphorus doping did not enhance the photocatalytic

activity for phenol degradation at any dopant loading (i.e., $y = 0.01$ – 0.5), though phosphorus uniformly doped into the $g\text{-C}_3\text{N}_4$ structure (Figure S4). Reactivity increase was observed for atrazine degradation only on $\text{MCE}_{0.01}$ that had the lowest phosphorus doping level (0.6 ± 0.1 and $0.3 \pm 0.02 \text{ m}^2$ (mol of photons) $^{-1}$ for $\text{MCE}_{0.01}$ and MC, respectively), as shown in Figure S5. The experimental results are in agreement with DFT simulation results with carbon-doped $g\text{-C}_3\text{N}_4$ showing an enhanced activity compared to that of phosphorus-doped $g\text{-C}_3\text{N}_4$. The carbon-doped supramolecule-based $g\text{-C}_3\text{N}_4$ with an optimum photocatalytic activity ($\text{MCB}_{0.07}$), undoped supramolecule-based $g\text{-C}_3\text{N}_4$ (MC), and conventional $g\text{-C}_3\text{N}_4$ (U and M) were selected for further material characterization and water treatment applications.

Characterization of $g\text{-C}_3\text{N}_4$. Previous studies have confirmed that melamine and cyanuric acid formed a supramolecular complex for $g\text{-C}_3\text{N}_4$ synthesis by XRD and FTIR.^{34,35,38} All $g\text{-C}_3\text{N}_4$ samples had a similar XRD pattern that could be ascribed to a typical graphite-like structure (Figure S6), and the introduction of cyanuric acid and/or barbituric acid may promote polymer-like growth and more defects in $g\text{-C}_3\text{N}_4$.^{44,48,74} Infrared spectroscopic analysis of each photocatalyst (Figure S7) showed absorption bands characteristic of $g\text{-C}_3\text{N}_4$: six bands in the 1200 – 1650 cm^{-1} region for stretching modes of C–N heterocycles⁷⁵ and one band at 805 cm^{-1} for triazine.⁷⁶ The characteristic binding energy of $g\text{-C}_3\text{N}_4$ was also observed in XPS spectra of each photocatalyst (Figure S8).^{28,77–79} The results are very consistent with the previous reports,^{28,75–80} confirming the presence of $g\text{-C}_3\text{N}_4$.

The morphology of $g\text{-C}_3\text{N}_4$ was characterized by SEM and TEM, as shown in Figure 2a. U exhibited a porous structure, possibly due to a large amount of gas production in the thermal polycondensation of urea (e.g., NH_3 and H_2O).⁸¹ A typical condensed, layered structure of M was observed with the presence of fewer pores, likely due to a lesser extent of structural reorganization and reduced gas emission.^{24,82} The addition of cyanuric acid created a loose, porous structure in MC, as expected from the self-templating of cyanuric acid with limited thermal stability.⁴⁴ Further introduction of barbituric acid for $\text{MCB}_{0.07}$ synthesis did not lead to any notable change in the sample morphology, possibly because of the low loading of barbituric acid (i.e., 0.07 g). The morphology of supramolecule-based $g\text{-C}_3\text{N}_4$ is largely determined by the surface energy of the hydrogen-bonded supramolecular complex in a solvent.^{34,35,38} A pancake-like structure and an irregular rod-/particle-like structure were observed for the supramolecular complex in ethanol and water, respectively (Figure S9). Accordingly, our samples showed a distinct porous structure compared to that reported by Shalom et al.³⁵ because ethanol rather than water was used in our work.

The surface area and porosity of $g\text{-C}_3\text{N}_4$ samples were characterized by liquid N_2 adsorption (Figure 2a), and the adsorption isotherms and pore size distribution (Figure S10) indicated that U, MC, and $\text{MCB}_{0.07}$ mainly contained mesopores. M had the lowest BET surface area and pore volume in all $g\text{-C}_3\text{N}_4$ samples, as supported by the SEM and TEM results. The BET surface area and pore volume of MC increased by 8.0- and 6.6-fold compared to those of M and were also higher than those of U. $\text{MCB}_{0.07}$ had the highest surface area and pore volume compared to other $g\text{-C}_3\text{N}_4$ samples.

