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**A novel visible-light-driven photocatalytic chlorine activation
process for carbamazepine degradation in drinking water**

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26 Graphical abstract:

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ABSTRACT:

Photolysis of free chlorine (HOCl/ClO^-) is an advanced oxidation process (AOP) to produce hydroxyl ($\text{HO}\bullet$) and other radicals for refractory micropollutant degradation. However, HOCl/ClO^- is only conducive to activation and production of radicals by Ultraviolet (UV) light. For the first time we show the use of visible light ($>400\text{ nm}$) to produce $\text{HO}\bullet$ and $\text{ClO}\bullet$, through use of graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) and photogenerated h_{vb}^+ , e_{cb}^- and $\text{O}_2^{\bullet-}$ in the presence of HOCl/ClO^- , which termed visible light $\text{g-C}_3\text{N}_4$ -enabled chlorine AOP (VgC-AOP). The VgC-AOP increased the pseudo-first order degradation rate constant of a model micropollutant, carbamazepine (CBZ), by 16 and 7 times higher than those without $\text{g-C}_3\text{N}_4$ and HOCl/ClO^- , respectively, and remained active over multiple use cycles. Effects of water quality (pH, alkalinity, Cu(II) and natural organic matter (NOM)) and operational conditions ($\text{g-C}_3\text{N}_4$ and HOCl/ClO^- concentrations, irradiation wavelength and dose) were investigated. Of particular significance is its superior performance in the presence of NOM, which absorbs less light at visible light wavelengths and scavenges less surface-bonded reactive species, compared against UV/ TiO_2 or UV/chlorine AOPs. The VgC-AOP is practically relevant, feasible and easily implementable, and it expands the potential types of light sources (e.g., LEDs, solar light).

1. INTRODUCTION

Advanced oxidation processes (AOPs) are promising treatment strategies to be integrated into conventional water and wastewater treatment plants to degrade micropollutants.¹ AOPs degrade micropollutants by producing hydroxyl radicals (HO•), sulfate radicals (SO₄•⁻), or reactive chlorine species (RCS).²⁻⁴ A common AOP strategy applied in full-scale practice to produce HO• is by the ultraviolet light with hydrogen peroxide (H₂O₂),⁵ and more recently with free chlorine (HOCl/OCl⁻) to produce both HO• and RCS.⁶⁻⁹ Bolton and co-workers^{10,11} suggest lower energy AOPs that use visible light, including wavelengths present in the solar spectrum, would be advantageous, especially for off-grid industrial applications (e.g., treatment of oil-shale processing water). If demonstrated to have high radical yields, solar-based AOPs potentially would reduce energy consumption, and eliminate reliance upon fragile UV lamps containing hazardous mercury. The challenge has been that only a small fraction (<4%) of the solar spectrum occurs at near-UV wavelengths, and many heterogeneous photocatalysts activated at longer wavelengths exhibit low quantum yield production of HO•.¹² Therefore, a need exists to discover materials for efficient AOPs capable of operating in visible light.

The performance of heterogeneous photocatalytic AOPs depends primarily on the high-energy hole-electron ($h_{vb}^+ - e_{cb}^-$) pairs which form at an energy levels equal to or higher than their bandgaps.¹³ The photo-induced h_{vb}^+ either degrades micropollutants directly or oxidizes H₂O/HO⁻ to produce HO• to degrade micropollutants indirectly if the valence band (VB) potential of photocatalyst is higher than E⁰(HO•/H₂O) or E⁰(HO•/HO⁻).¹⁴ The photo-induced e_{cb}^- at the conduction band (CB) mainly reduces oxygen adsorbed on photocatalyst surface to form superoxide radicals (O₂•⁻).¹⁵ Graphitic carbon nitride (g-C₃N₄) is a commonly studied low-cost non-metallic

photocatalyst that can be activated under visible light spectrum ($<470\text{ nm}$), which accounts for 15% of sunlight.¹⁶ Unlike the noble-metal and non-metal doped metal oxide photocatalysts, for example, Au-, Pt- or N- doped TiO_2 , the material preparation process of $\text{g-C}_3\text{N}_4$ is much simpler and less costly.¹⁷ However, the VB potential (around 1.4 V) of $\text{g-C}_3\text{N}_4$ is too low to oxidizes $\text{H}_2\text{O}/\text{HO}^-$ to produce $\text{HO}\bullet$, which greatly limits its photocatalytic micropollutant degradation since $\text{O}_2^{\bullet-}$, instead of $\text{HO}\bullet$, are mainly formed in the process.¹⁸ $\text{O}_2^{\bullet-}$ is a much weaker oxidant, whose redox potential is (-0.33 V), than $\text{HO}\bullet$.¹⁹

One strategy has recently been reported to enhance the photocatalytic micropollutant degradation efficiency under visible light irradiation by the combined use of photocatalysts with chemical oxidants, including ozone (O_3), hydrogen peroxide (H_2O_2), peroxymonosulfate (PMS, HSO_5^-), or peroxydisulfate (PDS, $\text{S}_2\text{O}_8^{2-}$).²⁰⁻²⁵ Xiao et al. (2017) reported that the combined use of 0.1 g/L bulk $\text{g-C}_3\text{N}_4$ and O_3 at 45 mg/L enhanced the oxalic acid (OA) degradation rate constant by 84 times compared with that in the absence of $\text{g-C}_3\text{N}_4$.²² The synergistic enhancement of the OA degradation is mainly due to the enhanced production of $\text{HO}\bullet$ from the activation of O_3 by photo-induced e_{cb}^- , which is either exposed or diffuses to aqueous phase as hydrated electrons (e_{aq}^-), and $\text{O}_2^{\bullet-}$ at reaction rate constants of 3.6×10^{10} and $1.5 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$, respectively (Eqs. S1–3 in Table S1).²⁶ Similarly, the combined use of 0.5 g/L $\text{g-C}_3\text{N}_4$ and H_2O_2 (10 mM), PMS (1.0 mM) or PDS (5.0 mM) can enhance the $\text{HO}\bullet$ or $\text{SO}_4^{\bullet-}$ production through the activation of H_2O_2 , PMS or PDS by the photo-induced species, like e_{cb}^- , h_{vb}^+ and/or $\text{O}_2^{\bullet-}$ (Eqs. S4–9 in Table S1).^{23-25,27}

However, PMS and PDS are seldom used in drinking water treatment processes due to the problem of residual sulfate ions.²⁸ O_3 and H_2O_2 have been used in the UV/ O_3 and UV/ H_2O_2 AOPs in drinking water treatment plants, but the practicality of the activation

of O₃ and H₂O₂ by g-C₃N₄ photocatalysis will be offset by the high oxidant dosage (45 mg/L O₃ and 10 mM H₂O₂) and necessity of additional chlorine to quench residual H₂O₂ after treatment.^{22,23,29} Chlorine, on the other hand, emerges as a potentially more viable alternative, because it has been widely used in drinking water treatment as a low-cost disinfectant, and is able to be produced cost-effectively on-site. Furthermore, unreacted chlorine serves as a secondary disinfectant to provide residual protection in water distribution system. HOCl and ClO⁻ (pK_a = 7.5) can be activated by O₂^{•-} to produce HO• at $7.5 \pm 0.38 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and by e_{aq}⁻ to produce O•⁻ at $7.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively (Eqs. 1 and 2).^{30,31} Therefore, we hypothesize that e_{cb}⁻ and O₂^{•-} generated from the visible-light-driven g-C₃N₄ photocatalytic process can activate chlorine to produce larger amounts of HO• than either the visible-light-driven chlorine process or visible-light-driven g-C₃N₄ photocatalytic process. The visible light g-C₃N₄-enabled chlorine AOP (VgC-AOP) has the potential to be more practically relevant, feasible and easily implementable, compared with the activation of PMS, PDS and H₂O₂, by activating the residual chlorine present in tap water and treated reused wastewater for enhancing the micropollutant degradation.

