Preparation of oxygen-doped graphitic carbon nitride and its visible-light photocatalytic performance on bisphenol A degradation

Rong Tang, Renli Ding and Xianchuan Xie

ABSTRACT

A novel metal-free oxygen-doped graphitic carbon nitride (O-g-C3N4) was synthesized by the pre-treatment of bulk graphitic carbon nitride (g-C3N4) with hydrogen peroxide (H2O2), and combined with high-temperature calcination treatment. The obtained 2-O-g-C3N4 catalyst exhibits high activity in visible light photocatalytic degradation of bisphenol A (BPA) with a mineralization rate as high as 62.3%. According to the characterization results of X-ray diffraction, transmission electron microscopy, UV-visible spectroscopy, Brunauer–Emmett–Teller and photoluminescence spectroscopy analyses, the markedly higher visible-light-driven oxidation activity of 2-O-g-C3N4 is attributed to the larger specific surface area, wider range of light responses and low charge recombination rate. Moreover, the trapping experiment shows that superoxide radicals (·O2−) are the dominant active species in the BPA decomposition process over 2-O-g-C3N4. This study presents a simple and environment-friendly method to synthesise oxygen-doped graphitic carbon nitride.

Key words | bisphenol A, graphite carbon nitride, oxygen doping, semiconductor, superoxide radicals, visible-light photocatalysis

INTRODUCTION

Semiconductor photocatalyst technology can be used for the decomposition of pollutants in the environment, which is an effective way to solve problems of environmental pollution (Asahi et al. 2001). Environmental pollution caused by emerging pollutants (endocrine disruptors, pharmaceuticals, pesticides, etc.) has become a major threat to human health and aquatic life. Especially, bisphenol A (BPA), as a typical endocrine disruptor, is widely used in the production of polycarbonate plastics, epoxy resins, strong adhesives, rubber antioxidants, flame retardants, fungicides and antioxidants. Exposure to BPA can potentially lead to the disruption of normal endocrine function and inhibition of the nerve conduction system (Mizuta et al. 2017). Previous reports showed that both BPA and its halogen can be degraded by photocatalysis treatment (Eriksson et al. 2004).

In the process of photocatalytic reaction, semiconductor photocatalysts will produce excited high-energy states of electron and hole pairs. The holes are responsible for the degradation of organic compounds and can react with water or hydroxyl ions to produce hydroxyl radicals. The hydroxyl radicals are nonselective powerful oxidant species capable of converting organic pollutants into relatively innocuous end products such as CO2 and H2O (Gutierrez-Mata et al. 2017). At the same time, electrons react with oxygen to form superoxide radicals, and superoxide radicals also have strong oxidation capacity (Wang et al. 2013). However, traditional semiconductor photocatalysts, such as TiO2, have some shortcomings of narrow spectral response range, low solar energy utilization and low electron hole mobility (Zhang et al. 2013a, 2013b, 2013c; Mao et al. 2013). In order to solve the above problems, exploring high performance, low cost, stable visible light catalysts is of great importance.

Graphitic carbon nitride (g-C3N4), a metal-free photocatalyst with a narrow band gap of 2.7 eV, has the advantages of rich raw material, low cost, simple synthesis and visible light response (Jiang et al. 2014). It shows great potential for photocatalytic hydrogen evolution, contaminant elimination and CO2 reduction (Wang et al. 2009a, 2009b, 2009c; Mao et al. 2013). However, it also suffers from low carrier separation efficiency and small specific surface area, which limits its application in the environment (Wang et al. 2013, 2014).
Recently, a variety of strategies have been proposed to modify the g-C₃N₄, including loading with noble metals or doping by non-metals, integrating with other semiconductors, and varying the g-C₃N₄ morphology. Among them, non-metal (Wu et al. 2008; Liu et al. 2010; Yan et al. 2012; Ma et al. 2015; Zhou et al. 2015; Wang et al. 2017) doping is an efficient method to promote the photocatalytic activity. Recently, (Liu et al. 2017) reported the development of chlorine (Cl) intercalated g-C₃N₄ which exhibited outstanding photocatalytic performance for water splitting, CO₂ reduction, and liquid air contaminants removal. Li et al. (2012) synthesized oxygen-doped g-C₃N₄ by a hydrothermal method using H₂O₂, which showed high photocatalytic activity under visible light irradiation. Subsequently, Huang et al. (2015) reported a porous oxygen-doped g-C₃N₄ catalyst synthesized by condensation of melamine and H₂O₂, which exhibited higher H₂ evolution activity than bulk g-C₃N₄. Although O-doped g-C₃N₄ has been studied for a long time, it is still a challenge to realize the controllable O doping and enhance the photocatalytic performance of the photocatalyst.