Bulk carbon and nitrogen contents of $g\text{-C}_3\text{N}_4$ were also analyzed (Figure 2a), and U and M had the same carbon to

nitrogen (C/N) mass ratio of 0.59. The addition of cyanuric acid for MC synthesis increased C/N mass ratio to 0.60, and the addition of barbituric acid for $\text{MCB}_{0.07}$ synthesis further increased the C/N mass ratio to 0.61.

Optical properties of $g\text{-C}_3\text{N}_4$, including band gap and optical absorption, were characterized to evaluate its capability of harvesting and utilizing visible photons. $g\text{-C}_3\text{N}_4$ is an indirect band gap photocatalyst,⁸³ and all $g\text{-C}_3\text{N}_4$ samples had a similar band gap of 2.72 eV (harvesting photons with $\lambda \leq \text{ca. } 460 \text{ nm}$, Figure S11), which is in agreement with previous research and our DFT simulation results for undoped $g\text{-C}_3\text{N}_4$.^{24,26,81} The addition of cyanuric acid and barbituric acid did not change the band gap of $g\text{-C}_3\text{N}_4$, in contrast to DFT predictions, likely due to the low dopant level (C/N mass ratio of 0.61 vs 0.59). Nevertheless, $\text{MCB}_{0.07}$ showed noticeable band-tail absorption in the visible light region ($>460 \text{ nm}$) compared to undoped $g\text{-C}_3\text{N}_4$ (U, M, and MC in Figure S11), likely due to the presence of midgap states, i.e., the electronic states located within the band gap. The midgap states can accommodate photoexcited electrons from the valence band, resulting in the absorption of photons with energies smaller than the band gap for photocatalytic reactions.^{51,84,85} In addition to intrinsic photon absorption as reflected by the band gap, the morphology, structure, and particle size of $g\text{-C}_3\text{N}_4$ in reaction suspension may also impact the photon absorption due to light reflection and scattering on materials.⁴⁸ U had the highest absorption of visible light ($\lambda > 400 \text{ nm}$), followed by the other samples (i.e., M, MC, and $\text{MCB}_{0.07}$) with similar optical absorption, as shown in Figure S12. Increased photon absorption of U may improve the photocatalytic activity for contaminant degradation.

Improved charge separation may enhance the photocatalytic activity of $g\text{-C}_3\text{N}_4$ because of an increased amount of charge carriers for photocatalytic reactions. PL intensity, representative of radiative charge recombination, was used as an indirect evidence to characterize charge separation. The PL intensity of U, MC, and $\text{MCB}_{0.07}$ was similar and significantly lower than that of M (Figure S13), and it suggests that charge recombination may be the most pronounced in M, and its photocatalytic performance may be limited. The PL peak of U, MC, and $\text{MCB}_{0.07}$ also red-shifted compared to that of M (Figure S13). The reduction of PL intensity and red-shifted peaks indicate that the addition of cyanuric acid and barbituric acid for the preparation of supramolecule-based $g\text{-C}_3\text{N}_4$ may lower the charge recombination compared to M derived from melamine only. Holes are generally less mobile than electrons (i.e., diffusion length of several nanometers vs micrometers),⁸⁶ and increased surface area and porosity in U, MC, and $\text{MCB}_{0.07}$ could facilitate the migration of holes to the surface and subsequent reactions with contaminants rather than recombination with electrons.⁴³ Carbon dopants may also facilitate hole localization and improve the reaction between charge carriers and contaminants, as suggested by DFT simulations. Nevertheless, the PL only qualitatively characterizes the extent of radiative charge recombination but not nonradiative charge recombination (dissipation as heat rather than photon emission), and it may not necessarily explain the photocatalytic activity. For example, the PL intensity of U and MC was lower compared to that of $\text{MCB}_{0.07}$, which suggested that U and MC might exhibit an increased charge separation. In contrast, the photocatalytic activity of $\text{MCB}_{0.07}$ was equal to or higher than that of U and MC for contaminant degradation (Figure 2b). More quantitative analyses such as time-resolved fluorescence measurements^{43,44} and theoretical simulations for charge

lifetime^{87,88} are needed to correlate photocatalytic activity with the charge separation.