In this study, g-C₃N₄ was synthesized and studied as a photocatalyst capable of generating h_{vb}⁺, e_{cb}⁻ and O₂^{•-} and activating free chlorine in model waters containing realistic environmental solutes (NOM, alkalinity, etc.) under visible light irradiation to degrade carbamazepine (CBZ). CBZ is selected as model compound because it is a frequently detected recalcitrant micropollutant in the source water. The removal efficiency of CBZ in conventional drinking water treatment plants is less than 50%.^{32,33} AOP is thus needed to remove it from drinking water. In addition, its second order rate

constants towards HO• and RCS have been well studied. The objectives of this study are to (1) identify the radical species and propose the chlorine activation mechanism in the visible light g-C₃N₄-enabled chlorine AOP (VgC-AOP); (2) examine the synergistic enhancement in the organic micropollutant degradation by the VgC-AOP; and (3) evaluate VgC-AOP performance in degrading CBZ under different g-C₃N₄ and chlorine dosages, light sources, and water matrices for multiple cycles.

2. MATERIALS AND METHODS

2.1. Chemicals. The general chemicals used in and solutions/g-C₃N₄ prepared for this study are listed on Text S1.

2.2. Experimental setup and procedures. The experimental set-up used for the CBZ degradation tests is shown in Figure S1. A cylindrical reactor with a diameter of 7.5 cm containing 100 mL solution (2.5 cm in depth) was placed on a magnetic stirring plate. An LED lamp was placed 8 cm above the bottom of the cylindrical reactor and the distance of the LED lamp to the solution surface is 6.5 cm. Three different light sources, i.e., a 45 W multi-wavelength LED (45 W 450 nm visible LED), a 5 W single wavelength LED emitting light at 450 nm (5W 450 nm LED), and a 5 W single wavelength LED emitting light at 420 nm (5W 420 nm LED), were selected. The 45 W 450 nm visible LED was used as the light source in most studies unless otherwise stated. The irradiation spectrum and intensity of different LEDs (45 W 450 nm visible LED, 5 W 450 nm LED, and 5W 420 nm LED) was measured by NIST Traceable Light Measurement Systems (InternationalLight Technologies) at the surface of the reacting solutions (6.5 cm beneath the LED lamp center) with their spectra shown in Figure S2. The irradiation intensities at wavelengths lower than 470 nm of 45 W 450 nm visible LED, 5 W 450 nm LED, and 5W 420 nm LED are 16.9, 11.4 and 4.6 mW/cm², respectively.

Tests of the CBZ degradation kinetics in the VgC-AOP were conducted as described on Text S2. The radical species generated in the VgC-AOP were determined by competition kinetics using NB, BA, and DMOB as probe compounds.^{6,35} The experiments were conducted in a similar manner as previously described and illustrated in Figure S1. Additionally, electron paramagnetic resonance (EPR) spectroscopy (Bruker EMX-E spectrometer) was applied for the investigation of radical generation, using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the spin trapping reagent.³⁶ The role of different reactive species in chlorine activation was indirectly investigated by adding oxalate ion ($h_{\nu b}^+$ scavenger) and deoxygenation ($O_2^{\bullet -}$ scavenger).

Water matrix effects were investigated by varying pH from 6.0 to 8.0, since pHs of drinking water usually range from 6.5 to 8.5 and for effective disinfection with chlorine, the pH should preferably be less than 8.0 as recommended by WHO (2011),^{37,38} and adding varying levels of bicarbonate, NOM, or copper ion (Cu^{2+}) at pH 7.0. Copper was added because it can co-exist with chlorine in drinking within premise plumbing.

The reusability and stability of g-C₃N₄ were examined by conducting five consecutive CBZ degradation experiments under the same experimental conditions. The g-C₃N₄ after five cycles were collected for further characterization, including SEM, XPS and UV-Vis DRS, to examine its structural changes after reaction.

2.3. Analytical methods. The concentrations of free chlorine were determined by a DPD colorimetric method.³⁹ Concentrations of CBZ, NB, BA and DMOB were determined by a reverse phase UPLC (VP series, Shimadzu) equipped with a Waters symmetry C18 column (4.6 mm × 150 mm, 5 μM particle size; Waters) and a UV detector. The flow rate was 1.0 mL/min and the mobile phase was a mixture of water (pH 3, adjusted using phosphoric acid) and methanol (55/45, v/v %).⁴⁰ The detection limits of CBZ, NB and BA are 0.06, 0.10, 0.04 and 0.13 μM, respectively.

Before and after reactions the g-C₃N₄ was subjected to material characterization. The surface morphology of the g-C₃N₄ samples were characterized by SEM. The elemental composition of the g-C₃N₄ were obtained by XPS (PHI 5600, Physical Electronics Inc., Al K α radiation (1486.8 eV), USA). The optical properties of the g-C₃N₄ were characterized by UV-Vis diffuse reflection spectroscopy (UV-vis DRS, PerlonElmer Lambda 950, USA).

3. RESULTS AND DISCUSSION

3.1. Enhanced CBZ degradation in the VgC-AOP. Figure 1 shows the CBZ degradation kinetics for control processes (dark/g-C₃N₄/chlorine, Vis/chlorine and Vis/g-C₃N₄) and the VgC-AOP with 1 g/L g-C₃N₄ and a free chlorine dosage of 5 mgCl₂/L, respectively. Negligible CBZ degraded during the dark/g-C₃N₄/chlorine process, indicating that g-C₃N₄ cannot 1) activate chlorine in the absence of light, nor 2) adsorb CBZ. For the other three processes, CBZ degradation kinetics follows the pseudo first order rates. The pseudo first order degradation rate constant (k') for the VgC-AOP is $0.0505 \pm 0.0005 \text{ min}^{-1}$, which is 16 and 7 times higher Vis/chlorine ($k'=0.0032 \pm 0.0001 \text{ min}^{-1}$) and Vis/g-C₃N₄ ($k'=0.0073 \pm 0.0014 \text{ min}^{-1}$) processes. The VgC-AOP also exhibits 4.6 times higher chlorine consumption (2.3 mgCl₂/L) compared with those of the Vis/chlorine (0.5 mgCl₂/L, which mainly due to the direct photolysis) and dark/g-C₃N₄/chlorine (0.5 mgCl₂/L). Figure S3 shows that the change in chlorine concentrations with g-C₃N₄ is due to adsorption and/or oxidation. The higher CBZ degradation rate constant and chlorine consumption in the VgC-AOP suggests that there is a synergistic enhancement in CBZ degradation by the VgC-AOP. The CBZ degradation rate constant is above the overall performance estimated by the superposition principle considering its subordinate processes (Text S3). The reaction stoichiometric efficiency (%RSE), defined as the moles of CBZ degraded divided by

the moles of chlorine consumed, in the VgC-AOP reached 5.2%, which was at a similar level to that reported in the UV-C/chlorine process.^{41,42}

3.2. Mechanism of the VgC-AOP. Radical species generated in the VgC-AOP for the CBZ degradation was determined using three probe compounds, NB, BA and DMOB.^{6,35} Neither NB, BA nor DMOB degraded in the control Vis/g-C₃N₄ experiments (Figure S4). For the VgC-AOP, Figure 2(a) shows BA degradation rate constants decreased from 0.0469 ± 0.0003 to less than $0.0258 \pm 0.0001 \text{ min}^{-1}$ ($p < 0.05$) in the presence of increasing NB concentrations (0 to 10 μM), while the NB concentration of 100 μM completely inhibited BA degradation. The addition of 100 μM NB consume about 85% of HO•, respectively, as calculated from the 2nd order reaction rate constants of NB and BA towards HO• at 3.9×10^9 and $5.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively (Eqs. 3 and 5, detailed calculation is in Text S4). Since NB only reacts with HO• (Eqs. 3 and 4), while BA reacts with both HO• and Cl• (Eqs. 5 and 6), the total inhibition of the BA degradation by excessive NB indicates that HO• but not Cl• is generated in the VgC-AOP.