In this paper, O-doped g-C₃N₄ (O-g-C₃N₄) was synthesized by the pre-treatment of bulk g-C₃N₄ with H₂O₂, and combined with high-temperature calcination treatment. The synthesized O-g-C₃N₄ not only possesses high surface area and low charge recombination rate but also extends the sufficient light absorption range, which significantly enhances the degradation efficiency of BPA under visible light irradiation. The result shows that O doping can induce intrinsic electronic and band structure modulation of the g-C₃N₄. In addition, trapping experiments were conducted to explore the mechanism of BPA degradation.

**MATERIALS AND METHODS**

**Preparation of oxygen-doped graphitic carbon nitride**

The preparation process of oxygen-doped graphitic carbon nitride is shown in Figure 1. Briefly, 20 g of melamine was placed in a porcelain crucible with a cover and calcined at 550 °C for 4 h with a heating rate of 2 °C/min to obtain graphitic carbon nitride (g-C₃N₄) (Wang et al. 2012; Zhang et al. 2012). Subsequently, 2 g g-C₃N₄ was placed in a 250 mL beaker, then a certain amount of hydrogen peroxide was added and the mixture was stirred for 20 min at 60 °C. After that, the resulting powders were washed with deionized water until pH was 7.0 and then collected to be dried at 60 °C. The resultant products were marked as 1-H₂O₂·g-C₃N₄ (the amount of hydrogen peroxide was 60 mL) and 2-H₂O₂·g-C₃N₄ (the amount of hydrogen peroxide was 120 mL), respectively. The above 1-H₂O₂·g-C₃N₄ and 2-H₂O₂·g-C₃N₄ powers were calcined at 550 °C for 2 h with a heating rate of 2 °C/min and denoted as 1-O·g-C₃N₄ and 2-O·g-C₃N₄, respectively.

Also, 2 g g-C₃N₄ was heated at 550 °C for 2 h with a heating rate of 2 °C/min in nitrogen and labeled as N₂·g-C₃N₄ (Huang et al. 2015). Apart from that, 2 g g-C₃N₄ and 120 mL H₂O₂ were added into the beaker of 250 mL, and stirred for 20 min at 60 °C. Then the product was transferred to a Teflon-lined stainless steel autoclave, and then heated at 150 °C for 5 h. The obtained products were labeled as SR·g-C₃N₄.

**Characterization of the photocatalysts**

Transmission electron microscopy (TEM) was used to observe the surface morphology and structure characteristic of the catalytic material using the JEOL JEM 2100 with the acceleration voltage of 200 kV. BET (Brunauer–Emmett–Teller) specific surface area analysis was carried out by an ASME2020 BET specific surface area analyzer (Micromeritics company). X-ray diffraction analysis (XRD) was measured by Beijing Puxi General Company’s XD-3 X-ray diffractometer with a scanning range of 10°–50°. Fourier transform infrared (FT-IR) spectra were measured by Nicolet Company’s NEXUS770 infrared spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Company’s ESCALAB 250 X-ray photoelectron spectrometer, using the RBD upgradeable PHI-5000C ESCA system (Perkin Elmer). The monochromator is a Mg Kα excitation light source (hν = 1,253.6 eV). The photoluminescence (PL) spectrum was measured on a Jobin Yvon SPEX Fluorolog-3-P spectroscope. Ultraviolet diffuse reflectance spectroscopy (UV-vis DRS) was measured on a Beijing Rayleigh Company’s UV1201 spectrometer with a wavelength range of 200–800 nm. Electron paramagnetic resonance (EPR) spectra were obtained on a JEOL JES-FA200 spectrometer. The Schottky curve was obtained on CHI 660E electrochemical workstation equipped with a standard three-electrode system (a platinum foil electrode as the counter electrode and an Ag/AgCl electrode as the reference electrode).