Relationship between Photocatalytic Activity and g-C₃N₄ Properties. Figure 2b shows photocatalytic degradation kinetics of phenol and persistent organic micropollutants on g-C₃N₄ in the phosphate buffer under simulated visible sunlight irradiation ($\lambda > 400$ nm, xenon lamp). MCB_{0.07} showed the highest photocatalytic activity for atrazine, sulfamethoxazole, and carbamazepine compared to that of other g-C₃N₄ samples, and its reactivity was on par with U for phenol degradation. M had the lowest reactivity compared to that of its counterpart g-C₃N₄ samples. Of the four probe contaminants, atrazine is the most photocatalytically degradable on g-C₃N₄ samples (except for U), and carbamazepine is the most persistent in photocatalytic reactions. Atrazine degradation was also explored on MCB_{0.07} over four repeated cycles, and no reactivity loss or morphological/chemical property change of the photocatalyst was observed (Figure S14).

The measured photocatalytic activity for contaminant degradation could be influenced by mass transfer and contaminant adsorption on g-C₃N₄. Nonetheless, mass transfer limitation was eliminated in the reaction (see the Supporting Information), and no contaminant adsorption was measured in the dark experiments. In addition, all g-C₃N₄ samples in our study showed a similar negative ζ -potential (i.e., -28.5 to -37.8 mV at pH 7.3), and they were not expected to interact strongly with neutral contaminants in the reaction solution at pH 7.3 (pK_a 's of phenol, atrazine, sulfamethoxazole, and carbamazepine are 10.0, 1.7, 1.4/5.8, 2.3/13.9, respectively).^{89–92}

The enhancement of photocatalytic activity could be determined by the following key photocatalyst properties: (i) an increased surface area, (ii) improved light harvesting, and (iii) promoted charge separation. Photocatalysis is a surface-mediated reaction, and the increased surface area provides more active sites for the contaminants to reside and react. The improvement of light harvesting and charge separation enables the generation of more electrons and holes for photocatalytic reactions. MCB_{0.07} exhibited the highest surface area, and its reactivity outperformed M and MC for the degradation of all probe contaminants. The charge separation of MCB_{0.07} and MC was significantly promoted compared to M, and M showed the lowest reactivity for contaminant degradation. The low carbon doping of MCB_{0.07} did not change its band gap, but midgap states possibly increased visible light absorption and photocatalytic activity. The results indicate that the enhanced surface area, visible light absorption, and charge separation of MCB_{0.07} synergistically contribute to improving the photocatalytic activity.^{26,44,48}

Selective Contaminant Degradation on g-C₃N₄. It is worth noting that g-C₃N₄ is selective for contaminant degradation, e.g., MCB_{0.07} is 1.8 times more reactive for the degradation of atrazine than phenol; however, U is 3.9 times more reactive for the degradation of phenol than atrazine. Similar selective degradation of sulfamethoxazole was also observed in comparison with phenol or atrazine. To understand the mechanism of selective contaminant removal, we explored the significance of the ROS and hole for the photocatalytic degradation of phenol and atrazine. Scavenger tests were conducted to quench the reactions between contaminants and a specific oxidative species, and the inhibition of reactivity was used to evaluate the contribution of the specific oxidative species to photocatalytic degradation. The results, as shown in

Figure S15a, indicated that the addition of *tert*-butyl alcohol, a $\cdot\text{OH}$ scavenger, reduced the reactivity for phenol degradation by 60% on U compared to 33% on MCB_{0.07}. The $\cdot\text{OH}$ scavenger test also showed 55% of reactivity inhibition for atrazine degradation on U, in contrast to no inhibition for atrazine degradation on MCB_{0.07}. However, the addition of ammonium oxalate, a hole scavenger, significantly inhibited the reactivity for phenol and atrazine degradation on both U and MCB_{0.07} from 74 to 86%. The addition of L-histidine, a $^1\text{O}_2$ scavenger, reduced the reactivity of phenol degradation by 76% on U compared to 55% on MCB_{0.07} and fully inhibited the reactivity for atrazine degradation on both U and MCB_{0.07}.