The generation of HO• in VgC-AOP is further confirmed by an EPR spin-trap technique using DMPO as the probe. The signals of the DMPO–HO• adducts are observed in the spectrum of the VgC-AOP but not in the visible light g-C₃N₄ (Vis/g-C₃N₄) or visible light chlorine (Vis/chlorine) processes (Figure S5).

As shown in Figure 2(b), the DMOB degradation rate constants decreased by about 81% from 0.0863 ± 0.0009 to $0.0159 \pm 0.0003 \text{ min}^{-1}$ ($p < 0.05$) upon increasing NB

218 concentrations (0 to 200 μM , respectively). The addition of 200 μM NB consumes 90%
 219 of $\text{HO}\bullet$, as calculated from the 2nd order reaction rate constants of NB and DMOB
 220 towards $\text{HO}\bullet$ at 3.9×10^9 and $7.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively (Eqs. 3 and 7, detailed
 221 calculation is in Text S4). Since NB only reacts with $\text{HO}\bullet$ (Eqs. 3 and 8), while DMOB
 222 reacts with both $\text{HO}\bullet$ and $\text{ClO}\bullet$ (Eqs. 7 and 9), the 90% reduction of $\text{HO}\bullet$ concentration
 223 but 81% decay of DMOB degradation rate constant in the presence of 200 μM NB
 224 indicates that $\text{ClO}\bullet$ is also produced in the system. The experiments using the three
 225 probe compounds suggest that the major radical species generated in the VgC-AOP are
 226 $\text{HO}\bullet$ and $\text{ClO}\bullet$. The steady-state concentrations of $\text{HO}\bullet$ and $\text{ClO}\bullet$ in the VgC-AOP was
 227 then determined to be $3.1 \times 10^{-14} \text{ M}$ and $2.4 \times 10^{-13} \text{ M}$, respectively, by simultaneously
 228 degrading 2.0 μM NB and 5.0 μM DMOB (Figure S6, see Text S5 for details). The
 229 steady-state concentration of $\text{ClO}\bullet$ is about 7.8 time higher than that of $\text{HO}\bullet$.

230 The photo-induced species in the VgC-AOP responsible for the chlorine activation
 231 were further investigated. Figure 3 shows the CBZ degradation rate constants by the
 232 VgC-AOP in the presence of oxalate ions (a h_{vb}^+ scavenger) at dissolved oxygen (DO)
 233 concentrations of 8.3 and 0.5 mg/L. In the presence of oxalate ions, the CBZ
 234 degradation rate constant decreases by 19%, which is due to the inhibition of $\text{ClO}\bullet$
 235 produced from the HOCl/ClO^- activation and the direct oxidation by h_{vb}^+ . h_{vb}^+ has a VB
 236 edge potential of 1.52 V (Text S6), which is higher than that of $\text{E}^0(\text{ClO}\bullet/\text{ClO}^-)$, and the
 237 reaction produces $\text{ClO}\bullet$ from the activation of HOCl/ClO^- (Eq. 10). The steady-state
 238 concentration of $\text{ClO}\bullet$ is $1.26 \times 10^{-13} \text{ M}$, which could account for 53% of the total $\text{ClO}\bullet$
 239 concentration (see Text S5 for details), but it only contributes about 3.2% to the CBZ

degradation (see Text S5 for details). The contribution is larger than that calculated from the second order rate constant ($9.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) between $\text{ClO}\bullet$ and CBZ in solution phase (Eq. 11), which may be due to degradation of CBZ by the surface-bounded $\text{ClO}\bullet$. The remaining 16% of the CBZ degradation is attributed to the direct oxidation by h_{vb}^+ , since h_{vb}^+ is the only reactive species degrading CBZ in the Vis/g- C_3N_4 process.⁴³

As shown in Figure 2(b), the CBZ degradation rate constants (k') decreased by 42% with decreasing solution DO from 8.3 to 0.5 mg/L. Since HOCl can be activated by $\text{O}_2^{\bullet-}$ to produce $\text{HO}\bullet$,³⁰ the 42% decrease in the k' at the low DO concentration is mainly because that the concentrations of $\text{O}_2^{\bullet-}$ available in activating chlorine drops by 94% (see Text S7 for details), as the reaction between DO and e_{cb}^- is much inhibited (Eq. 12). However, k' at the low DO concentration is still 3.5x higher than that in the absence of chlorine. The activation of ClO^- by e_{cb}^- is promoted in the lower DO environment (i.e., less e_{cb}^- will be trapped by O_2), and >13x more e_{cb}^- will be available for ClO^- activation (see Text S7 for details). This suggests that e_{cb}^- , in addition to $\text{O}_2^{\bullet-}$, contributes to the chlorine activation by producing $\text{O}\bullet^-$ and then to $\text{HO}\bullet$ as shown in Eq. 2.³¹ $\text{HO}\bullet$ will be partially scavenged by HOCl/ClO^- to produce $\text{ClO}\bullet$, which accounts for 47% of the total $\text{ClO}\bullet$ concentrations and contributes to 2.8% of the CBZ degradation (Eqs. 13 and 14). Based on the previously section, the contributions of h_{vb}^+ , $\text{HO}\bullet$ and $\text{ClO}\bullet$ to the CBZ degradation at normal DO level are 16%, 78% and 6%, respectively (see Text S5 for details).

Scheme 1 shows the proposed chlorine activation and CBZ degradation mechanism in the VgC-AOP. As g-C₃N₄ absorbs visible lights at wavelengths shorter than 470 nm there is production of h_{vb}^+ and e_{cb}^- at valence and conduction bands, respectively. h_{vb}^+ can oxidize HOCl/ClO⁻ to produce ClO•. e_{cb}^- reacts rapidly with O₂ to produce O₂^{•-}, which subsequent activates HOCl to produce HO•. e_{cb}^- also reacts with ClO⁻ directly to produce O•⁻ and then convert into HO•. HO• will be partially scavenged by HOCl/ClO⁻ to produce ClO•. h_{vb}^+ , HO• and ClO• are thus responsible for the CBZ in the process. The synergistic enhancement in the CBZ degradation by the VgC-AOP is attributed to the production of HO• and ClO• from the chlorine activation by photo-induced h_{vb}^+ , e_{cb}^- and O₂^{•-}. The synergism is much more significant than combining g-C₃N₄ photocatalysis with PMS, PDS or H₂O₂.

3.3. Influencing factors on CBZ degradation.

3.3.1. Effects of g-C₃N₄ and chlorine dosages. Figure 4 shows data and fitted k' values for the VgC-AOP at pH 7.0. As shown in Figure 4(a), with a 4x increase in g-C₃N₄ dosages from 0.5 to 2.0 g/L, the CBZ degradation rate constants increase by 2.3x from 0.0287 ± 0.0018 to $0.0649 \pm 0.0017 \text{ min}^{-1}$ ($p < 0.05$). The increasing catalyst doses (i.e., more surface area) promote the generation of reactive sites (h_{vb}^+ , e_{cb}^-) and O₂^{•-} (Scheme 1), and thus generates more reactive species through the HOCl activation, which further leads to more rapid CBZ degradation.⁴⁴