**Evaluation of photocatalytic activity**

The photocatalytic activities of the samples were evaluated by the degradation of BPA under visible light irradiation. In a typical process, 0.02 g catalyst was added into 50 mL...
BPA solution (10 mg/L) in a quartz tube reactor at room temperature. The mixture was stirred in the dark for 30 min to reach adsorption–desorption equilibrium before a 500 W Xe lamp was turned on. At given time intervals (30 min) of irradiation, 1.5 mL of suspension was withdrawn and then filtered. The concentration of BPA was determined by a high performance liquid chromatograph (e2685, Waters) equipped with a UV-vis detector (2489, Waters). The mobile phase was 85% methanol and 15% water. The detect wavelength was 230 nm and the column temperature was 30 °C.

RESULTS AND DISCUSSION

Characterization of the photocatalyst

The morphology of bulk g-C3N4 and 2-O-g-C3N4 was investigated via TEM. As shown in Figure 2(a) and 2(b), bulk g-C3N4 presents a thick and interlayer-like structure, while the morphology of 2-O-g-C3N4 is obviously changed, whereby it is thinned and fragmentized. The difference may be ascribed to the treatment process of 2-O-g-C3N4, during which the gas would generate to destroy the layered structure of the photocatalyst. To further understand the thickness of g-C3N4 and 2-O-g-C3N4, Atomic force microscopy (AFM) measurement was carried out. The thickness of g-C3N4 and 2-O-g-C3N4 is 19.0 nm and 7.2 nm (Figure 2(c) and 2(d)), respectively. Obviously, the thickness of 2-O-g-C3N4 is smaller than that of g-C3N4. The result is consistent with the results of TEM.

The specific surface area of the photocatalyst is shown in Table 1. The specific surface area of g-C3N4 is 5.71 m²/g, while that of 2-H2O2-g-C3N4, 1-O-g-C3N4, and 2-O-g-C3N4 is 10.12, 11.80 and 42.72 m²/g, respectively. Obviously, the specific surface area of 2-H2O2-g-C3N4 is higher than that of g-C3N4, which is due to the porous structure of 2-H2O2-g-C3N4. The specific surface area of 2-O-g-C3N4 further increases, which is ascribed to the fact that 2-O-g-C3N4 was exfoliated and fragmented due to the formation of gas generated during high-temperature treatment. The specific surface area of 1-O-g-C3N4 is lower than that of 2-O-g-C3N4, which is probably because the amount of oxygen-functionalized groups in 1-H2O2-g-C3N4 is lower and the gas generated during high-temperature treatment is less. It is reasonable to speculate that the increase of specific surface area can increase the photocatalytic reactive sites, which is conducive to the adsorption of pollutants, thereby enhancing the photocatalytic performance (Wang et al. 2017).

The change of morphology through oxygen doping can also be confirmed by the results of XRD. As shown in Figure 3(a), the XRD pattern of the pristine g-C3N4 shows two main reflections at 2θ = 13.1° and 27.2° which refer to the (100) and (002) planes of hexagonal graphitic carbon nitride (Jayaramana et al. 2013). The strong peak at 27.2° indexed as (002) is attributed to the lamellar packing of graphite in the π-conjugate plane (Wang et al. 2009a, 2009b, 2009c). For 1-O-g-C3N4 and 2-O-g-C3N4, there is a slight shift of (002) to higher angles, suggesting the decrease of interlayer distance in O-g-C3N4 (Ho et al. 2015). At the same time, it can be seen that the intensity of the diffraction peaks of 1-O-g-C3N4 and 2-O-g-C3N4 is weakened due to the stripping of the bulk g-C3N4 during the modification process. While there is no obvious change in the full widths at half maxima of the (002) peaks between bulk g-C3N4 and O-g-C3N4 (Lucy et al. 2013). The weak characteristic peak at 13.1° is indexed as (100) (Chang et al. 2013). The decrease of the (100) peak of O-g-C3N4 is due to the destruction of heptazine (Niu et al. 2012) which leads to the reduction of heptazine.