We propose that the production of oxidative species on g-C₃N₄ is structurally sensitive, i.e., different g-C₃N₄ generates different types and amounts of oxidative species. Phenol is known to be more reactive with $\cdot\text{OH}$ than atrazine with $\cdot\text{OH}$, and the second-order rate constant of $\cdot\text{OH}$ -phenol is 5.9-fold higher than that of $\cdot\text{OH}$ -atrazine (1.4×10^{10} vs 2.4×10^9 s⁻¹ M⁻¹).^{93,94} U may generate more $\cdot\text{OH}$ than MCB_{0.07}, and quenching $\cdot\text{OH}$ had more pronounced inhibition for phenol degradation. MCB_{0.07} may produce a significant amount of other ROS, e.g., $\text{O}_2^{\cdot-}/\text{HO}_2^{\cdot}$ and $^1\text{O}_2$, to facilitate atrazine degradation. Though $\cdot\text{OH}$ is generally more reactive (second-order reaction rate constant between ROS and organics are 10^6 – 10^{10} , 10^3 – 10^{10} , or $<10^8$ M⁻¹ s⁻¹ for $\cdot\text{OH}$, $^1\text{O}_2$, or $\text{O}_2^{\cdot-}/\text{HO}_2^{\cdot}$, respectively),^{95–97} its steady-state concentration is orders of magnitude lower in water compared to that of other ROS.^{98,99} The other ROS, especially $^1\text{O}_2$, may be a leading contributor to atrazine degradation; quenching $\cdot\text{OH}$ had a negligible effect on atrazine degradation on MCB_{0.07}, but quenching $^1\text{O}_2$ completely deactivated photocatalytic atrazine degradation. In contrast, U could produce $\cdot\text{OH}$ as one dominant ROS, and hence atrazine degradation on U is slower, and quenching $\cdot\text{OH}$ reduces the reactivity significantly. The hole and $^1\text{O}_2$ are the most dominant oxidative species for contaminant degradation, regardless of g-C₃N₄ properties. $\text{O}_2^{\cdot-}$ and H_2O_2 were also identified in the photocatalytic degradation of phenol on U, and their contribution to reaction kinetics was also critical (Figure S15b). A recent study also demonstrated that the production of oxidative species is structurally sensitive, with g-C₃N₄ nanosheets producing more H_2O_2 than its bulk counterpart.⁷¹

The exploration of the structural sensitivity is significant for the application of g-C₃N₄ in contaminant degradation because we may tailor the synthesis and properties of g-C₃N₄ to selectively degrade a certain group of highly toxic, low concentration contaminants with minimized inhibition from cocontaminants, natural water constituents, or foulants. It may also be useful for designing photocatalysts for selective oxidation and conversion of contaminants to value-added products (e.g., benzene oxidation to phenol).¹⁰⁰ Further study is required to quantitatively analyze the production of oxidative species and identify key g-C₃N₄ properties for the selective generation of oxidative species and degradation of contaminants. Factors beyond the generation of oxidative species, such as the affinity of g-C₃N₄ to contaminants, may also be important for the selectivity in contaminant degradation. The affinity between the photocatalyst and contaminant may be tailored for selective reactions.

Performance Comparison in Matrixes Representative of Water and Wastewater Treatment. For all experiments conducted in the simulated and real water samples and with both fresh and aged MCB_{0.07}, little to no inhibition was

observed in atrazine degradation, as shown in Figure S16. The excellent photocatalytic performance of g-C₃N₄ in complex water matrixes may be attributed to the large surface area, high porosity, the polymeric nature of the material without metal loading, and the selective ROS production.