As shown in Figure 4(b), with a 4x increase in chlorine dosages from 0.5 to 2.0 mgCl₂/L, the CBZ degradation rate constants increase by 1.3x from 0.0328 ± 0.0039 to $0.0438 \pm 0.0004 \text{ min}^{-1}$ ($p < 0.05$), which is only about 60% compared with that with increasing g-C₃N₄ dosages. A further 2.5x increase in chlorine dosages from 2.0 to 5.0

mgCl₂/L only increases the CBZ degradation rate constants by about 0.15x from 0.0438 ± 0.0004 to 0.0505 ± 0.0005 min⁻¹ (p<0.05). The slow increase of the CBZ degradation rate constants above chlorine dosages of 2.0 mgCl₂/L may be due to the limited reactive sites on g-C₃N₄. This phenomenon reveals that the generation of photo-induced reactive species is the rate determined step in the VgC-AOP under the testing conditions. Simultaneously, the increasing chlorine concentrations increase the quenching of HO• due to the high reaction rate constants between HOCl/ClO⁻ and HO• at 2.9 × 10⁹ M⁻¹ s⁻¹ and 8.8 × 10⁹ M⁻¹ s⁻¹, respectively (Eqs. 13 and 14). The excessive chlorine consumes more HO• to ClO•, whose second order rate constant towards CBZ is 9.2 × 10⁷ M⁻¹ s⁻¹, and further inhibits the CBZ degradation.^{6,42}

3.3.2. Effects of irradiation intensity and wavelength. Figure 5 shows irradiation intensity and *k'* data for LEDs emitting light at 420 or 450 nm (Figure S2 shows emission spectra for each LED). The irradiation intensity at wavelengths lower than 470 nm of 45 W 450 nm visible LED, 5 W 450 nm LED, and 5W 420 nm LED is 16.9, 11.4 and 4.6 mW/cm², respectively, as shown in Figure 5(a). While the 45W and 5W 450 nm LED share the same light spectra (Figure S2), the former produces only 40% higher intensity than the 5W LED. Figure 5(b) shows the observed (*k'*, min⁻¹) and intensity-normalized (*k_{hv}*, min⁻¹(W/cm²)⁻¹) pseudo first-order CBZ degradation rate constants for VgC-AOP using these LEDs (see Figure S7 for their degradation kinetics and Text S8 for normalized rate constant calculation). Values for *k'* in the process under 45W 450 nm visible LED and 5W 450 nm LED increase proportionally with increasing light intensities, but their *k_{hv}* values are equivalent (9.5 min⁻¹(W/cm²)⁻¹). Therefore, radical production during the VgC-AOP is directly proportional to irradiation intensity. The *k_{hv}* for 420 nm versus 450 nm LED is 1.7x higher, suggesting that the process produces larger amounts of radicals for the CBZ degradation at shorter wavelengths.

The chlorine decay trends follow the same trends as CBZ as a function of k_{hv} for irradiance intensity and wavelength (Figure S8, see Text S9 in the SI for details).

3.3.3. Reusability and stability. Many publications overlook potential aging of photocatalysts. As an initial assessment, the as-prepared g-C₃N₄ photocatalyst was collected and reused for five consecutive CBZ degradation tests under the same conditions. Figure 6 shows k values remained the same after five cycles, suggesting acceptable material stability and potential reusability of the g-C₃N₄ in the process. The high stability of g-C₃N₄ in the process is because HO• prefers to react with organics components in the water and will not primarily attack g-C₃N₄ as reported by Xiao et al. (2017).⁴⁵ A similar conclusion was reached based upon material characterization. The g-C₃N₄ after five consecutive cycles were further characterized and compared with the freshly prepared g-C₃N₄ using SEM, UV-Vis DRS and XPS to investigate its changes in the process (Figure S9). From SEM imaging, the morphology of g-C₃N₄ after five cycles remains the same as the original one. Based upon UV-Vis DRS, the absorption spectrum of the used g-C₃N₄ is the same as the original one, suggesting that the process does not affect the light absorption property of g-C₃N₄. As indicated in the XPS, the C content of g-C₃N₄ remained the same, while the used g-C₃N₄ has a 1.7% and 0.07% increase in O and Cl content, respectively, and a 2.8% decrease in N content compared with the original g-C₃N₄ (as shown by the elemental composition of the original and used g-C₃N₄ in SI Table S2). The increase of O and decrease of N may be due to substitution of N by O during the oxidation process, while the presence of Cl content on g-C₃N₄ may because of the surface modification of g-C₃N₄ during the reactions between HOCl/CIO⁻ and photo-induced $h_{vb}^+/O_2^{\bullet-}/e_{cb}^-$. The replacement of N with O and the presence of trace amount of Cl content does not affect the properties of g-C₃N₄, which allows the CBZ degradation efficiency remain the same using recycled g-C₃N₄.

3.3.4. *Impacts of water matrices.* The impacts of water matrices, including pH, HCO_3^- , Cu^{2+} and NOM, on the VgC-AOP are summarized in Figure 7. pH levels between 6.0 to 8.0 showed comparable k' values ($0.043 \pm 0.0008 \text{ min}^{-1}$, $p > 0.05$). In contrast, for UV/chlorine AOPs, their oxidative efficiency decreases as HOCl deprotonates with increasing pHs, because ClO^- quenches $\text{HO}^\bullet$ 4.4x faster than HOCl.⁴⁶ However, during the VgC-AOP, the unchanged k' values at pHs from 6.0 to 8.0 is mainly because ClO^- reacts with e_{cb}^- about 1000x ($7.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) faster than HOCl reacts with $\text{O}_2^{\bullet -}$ ($7.5 \pm 0.38 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$), which offsets the stronger scavenging of $\text{HO}^\bullet$ cause by the increasing ClO^- concentrations with increasing pHs.

As shown in Figure 7, at bicarbonate levels of 0, 0.5, 1.0, and 2.0 mM, the CBZ degradation rate constants (k') are 0.0438 ± 0.0004 , 0.0481 ± 0.0023 , 0.0425 ± 0.0035 , and $0.0471 \pm 0.0078 \text{ min}^{-1}$, respectively. The P-value of this set of data is greater than 0.05 ($p > 0.05$), suggesting the difference of k' with increasing bicarbonate levels is insignificant. Therefore, increasing bicarbonate levels (0.5–2.0 mM) did not affect the CBZ degradation in the VgC-AOP. Even with increasing pHs from 7.0, the pH used in our investigation, to 8.0, the portion of CO_3^{2-} increases from 0.05% to 0.5%, since the pKa of bicarbonate (HCO_3^-) and carbonate ion (CO_3^{2-}) is 10.3. In theory, the pseudo first order $\text{HO}^\bullet$ scavenging rate constants towards 2.0 mM bicarbonate ($\text{HCO}_3^-/\text{CO}_3^{2-}$) increase from 1.7×10^4 to $2.1 \times 10^4 \text{ s}^{-1}$ as calculated from their second order rate constants towards $\text{HO}^\bullet$ shown in Eqs. 15 and 16. Such a small increase will not cause significant inhibition on CBZ degradation.

The unaffected k' values ($p > 0.05$) across the range of carbonate alkalinities can be explained by the negatively charged surface of g- C_3N_4 which likely repulses HCO_3^- , and reduces concentrations of HCO_3^- on/near the surface of g- C_3N_4 . As a result, the scavenging of reactive sites and radical species on/near the surface of g- C_3N_4 by HCO_3^-

359 is greatly inhibited. On the contrary, k' was reduced by about 20% in the UV/chlorine
 360 process in the presence of 1.0 mM HCO_3^- ,⁹ due to the scavenging of $\text{Cl}\cdot$ and $\text{HO}\cdot$ to
 361 less reactive carbonated radical (i.e. $\text{HCO}_3^{\cdot-}$ and $\text{CO}_3^{\cdot-}$) as shown in Eqs. 15 and 17. In
 362 the g-C₃N₄/TiO₂ photocatalytic process, k' was reduced by 64% and 84% at HCO_3^-
 363 concentration of 1.5 and 5.0 mM, respectively,⁴⁷ due to the competition of HCO_3^- with
 364 organic pollutants for active sites and scavenging of h_{vb}^+ and radicals (Eqs. 15 and 18).