Figure 3(b) shows the FT-IR spectra of bulk g-C3N4 and modified g-C3N4. For bulk g-C3N4, the broad peak between 3,137 cm⁻¹ and 3,436 cm⁻¹ corresponds to the N-H stretching vibration. The two absorption bands located at 1,588 cm⁻¹ and 1,721 cm⁻¹ belong to the C=N stretching vibration. The peaks at 1,274, 1,346 and 1,504 cm⁻¹ are...
ascribed to C-N stretching vibration in the aromatic ring, and the sharp band at 819 cm$^{-1}$ corresponds to the stretching vibration of triazine ring structure (Fu et al. 2014). Obviously, 2-O-g-C$_3$N$_4$ shows a new peak at 1,121 cm$^{-1}$, which is ascribed to the C-O stretching vibration (Devendran et al. 2014). This indicates that oxygen may exist in the form of C-O in 2-O-g-C$_3$N$_4$. Moreover, there is no significant change in the spectra of 1-H$_2$O$_2$-g-C$_3$N$_4$, 2-H$_2$O$_2$-g-C$_3$N$_4$, SR-g-C$_3$N$_4$ and N$_2$-g-C$_3$N$_4$. The results indicate that the combination of H$_2$O$_2$ treatment and high-temperature calcination treatment plays a crucial role in the doping of oxygen.

The XPS spectra were obtained to investigate the elemental valence state and composition in bulk g-C$_3$N$_4$ and O-doped g-C$_3$N$_4$. As shown in Figure 4, the C 1s spectrum of bulk g-C$_3$N$_4$ (Figure 4(a)) shows three peaks at 283.7, 286.9 and 292.2 eV, corresponding to π excitation, C-NH$_2$ and graphite-phase C characteristic peaks (Guo et al. 2014).
In addition, a new weak peak appears at 285.4 eV for 2-H2O2-g-C3N4, 1-O-g-C3N4 and 2-O-g-C3N4, which may be due to the formation of C-O during the O-doping process. Meanwhile, as the amount of added H2O2 increases, the intensity of the peak (285.4 eV) in O-g-C3N4 further increases, indicating more oxygen-functional groups are loaded when more H2O2 is used. The N 1 s spectra of bulk g-C3N4 and modified g-C3N4 (Figure 4(b)) are divided into four peaks at 397.5, 399.4, 400.1 and 403.2 eV, which correspond to sp² hybridization of nitrogen (C-N-C), sp³ hybrid nitrogen (C3-N), amino functional group (C2-N-H) and π excitation, respectively. Compared with bulk g-C3N4, the proportion of N (sp²)/N (sp³) in 2-H2O2-g-C3N4, 1-O-g-C3N4 and 2-O-g-C3N4 decreased in sequence, which may be because N (sp²) was replaced by oxygen atoms in the process, indicating that the calcination treatment is conducive to the incorporation of O atoms. In addition, the O 1 s spectrum (Figure 4(c)) of bulk g-C3N4 shows a characteristic peak at 531.6 eV due to the adsorption of water, and no appearance of C-O or N-O signal peaks is observed in the spectrum. The 2-H2O2-g-C3N4 shows a peak at 532.3 eV which probably is due to the formation of C-O-C. Apart from the peak at 532.3 eV, 1-O-g-C3N4 and 2-O-g-C3N4 present a new peak at 530.1 eV, which has come from the C-OH bands (Lu et al. 2012). In order to reduce noise-to-signal ratio, the XPS spectra of 2-O-g-C3N4 were measured again and there was no obvious change in the O 1 s spectra peak of 2-O-g-C3N4 because of the low content of oxygen (Figure S1, supporting information, available with the online version of this paper). This is in agreement with the results of FT-IR.