Increased surface area and porosity may afford sufficient sites to interact with contaminants even when foulants or natural water constituents are at a high concentration (i.e., mM of foulants or constituents vs μ M of contaminants). Noble metals used in photocatalysis (e.g., Au) are reactive and susceptible to fouling,⁵⁵ and the polymeric nature of g-C₃N₄ with the presence of only carbon and nitrogen mitigates the likelihood of photocatalyst deactivation. In addition, the hydrophilic nature of g-C₃N₄ reduces the adsorption of organic or biological foulants, and the tri-s-triazine unit in g-C₃N₄ is not expected to bind strongly to the carboxylate group of NOM, in contrast to TiO₂.¹⁰¹

The selective production of ROS may also contribute to the minimal inhibition of photocatalytic activity in complex water matrixes. $\cdot$ OH is the most powerful, nonselective radical generated in most AOPs and is attractive for environmental applications because it can degrade most organic contaminants at near diffusion-limited rates.^{95,102,103} However, the nonselective destruction of contaminants can be easily compromised when nontarget chemicals are present, including NOM and other background constituents present in raw natural water or (partially) treated water and wastewater.^{104,105} In our system, MCB_{0.07} may generate other ROS predominantly rather than $\cdot$ OH, such as $^1\text{O}_2$ and $\text{O}_2^{\cdot-}/\text{HO}_2^{\cdot}$, which are more selective for contaminant degradation. For example, $^1\text{O}_2$ selectively oxidizes electron-rich moieties of contaminants with the presence of NOM,^{99,106} and $\text{O}_2^{\cdot-}/\text{HO}_2^{\cdot}$ facilitates the degradation of halogenated compounds because of the synergy of reductive dehalogenation and the oxidation of carbon backbones ($\text{O}_2^{\cdot-}/\text{HO}_2^{\cdot}$ can act as both a reductant and an oxidant).¹⁰⁷

Environmental Implication. Our study indicates that g-C₃N₄ is a promising visible-light-responsive photocatalyst for water treatment applications because it is prepared from earth abundant materials, it exhibits highly tunable properties, and it shows excellent performance for the removal of persistent organic micropollutants in complex water matrixes. N-rich organic wastes (e.g., urea) could be reused to synthesize g-C₃N₄, improving the sustainability of material production. We rationally designed supramolecule-based g-C₃N₄ with enhanced surface area and charge separation by soft-templating and nonmetal doping, and the material with improved photocatalytic performance, economic feasibility, sustainability, and robustness was obtained. DFT simulations were used to understand the mechanism of nonmetal doping for g-C₃N₄ that was largely unknown in previous studies, and simulation results successfully predicted the photocatalytic performance for contaminant degradation. Our study provides first insights into the rational material design guided by DFT simulations, which is highly needed for material-based research for environmental applications.

Selective contaminant degradation was observed on g-C₃N₄ with distinct properties, likely due to the difference in ROS production and interfacial interactions between the contaminant and the photocatalyst. The selectivity of g-C₃N₄ paves a new avenue for the smart design of photocatalysts for a wide range of applications.^{100,108} Little to no inhibition of the photocatalytic activity in complex water matrixes implies that g-

C₃N₄ is robust for water purification in the presence of natural water constituents and foulants. g-C₃N₄ is a versatile visible-light-responsive photocatalyst and holds promise for a range of environmental applications, including the development of point-of-use or point-of-entry water treatment units for small public water systems that are more susceptible to contamination^{109,110} and use as an antimicrobial material to prevent pathogen transmission and disease outbreaks.^{32,33}

Before g-C₃N₄ may be practically deployed, it is critical to understand the mechanism of ROS production and interfacial interactions between the contaminant and the photocatalyst. Photocatalyst stability for a long-term reaction should be evaluated by considering photocatalyst self-corrosion and deactivation with the presence of foulants. Immobilization of g-C₃N₄, combination of g-C₃N₄ with other photocatalysts, and optimized reactor design will minimize photocatalyst post-separation, reduce photocatalyst leaching, maximize solar energy harvesting, enhance mass transfer, and improve photon efficiency for reactions.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications Website at DOI: 10.1021/acs.est.6b02579.

Experimental and simulation details; spectral irradiance, photon fluence, and optical power density of the light source; description of water treatment process in GWP, wastewater treatment process in BRWRF, and water quality parameters; band gap, CBM, and VBM of g-C₃N₄; mass transfer evaluation; material characterization results; photocatalytic activity of g-C₃N₄ in a model buffer system with the presence of scavengers and in simulated/real complex water matrixes (PDF)

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Notes

The authors declare no competing financial interest.

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