365 Copper in drinking water can co-occur with chlorine (i.e., within premise plumbing).
 366 Values for k' increased, non-linearly, in proportion to Cu^{2+} concentration (Figure 7).
 367 Accelerated CBZ degradation in the presence of Cu^{2+} are mainly due to the electron-
 368 shuttle effect of Cu^{2+} , which not only enhanced the h_{vb}^+ and e_{cb}^- separation, but also
 369 maintained the generation rates of $\text{O}_2^{\cdot-}$.⁴⁸ Compared with O_2 , Cu^{2+} has a higher affinity
 370 towards g-C₃N₄ due to its positive charge and reacts with e_{cb}^- at a higher second order
 371 rate constant of $3.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (Eq. 19). The adsorbed Cu^{2+} likely out-competes O_2
 372 to boost the h_{vb}^+ and e_{cb}^- separation and produces Cu^+ , which then reacts with DO near
 373 the g-C₃N₄ surface to produce more $\text{O}_2^{\cdot-}$ (Eq. 20) to accelerate the CBZ degradation.⁴⁹
 374 However, the limited sites on g-C₃N₄ only allow a fixed amount of Cu^{2+} adsorbed on
 375 the photocatalyst surface to boost h_{vb}^+ and e_{cb}^- separation, which results in the plateau
 376 of the CBZ degradation rate constant at higher Cu^{2+} concentration.

As NOM concentrations increased from 0 to 4.0 mgDOC/L, proportional decreases were observed in k' from 0.0438 ± 0.0004 to $0.0229 \pm 0.0006 \text{ min}^{-1}$ ($p < 0.05$). NOM mainly acts as a radical scavenger (Eq. 21) and a competitor for free chlorine (Eq. 22). As represented in Table S3, the NOM inhibition on the CBZ degradation occurs mainly due to its competition of active sites and scavenging of radicals, which contributes to around 75% of the overall decay at all tested NOM concentrations. The contribution of chlorine consumption of the overall decay is about 24% at all tested NOM concentrations (calculated from Table S3). The 48% drop in k' at an NOM concentration of 4.0 mgDOC/L less significant than a 76% drop in CBZ degradation rate constant during the UV/chlorine AOPs in the presence 4.0 mgDOC/L NOM,⁵⁰ or the 67% drop during TiO_2 photocatalysis at an NOM concentration of only 1 mgDOC/L.⁵¹ Because NOM molar absorptivity decreases at longer wavelengths, irradiation at 400 to 470 nm resulted in < 1% drop in delivered light dosage for the 45 W 450 nm visible LED for 4 mgDOC/L (see Text S10 in the SI for detail calculation). Furthermore, the lower impact of NOM on efficiency VgC-AOP, compared against other AOPs, is because the tri-s-triazine unit in g- C_3N_4 has limited adsorption capacity of NOM due to its low affinity towards the carboxylate groups in NOM. The surface-bond reactive species on g- C_3N_4 are thus less affected compared with those in aqueous phase and those on TiO_2 .

4. ENGINEERING IMPLICATIONS

The activation of chlorine by visible-light-driven photocatalysis is a novel AOP capable of degrading micropollutants. The VgC-AOP is practically relevant, feasible and easily

implementable by activating the residual chlorine present in tap water and treated reused wastewater to enhance the micropollutant degradation in clear water tanks, service water reservoirs, point-of-use water purifiers, etc. Compared with the UV/chlorine AOP, the VgC-AOP may allow use of more efficient LEDs (i.e., efficiency and output wattage are higher for visible compared against ultraviolet wavelengths⁵²). Because 96% of the solar spectrum is > 400 nm, there is potential to use sunlight with VgC-AOP in off-grid industrial applications or even potentially in applications similar to SODIS – although additional research is needed how to add and separate g-C₃N₄ in these applications.

VgC-AOP exhibited less competition from common inorganic or organic dissolved solutes in water, compared against common homogeneous (UV/chlorine) or heterogeneous (UV/TiO₂) AOPs. Despite the possibility that h_{vb}^+ may be trapped by other organic components like DOM in real water matrix, the significant enhancement of radical yields still exists in the VgC-AOP, because HO•, which contributes to 78% of CBZ degradation, is generated from the activation of chlorine by e_{cb}^- and O₂^{•-}. Moreover, the same principle in activating chlorine can be extrapolated to other photocatalysts, and thus provides unlimited potentials to enhance the micropollutant degradation performance and reduce the energy consumption in the photocatalytic chlorination processes. A side benefit of the fast chlorine decay rate is that the process can be integrated to the end of the disinfection tank to achieve simultaneous advanced oxidation and chlorine reduction to meet the aesthetic chlorine concentration standard in the drinking water supply standard. VgC-AOP may produce less halogenated by-products compared with the UV/chlorine AOP, because the chlorine decay rates in the former process are much faster than the latter process, resulted in less free chlorine contact time and thus potentially less halogenated by-product formation. The

degradation pathways and byproducts of micropollutants in the VgC-AOP need further investigation, considering the electrophilic chlorine substitution mechanism.⁵³

ASSOCIATED CONTENT

Supporting Information

Chemicals; experimental procedures of CBZ degradation test; superposition principle; radical species for CBZ degradation; determination of the edge potential of VB and CB of g-C₃N₄; effect of DO; normalized rate constant with respect to the irradiation intensity; chlorine decay in the VgC-AOP; effect of NOM; Experimental set-up; irradiation spectrum of light sources; chlorine decay by the VgC-AOP and control processes; degradation of NB and DMOB by Vis/g-C₃N₄ process; EPR spectra of DMPO-•OH adducts in different systems; determination of the steady-state concentrations of HO• and ClO• in the VgC-AOP; effect of different light sources; effect of light sources on chlorine decay in the VgC-AOP and Vis/chlorine process; g-C₃N₄ characterization before and after 5 cycles VgC-AOP; reactions between photoinduced species and oxidants; elemental composition of g-C₃N₄ before and after 5 cycles VgC-AOP, and scavenging effect of NOM.

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Figure 1. The CBZ degradation by different processes. Conditions: pH = 7.0, [CBZ]₀ = 2.0 μM, [g-C₃N₄] = 1.0 g/L, [Free chlorine]₀ = 5.0 mgCl₂/L, and 45 W 450 nm visible LED. Pseudo first-order rate constants (k') calculated based upon regression analysis.

Figure 2. Influence of nitrobenzene (NB) on degradation kinetics of (a) benzoic acid ($BA_0 = 2.0 \mu\text{M}$) as a $\text{Cl}^\bullet$ probe, and (b) 1,4-dimethoxybenzene ($\text{DMOB}_0 = 5.0 \mu\text{M}$) as a $\text{ClO}^\bullet$ probe by the VgC-AOP. Other conditions: (a) 5 W 450 nm LED and (b) 45 W 450 nm visible LED, $\text{pH} = 7.0$, $[\text{g-C}_3\text{N}_4] = 1.0 \text{ g/L}$, and $[\text{Free chlorine}]_0 = 2.0 \text{ mgCl}_2/\text{L}$. Pseudo first-order rate constants (k') calculated based upon regression analysis.

Figure 3. The CBZ degradation rate constants by the VgC-AOP in the presence of different radical scavengers or at a low DO concentration. Conditions: pH = 7.0, $[\text{CBZ}]_0 = 2.0 \mu\text{M}$, $[\text{g-C}_3\text{N}_4] = 1.0 \text{ g/L}$, $[\text{Free chlorine}]_0 = 2.0 \text{ mgCl}_2/\text{L}$, and 45 W 450 nm visible LED, $[\text{Sodium oxalate}] = 2.0 \text{ mM}$, and $[\text{DO}] \approx 8.3 \text{ mg/L}$ (natural DO concentration) or 0.5 mg/L (low DO concentration). Pseudo first-order rate constants (k') calculated based upon regression analysis.