Figure 5(a) shows a PL plot of bulk g-C3N4 and modified g-C3N4. The emission peak attributed to the radiative recombination of photo-generated electron–hole pairs is used to evaluate the transfer and separation efficiency of photo-generated charge carriers. The spectral intensity of 2-H2O2-g-C3N4 is slightly reduced compared to that of bulk g-C3N4. This is because the introduction of the O atom effectively suppresses the recombination of photo-generated electrons and holes, which is consistent with the results reported by Li et al. (2012). The lower emission peak of 1-O-g-C3N4 and 2-O-g-C3N4 as compared to 2-H2O2-g-C3N4 suggests the recombination of charge carriers is further suppressed. The result shows that high-temperature treatment could promote O doping and further improve the electron–hole separation.

The photophysical properties of g-C3N4 and modified g-C3N4 were explored by UV-vis DRS and PL spectroscopy. Figure 5(b) shows the UV-vis DRS spectra of bulk g-C3N4 and modified g-C3N4. In order to display the UV-vis spectrum more clearly, Figure 2 has been separated into independent figures in the supporting information (Figure S2, available online). As seen from the figure, the absorption edge of bulk g-C3N4 is 460 nm, and the band gap is 2.78 eV. The absorption edge of 1-H2O2-g-C3N4 and 2-H2O2-g-C3N4 are similar to that of bulk g-C3N4, while the absorption edge of 1-O-g-C3N4 and 2-O-g-C3N4 shows a remarkable red-shift with intermediate band. The band gaps of 1-O-g-C3N4 and 2-O-g-C3N4 calculated by Kubelka–Munk method are 2.46 eV and 2.38 eV, respectively. In addition, no significant change can be seen in the SR-g-C3N4 as compared with g-C3N4, and the band gap of SR-g-C3N4 is about 2.72 eV. However, the absorption edge of N2-g-C3N4 shows a slight blue-shift, which may be due to the quantum confinement effect caused by a thinner layered structure (Tsunekawwas et al. 2000). It can be concluded that single high-temperature calcination treatment or H2O2 treatment shows little effect on the light harvesting ability of g-C3N4. However, the absorption edge broadens obviously after the combination of H2O2 treatment and high-temperature calcination treatment,
which is because the combined treatment can further promote the O doping and enhance the light absorption edge.

EPR analysis was carried out to determine the reactive species in the photocatalytic system. Figure 6(a) shows the EPR signals of DMPO–\(\cdot\)O\(_2\)/C\(_0\) in the presence of the g-C\(_3\)N\(_4\) and 2-O-g-C\(_3\)N\(_4\) after irradiation. The DMPO–\(\cdot\)O\(_2\)/C\(_0\) signal of 2-O-g-C\(_3\)N\(_4\) is stronger than that of g-C\(_3\)N\(_4\). The results clearly demonstrate the enhanced activity of the 2-O-g-C\(_3\)N\(_4\) to produce \(\cdot\)O\(_2\) radicals compared to g-C\(_3\)N\(_4\). While for the DMPO•OH signal (Figure 6(b)), there is no obvious difference between g-C\(_3\)N\(_4\) and 2-O-g-C\(_3\)N\(_4\) after irradiation. The results are consistent with the trapping experiment analysis.