Figure 4. The CBZ degradation by the VgC-AOP at different dosages of (a) $\text{g-C}_3\text{N}_4$ and (b) chlorine. Baseline conditions: $\text{pH} = 7.0$, $[\text{CBZ}]_0 = 2.0 \mu\text{M}$, $[\text{g-C}_3\text{N}_4] = 1.0 \text{ g/L}$, and $[\text{Free chlorine}]_0 = 2.0 \text{ mgCl}_2/\text{L}$, 45 W 450 nm visible LED. Pseudo first-order rate constants (k') calculated based upon regression analysis.

Figure 5. Effects of different light sources on CBZ degradation (a) irradiation intensity at wavelengths lower than 470 nm (b) the observed and intensity-normalized CBZ degradation rate constants by the VgC-AOP. Conditions: $\text{pH}=7.0$, $[\text{CBZ}]_0 = 2.0 \mu\text{M}$, $[\text{g-C}_3\text{N}_4] = 1.0 \text{ g/L}$, and $[\text{Free chlorine}]_0 = 2.0 \text{ mg/L}$ as Cl_2 . Pseudo first-order rate constants (k') calculated based upon regression analysis.

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Scheme 1. Proposed chlorine activation and CBZ degradation mechanism in the VgC-AOP.

Supporting Information for:

A novel visible-light-driven photocatalytic chlorine activation process for carbamazepine degradation in drinking water

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Text S1. The general chemicals used in and solutions/g-C₃N₄ prepared for this study.

Carbamazepine (CBZ), nitrobenzene (NB), benzoic acid (BA), 1,4-dimethoxybenzene (DMOB), sodium hypochlorite (NaOCl) solution (4.0–5.0%), melamine, sodium thiosulphate (Na₂S₂O₃), sodium chloride (NaCl), sodium bicarbonate (NaHCO₃), and copper(II) chloride (CuCl₂) were purchased from Sigma-Aldrich. These chemicals were of reagent grade and used as received without further purification. Suwannee River reversed osmosis natural organic matter (NOM) isolates (cat. no. 2R101N) were purchased from the International Humic Substances Society. The NOM stock solution was prepared by adding NOM isolates in DDI water, stirring overnight, and filtering the solution through a 0.45 µm pore size fiber membrane (Whatman). Phosphoric acid (H₃PO₄) and methanol (MeOH) of HPLC grade were purchased from Fisher Scientific.

Text S2. Experimental procedures of CBZ degradation by the VgC-AOP.

Tests of the CBZ degradation kinetics in the VgC-AOP were conducted by preparing a 100 mL solution containing 2.0 mM phosphate or borate buffers. The solution was sequentially spiked with predetermined concentrations of CBZ, g-C₃N₄ and chlorine, and then was exposed to the selected LED irradiation. Aliquots (1.5 mL) were collected over time (5, 10, 15, 20 and 30 minutes), filtered (0.22 µm Polyethersulfone, Tianjin Jinteng), chlorine quenched with 5.0 µL of 0.1 M thiosulphate, and then analyzed for CBZ concentrations. Control tests were conducted by exposing CBZ to the g-C₃N₄/chlorine (without LED irradiation), Vis/chlorine (without adding g-C₃N₄) and Vis/g-C₃N₄ (without adding chlorine) processes using the similar approach. All experiments were at least duplicated. All data plots represent the average of the experimental data of the duplicated test results.

Text S3. The superposition principle considering its subordinate processes.

$$\text{Dark/g-C}_3\text{N}_4/\text{chlorine}: k' = 0 \text{ min}^{-1}$$

$$\text{Vis/chlorine} : k' = 0.0032 \pm 0.0001 \text{ min}^{-1}$$

$$\text{Vis/g-C}_3\text{N}_4 : k' = 0.0073 \pm 0.0014 \text{ min}^{-1}$$

$$\text{VgC-AOP}: k' = 0.0505 \pm 0.0005$$

The k' of VgC-AOP is much larger than the sum of the k' of Dark/ g-C₃N₄/chlorine, Vis/chlorine, and Vis/g-C₃N₄.

Text S4. Radical species for the CBZ degradation in the VgC-AOP.

Since NB, BA and DMOB all cannot be degraded by the Vis/g-C₃N₄ process according to our preliminary test. Therefore, the degradation of the three probes should be all attributed to the radical species generated from chlorine activation.

1.1 The steady-state concentration of HO•. In the VgC-AOP, when only BA or DMOB is used as the probe compound, the formation rate ($F_{HO\bullet}$) and the consumption rate ($R_{HO\bullet}$) of HO• can be expressed respectively as follows:

$$\text{Only BA: } F_{HO\bullet} - R_{HO\bullet} = 0; R_{HO\bullet} = Q_{BA} + Q_{HOCl/CIO^-} + Q_{other}$$

$$\text{Only DMOB: } F_{HO\bullet} - R_{HO\bullet} = 0; R_{HO\bullet} = Q_{DMOB} + Q_{HOCl/CIO^-} + Q_{other}$$

Q_{BA}/Q_{DMOB} , and Q_{other} are the rates of HO• consumption by BA/DMOB, HOCl/CIO⁻ and other scavengers, respectively.

$$[HO\bullet]_{ss,BA} = F_{HO\bullet} / (k_{HO\bullet,BA} * [BA] + Q_{HOCl/CIO^-} + Q_{other})$$

$$[HO\bullet]_{ss,DMOB} = F_{HO\bullet} / (k_{HO\bullet,DMOB} * [DMOB] + Q_{HOCl/CIO^-} + Q_{other})$$

When NB and BA/DMOB are used simultaneously as the probe compounds, the consumption rate ($R_{HO\bullet}$) of HO• can be expressed respectively as follows:

$$\text{NB and BA: } R_{HO\bullet} = Q_{BA} + Q_{NB} + Q_{HOCl/CIO^-} + Q_{other}$$

$$\text{NB and DMOB: } R_{HO\bullet} = Q_{DMOB} + Q_{NB} + Q_{HOCl/CIO^-} + Q_{other}$$

$$[HO\bullet]_{ss,BA'} = F_{HO\bullet} / (k_{HO\bullet,BA} * [BA] + k_{HO\bullet,NB} * [NB] + Q_{HOCl/CIO^-} + Q_{other})$$

$$[HO\bullet]_{ss,DMOB'} = F_{HO\bullet} / (k_{HO\bullet,DMOB} * [DMOB] + k_{HO\bullet,NB} * [NB] + Q_{HOCl/CIO^-} + Q_{other})$$

1.2 Competition with BA/DMOB for HO• in the presence of NB.

(1) 2.0 μM BA degradation in the presence of NB:

Assume the presence of NB will not affect the $F_{HO\bullet}$, then can get:

$$[HO\bullet]_{ss,BA'} / [HO\bullet]_{ss,BA} = (k_{HO\bullet,BA} * [BA] + Q_{HOCl/CIO^-} + Q_{other}) / (k_{HO\bullet,BA} * [BA] + k_{HO\bullet,NB} * [NB] + Q_{HOCl/CIO^-} + Q_{other})$$

Since Q_{other} is negligible or much smaller than Q_{BA} , Q_{NB} , and Q_{HOCl/CIO^-} , then can get:

$$[HO\bullet]_{ss,BA'} / [HO\bullet]_{ss,BA} = (k_{HO\bullet,BA} * [BA] + Q_{HOCl/CIO^-}) / (k_{HO\bullet,BA} * [BA] + k_{HO\bullet,NB} * [NB] + Q_{HOCl/CIO^-})$$

$$Q_{HOCl/CIO^-} = k_{HO\bullet,HOCl} * [HOCl] + k_{HO\bullet,CIO^-} * [CIO^-]$$

$$k_{HO\bullet,BA} = 5.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}; k_{HO\bullet,NB} = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}; k_{HO\bullet,HOCl} = 2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

¹; $k_{HO\cdot, ClO^-} = 8.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; $[HOCl]_{\text{average}} = 11.4 \text{ }\mu\text{M}$; $[ClO^-]_{\text{average}} = 3.8 \text{ }\mu\text{M}$.

When $[NB]$ is $100 \text{ }\mu\text{M}$, $[HO\cdot]_{ss,BA'}/[HO\cdot]_{ss,BA} = 15\%$, which means $[HO\cdot]_{ss'}$ dropped by 85% .

(2) 5.0 μM BA DMOB degradation in the presence of NB

Assume the presence of NB will not affect the $F_{HO\cdot}$, then can get:

$$[HO\cdot]_{ss,DMOB'}/[HO\cdot]_{ss,DMOB} = (k_{HO\cdot,DMOB}*[DMOB] + Q_{HOCl/ClO^-} + Q_{\text{other}})/(k_{HO\cdot,DMOB}*[DMOB] + k_{HO\cdot,NB}*[NB] + Q_{HOCl/ClO^-} + Q_{\text{other}})$$

Since Q_{other} is negligible or much smaller than Q_{DMOB} , Q_{NB} , and Q_{HOCl/ClO^-} , then can get:

$$[HO\cdot]_{ss,DMOB'}/[HO\cdot]_{ss,DMOB} = (k_{HO\cdot,DMOB}*[DMOB] + Q_{HOCl/ClO^-})/(k_{HO\cdot,DMOB}*[DMOB] + k_{HO\cdot,NB}*[NB] + Q_{HOCl/ClO^-})$$

$$Q_{HOCl/ClO^-} = k_{HO\cdot,HOCl}*[HOCl] + k_{HO\cdot,ClO^-}*[ClO^-]$$

$k_{HO\cdot,DMOB} = 7.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; $k_{HO\cdot,NB} = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; $k_{HO\cdot,HOCl} = 2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; $k_{HO\cdot,ClO^-} = 8.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; $[HOCl]_{\text{average}} = 11.4 \text{ }\mu\text{M}$; $[ClO^-]_{\text{average}} = 3.8 \text{ }\mu\text{M}$.

When $[NB]$ is $50 \text{ }\mu\text{M}$, $[HO\cdot]_{ss,DMOB'}/[HO\cdot]_{ss,DMOB} = 31\%$, which means $[HO\cdot]_{ss,DMOB'}$ dropped by 69% . When $[NB]$ is $100 \text{ }\mu\text{M}$, $[HO\cdot]_{ss,DMOB'}/[HO\cdot]_{ss,DMOB} = 19\%$, which means $[HO\cdot]_{ss,DMOB'}$ dropped by 81% . When $[NB]$ is $200 \text{ }\mu\text{M}$, $[HO\cdot]_{ss,DMOB'}/[HO\cdot]_{ss,DMOB} = 10\%$, which means $[HO\cdot]_{ss,DMOB'}$ dropped by 90% .

Text S5. Steady-state concentration of HO• and ClO• in the VgC-AOP.

(1) 2.0 μM NB and 5.0 μM DMOB simultaneously degradation by the VgC-AOP.

$$k_{\text{obs,NB}} = k_{\text{HO}\cdot,\text{NB}} \times [\text{HO}\cdot]_{\text{ss}}$$

$$k_{\text{obs,DMOB}} = k_{\text{HO}\cdot,\text{DMOB}} \times [\text{HO}\cdot]_{\text{ss}} + k_{\text{ClO}\cdot,\text{DMOB}} \times [\text{ClO}\cdot]_{\text{ss}}$$

$$k_{\text{HO}\cdot,\text{NB}} = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}; k_{\text{HO}\cdot,\text{DMOB}} = 7.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}; k_{\text{ClO}\cdot,\text{DMOB}} = 2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1};$$

From Figure S6, $k_{\text{obs,NB}}$ is 0.0072 min^{-1} and $k_{\text{obs,DMOB}}$ is 0.0430 min^{-1} .

So $[\text{HO}\cdot]_{\text{ss}}$ and $[\text{ClO}\cdot]_{\text{ss}}$ are $3.08 \times 10^{-14} \text{ M}$ and $2.39 \times 10^{-13} \text{ M}$, respectively.

(2) Contribution of h_{vb}^+ , HO•, and ClO• to the CBZ degradation.

Assume $k_{\text{obs},h_{\text{vb}}^+}$ and $k_{\text{ClO}\cdot,\text{cbz}} \times [\text{ClO}\cdot]_{\text{ss}}$ will not be affect by DO concentration.

$$k_{\text{obs,CBZ}} = k_{\text{HO}\cdot,\text{cbz}} \times [\text{HO}\cdot]_{\text{ss}} + k_{\text{ClO}\cdot,\text{cbz}} \times [\text{ClO}\cdot]_{\text{ss}} + k_{\text{obs},h_{\text{vb}}^+} \text{ and } [\text{HO}\cdot]_{\text{ss}}/[\text{ClO}\cdot]_{\text{ss}} = 7.76$$

	Overall	h_{vb}^+	HO•	ClO•
Normal DO (min^{-1})	0.0438	16.0%	78% (0.034)	6.0%
Low DO (min^{-1})	0.0254	27.1%	62.2% (0.016)	10.7%

(3) 200 μM NB and 5.0 μM DMOB simultaneously degradation by the VgC-AOP.

In the presence of 200 μM NB, which can compete with 5.0 μM DMOB for about 95.71% of HO•, most of the DMOB will be degraded by ClO•.

$$k_{\text{obs,DMOB}} = k_{\text{HO}\cdot,\text{DMOB}} \times [\text{HO}\cdot]_{\text{ss}} + k_{\text{ClO}\cdot,\text{DMOB}} \times [\text{ClO}\cdot]_{\text{ss}},$$

$$k_{\text{HO}\cdot,\text{DMOB}} \times [\text{HO}\cdot]_{\text{ss}} \approx 0$$

From Figure 2, $k_{\text{obs,DMOB}}$ is 0.0159 min^{-1} .

$$\text{So } [\text{ClO}\cdot]_{\text{ss}} \text{ is } 1.26 \times 10^{-13} \text{ M}$$

As most HO• was quenched by NB, the ClO• responsible for DMOB degradation in the presence of 200 μM NB should be mostly produced from chlorine activation by h_{vb}^+ .

$$[\text{ClO}\cdot]_{\text{ss}}/[\text{ClO}\cdot]_{\text{ss}} = 52.86\%,$$

So the contribution of ClO• produced from chlorine activation by h_{vb}^+ is 3.2%.

Text S6. Determination of the edge potential of VB and CB of the as-prepared g-C₃N₄.

The edge potential of VB of the as-prepared g-C₃N₄ can be obtained from the valance XPS spectra (Figure a), which is around 1.52 eV. The band gap of the as-prepared g-C₃N₄ can be calculated from the UV-DRS spectra (Figure b), which is about 2.64 eV (470 nm). The edge potential of CB can be calculated as followed:

$$E_{CB} = E_g - E_{VB} = 2.64 - 1.52 = 1.12 \text{ eV}$$

Text S7. Effect of DO on the CBZ degradation.

(1) Formation rate of $O_2^{\bullet-}$ at the normal and low DO concentration.

In the VgC-AOP, $O_2^{\bullet-}$ can be generated through the reaction between O_2 and e_{aq}^- .