Mott-Schottky analysis was carried out to investigate the band structures of the bulk g-C\(_3\)N\(_4\) and 2-O-g-C\(_3\)N\(_4\). The Mott-Schottky equation describes the relationship between the differential capacitance of space charge layer (C) of the semiconductor and the potential of the semiconductor (E). According to the equation, the drawing of E should be a straight line, that is, a Mott–Schottky plot. The intercept of the linear extension line on the x-axis can get the flat
band potential. The positive slopes of the Mott-Schottky plots indicate the n-type semiconducting feature of both g-C\textsubscript{3}N\textsubscript{4} and 2-O-g-C\textsubscript{3}N\textsubscript{4}, as shown in Figure 7(a) and 7(b). Furthermore, the flat-band potential for n-type semiconductors can be approximately regarded as the conduction band (Xu et al. 2015a, 2015b; Luo et al. 2016). As can be seen, the flat-band potential of g-C\textsubscript{3}N\textsubscript{4} and 2-O-g-C\textsubscript{3}N\textsubscript{4} were −0.79 and −0.49 eV, respectively (vs NHE.

**Figure 5** | (a) PL spectra and (b) UV-vis spectra of bulk g-C\textsubscript{3}N\textsubscript{4} and modified g-C\textsubscript{3}N\textsubscript{4}.

**Figure 6** | EPR spectra of (a) DMPO-O\textsubscript{2} and (b) DMPO-OH for bulk g-C\textsubscript{3}N\textsubscript{4} and 2-O-g-C\textsubscript{3}N\textsubscript{4}.

**Figure 7** | Mott-Schottky plots for (a) bulk g-C\textsubscript{3}N\textsubscript{4} and (b) 2-O-g-C\textsubscript{3}N\textsubscript{4}.
(normal hydrogen electrode)) according to the intercepts with the x-axis. The difference in the conduction band between g-C$_3$N$_4$ and 2-O-g-C$_3$N$_4$ shows that O doping changed the band structure of g-C$_3$N$_4$.

**Evaluation of photocatalytic activity**

Photodegradation of BPA under visible light irradiation was used to evaluate the photocatalytic performance of bulk g-C$_3$N$_4$ and O-doped g-C$_3$N$_4$ (0.4 g/L), and the results are shown in Figure 8(a). The degradation efficiency of BPA is 12, 9.0 and 8.3% for bulk g-C$_3$N$_4$, 2-H$_2$O$_2$-g-C$_3$N$_4$ and SR-g-C$_3$N$_4$, respectively, indicating that single H$_2$O$_2$ treatment or hydrothermal treatment cannot improve the performance of the photocatalyst in photocatalytic degradation of BPA. According to the results of characterization, 2-H$_2$O$_2$-g-C$_3$N$_4$ and SR-g-C$_3$N$_4$ have similar absorption edges to that of bulk g-C$_3$N$_4$ and the recombination of photo-generated electrons and holes has no significant change. Thus, these three photocatalysts possessed similar activity.

As for N$_2$-g-C$_3$N$_4$, the photocatalytic degradation efficiency increases to 22.6% due to the increase of specific surface area of N$_2$-g-C$_3$N$_4$ after calcination treatment under nitrogen, and the enlarged surface area provides more active sites for photocatalysis and facilitates the electron transport (Zhang et al. 2015). The photocatalytic degradation efficiency of BPA by 1-O-g-C$_3$N$_4$ and 2-O-g-C$_3$N$_4$ is 42.0% and 63.0%, respectively, which is attributed to the larger specific surface area, wider range of light responses and low charge recombination rate. The difference in the photocatalytic degradation efficiency between 1-O-g-C$_3$N$_4$ and 2-O-g-C$_3$N$_4$ is mainly due to the different amount of oxygen doping. As compared to the reported Ag-decorated S-doped g-C$_3$N$_4$ photocatalyst (Oh et al. 2018), 2-O-g-C$_3$N$_4$ possessed similar activity without noble metal. The assistance of UV and/or H$_2$O$_2$ was needed for more efficient degradation and mineralization of BPA (Bechambia et al. 2015; Moussavi et al. 2018).