The formation rate of $O_2^{\bullet-}$ can be expressed as followed:

$$F(O_2^{\bullet-}) = k_{O_2, e_{aq}^-} [O_2] [e_{aq}^-]$$

$$k_{O_2, e_{aq}^-} = 1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$

When the DO concentration decreased from 8.3 to 0.5 mg/L, the formation rate of ($F(O_2^{\bullet-})$) theoretically will also decrease by 94%, leading to a same decrease in $HO^\bullet$ formation rate ($F(HO^\bullet)$) as followed:

$$F(HO^\bullet) = k_{O_2^{\bullet-}, HOCl} [O_2^{\bullet-}] [HOCl]$$

(2) Competition of e_{cb}^- at normal and low DO concentration.

e_{aq}^- can react with O_2 and ClO^- to produce $O_2^{\bullet-}$ and $O^\bullet$ as followed:

$$F(O_2^{\bullet-}) = k_{O_2, e_{aq}^-} [O_2] [e_{aq}^-]$$

$$F(O^\bullet) = k_{ClO^-, e_{aq}^-} [ClO^-] [e_{aq}^-]$$

The portion of e_{aq}^- that can react with ClO^- can be expressed as followed:

$$P_{ClO^-, e_{aq}^-} = k_{ClO^-, e_{aq}^-} [ClO^-] / (k_{ClO^-, e_{aq}^-} [ClO^-] + k_{O_2, e_{aq}^-} [O_2])$$

[O ₂]	[ClO ⁻] (pH 7)	P _{ClO⁻, e_{aq}⁻}
0.259 mM (8.5 mg/L)	0.007 mM	1%
0.016 mM (8.5 mg/L)	0.007 mM	13.1%

Text S8. Normalized rate constant with respect to the irradiation intensity of different light sources.

The normalized rate constants were calculated as followed:

$$k_n = k_{obs}/I$$

Where k_n is normalized rate constant, k_{obs} is observed rate constant and I is effective intensity (< 470 nm) of different light sources.

Text S9. Chlorine decay in the VgC-AOP using different light sources.

The chlorine decay in the VgC-AOP can be attributed to direct photolysis and photocatalytic activation. Figure S8(a) shows the chlorine decay rate constant in Vis/g-C₃N₄/chlorine process using different light sources and Figure S8(b) shows the direct photolysis of chlorine using different light sources, so the chlorine decay resulted from the photocatalytic activation can be expressed as followed:

$$k_{\text{activation}} = k_{\text{overall}} - k_{\text{photolysis}}$$

Therefore, the chlorine photocatalytic activation rate ($k_{\text{activation}}$) with respect to different irradiations can be calculated. The sequence of the activation rates of different light sources follows $k_{\text{activation},45\text{W } 450\text{ nm visible LED}} < k_{\text{activation},5\text{W } 450\text{ nm LED}} < k_{\text{activation},5\text{W } 420\text{ nm LED}}$.

Text S10. Effect of NOM on CBZ degradation.**(1) Chlorine consumption in the presence of NOM for 30 minutes:**

Initial chlorine (mg/L as Cl ₂)	2.0	2.0	2.0	2.0
NOM concentration (mg/L as C)	0	1	2	4
Residual chlorine (mg/L as Cl ₂)	2.0	1.69	1.39	0.98

(2) Light filtering

The light filtering effect of NOM at different concentration is calculated as following:

$$R_f = \frac{I_{a,NOM}}{I_0}$$
$$I_{a,NOM} = \sum I_\lambda * \epsilon_{\lambda,NOM} * C_{NOM}$$

Where R_f is the rate of the light filter by the NOM, $I_{a,NOM}$ is the irradiation absorbed by NOM. I_λ is the irradiation intensity at a particular wavelength range from 370–470 nm. $\epsilon_{\lambda,NOM}$ is the absorption coefficient at a particular wavelength range from 370–470 nm. C_{NOM} is the NOM concentration.

The NOM absorption spectrum is shown as follow:

Figure S1. Experimental set-up for the degradation of CBZ (a) 45 W 450nm visible LED (b) 5 W 450/420 nm LED.

Figure S2. The irradiation spectrum of different light sources.

Figure S3. The chlorine decay by different processes. Conditions: pH=7.0, [CBZ]₀ = 2.0 μ M, [g-C₃N₄] = 1.0 g/L, [Free chlorine]₀ = 5.0 mgCl₂/L, and 45 W 450 nm visible LED

Figure S4. (a) BA and (b) DMOB degradation by the Vis/g-C₃N₄ process in the presence of 2 μM NB. Conditions: (a) 5 W 450 nm LED and (b) 45 W 450 nm visible LED, pH = 7.0, [BA]₀ = 2.0 μM, [DMOB]₀ = 5.0 μM, and [g-C₃N₄] = 1.0 g/L.

Figure S5. EPR spectra of DMPO–•OH adducts in the systems of Vis/chlorine/DMPO, Vis/g-C₃N₄/DMPO, and VgC-AOP/DMPO. Conditions: [DMPO]₀ = 0.42 M, [g-C₃N₄] = 2.0 g/L, [Free chlorine]₀ = 5.0 mgCl₂/L, and 90 W 450 nm visible LED.

Figure S6. NB and DMOB simultaneously degradation by the VgC-AOP. Conditions: pH = 7.0, [NB]₀ = 2.0 μ M, [DMOB]₀ = 5.0 μ M, [g-C₃N₄] = 1.0 g/L, [Free chlorine]₀ = 2.0 mgCl₂/L, and 45 W 450 nm visible LED. Pseudo first-order rate constants (k') calculated based upon regression analysis.

Figure S7. Effect of different light sources on CBZ degradation by the VgC-AOP. Conditions: pH=7.0, [CBZ]₀ = 2.0 μ M, [g-C₃N₄] = 1.0 g/L, and [Free chlorine]₀ = 2.0 mgCl₂/L. Pseudo first-order rate constants (k') calculated based upon regression analysis.

Figure S8. Chlorine decay in the (a) VgC-AOP and (b) Vis/chlorine process using different light sources. Conditions: pH=7.0, $[\text{CBZ}]_0 = 2.0 \text{ } \mu\text{M}$, $[\text{g-C}_3\text{N}_4] = 1.0 \text{ g/L}$, and $[\text{Free chlorine}]_0 = 2.0 \text{ mgCl}_2/\text{L}$. Pseudo first-order rate constants (k') calculated based upon regression analysis.

Figure S9. SEM images of (a) virgin $\text{g-C}_3\text{N}_4$ and (b) used $\text{g-C}_3\text{N}_4$, (c) UV-DRS spectra of $\text{g-C}_3\text{N}_4$, and (d) High-resolution Cl 2p of the used $\text{g-C}_3\text{N}_4$.

Table S1. Reactions between photoinduced species and oxidants.

<i>Reaction</i>	Rate constant	No.
$O_3 + e_{aq}^- \rightarrow O_3^{\bullet-}$	$k = 3.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	Eq. S1
$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2$	$k = 1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Eq. S2
$O_3^{\bullet-} + H^+ \rightarrow HO_3^{\bullet-} \rightarrow HO\bullet + O_2$	$k = 2.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	Eq. S3
$H_2O_2 + e_{aq}^- \rightarrow HO\bullet + OH^-$	$k = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	Eq. S4
$H_2O_2 + O_2^{\bullet-} \rightarrow HO\bullet + OH^- + O_2$	$k = 0.13 \text{ M}^{-1} \text{ s}^{-1}$	Eq. S5
$HSO_5^- + e_{aq}^- \rightarrow SO_4^{\bullet-} + OH^-$	$k = 8.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Eq. S6
$HSO_5^- + h_{\nu b}^+ \rightarrow SO_5^{\bullet-} + H^+$		Eq. S7
$S_2O_8^{2-} + e_{aq}^- \rightarrow SO_4^{\bullet-} + SO_4^{2-}$	$k = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	Eq. S8
$S_2O_8^{2-} + h_{\nu b}^+ \rightarrow S_2O_8^{\bullet-}$		Eq. S9

Table S2. Elemental composition of g-C₃N₄ before and after the VgC-AOP.

Sample	C	N	O	Cl
Before (Mass Conc.)	37.29%	61.99%	0.71%	0.00%
After (Mass Conc.)	37.34%	59.15%	2.42%	0.07%

Table S3. Scavenging effect of NOM on CBZ degradation.

NOM Conc. (mg/L)	0	1	2	4
k_{obs}	0.0438	0.0363	0.0322	0.0229
Total decay	—	17.12%	26.26%	47.72%
Inner filter effect	—	0.16%	0.31%	0.62%
Chlorine consumption	—	3.52%	6.93%	11.77%
Radical scavenging and active sites competition	—	13.44%	19.01%	35.33%