Dynamic fitting of the results of BPA degradation over g-C$_3$N$_4$ and modified g-C$_3$N$_4$ was carried out, and the

---

**Figure 8** | (a) Photocatalytic degradation curve, (b) dynamic fitting curve and (c) adsorption curve of bulk g-C$_3$N$_4$ and modified g-C$_3$N$_4$. 
reaction process accorded with the pseudo first order kinetic model:

\[ r = -\frac{dC_t}{dt} = kC_t \]  
\[ \ln \left( \frac{C_0}{C_t} \right) = kt \]

Here \( r \) is the reaction rate, \( C_t \) is the concentration of BPA in the reaction time \( t \), \( C_0 \) is the initial concentration of BPA in the solution and \( k \) is the reaction rate constant.

The fitting results of pseudo first order dynamics are shown in Figure 8(b). The figure shows a linear relationship between g-C3N4/modified g-C3N4 and ln(\( C_0/C_t \)). The \( k \) value for g-C3N4 and 2-O-g-C3N4 are 0.000687 min\(^{-1}\) and 0.00578 min\(^{-1}\), respectively. This further indicates that the photocatalytic activity of 2-O-g-C3N4 has been greatly improved compared with that of g-C3N4. Moreover, the BPA degradation efficiency can be promoted as the amount of 2-O-g-C3N4 photocatalyst increases (Figure S3, supporting information, available online).

Photocatalytic reaction mechanism

The mechanism of photocatalysis was investigated by species trapping experiments to determine the main active species generated during the photocatalytic process. Scavengers of tert-butanol, potassium iodide and \( p \)-benzoquinone were separately added to trap \(-\text{OH}\), \( h^+ \) and \(-\text{O}_2^-\), respectively (Van Doorslaer et al. 2012; Jaafarzadeh et al. 2017; Ahmadi & Ghanbari 2018). As shown in Figure 9, benzoquinone significantly inhibits the photocatalytic degradation, indicating that \(-\text{O}_2^-\) is the dominant species during the photocatalytic process. In addition, the photocatalytic degradation process of BPA by 2-O-g-C3N4 was analyzed, and the main process are listed as follows.

\[ \text{O}_2 + e^- \rightarrow -\text{O}_2^- \]  
\[ 2\text{O}_2^- + 4\text{H}_2\text{O} \rightarrow 3\text{H}_2\text{O}_2 + 2\text{OH}^- \]  
\[ \text{H}_2\text{O}_2 + e^- \rightarrow -\text{OH} + \text{OH}^- \]  
\[ -\text{O}_2^- + \text{BPA} \rightarrow \text{BPA degradation intermediates} \quad \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{organic acids} \]  
\[ -\text{OH} + \text{BPA} \rightarrow \text{BPA degradation intermediates} \quad \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{organic acids} \]  
\[ h^+ + \text{BPA} \rightarrow \text{BPA degradation intermediates} \quad \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{organic acids} \]

According to the previous literature, the main BPA degradation pathway may be hydroxylation reaction in the photocatalytic system (Oh et al. 2018). In the process of photocatalytic degradation of BPA, BPA may be first oxidized to 4-[2-(3,4-dihydroxyphenyl)propan-2-yl]-quinone, 3,4-dihydroxybenzoic acid or dicarboxylic acid. Finally, these BPA intermediates can be further mineralized to harmless organic acids, CO\(_2\) and H\(_2\)O.

CONCLUSIONS

Herein, oxygen-doped g-C\(_3\)N\(_4\) (O-g-C\(_3\)N\(_4\)) was obtained by the pre-treatment of bulk g-C\(_3\)N\(_4\) with H\(_2\)O\(_2\), and combined with high-temperature calcination. Compared with the bulk g-C\(_3\)N\(_4\), the structure of O-g-C\(_3\)N\(_4\) has been changed obviously. The O-g-C\(_3\)N\(_4\) has larger specific surface area, wider range of light responses and lower charge recombination rate and shows excellent performance on the photocatalytic degradation of BPA. In addition, it was found that, compared to photocatalyst with a single H\(_2\)O\(_2\) treatment (H\(_2\)O\(_2\)-g-C\(_3\)N\(_4\)) or high-temperature calcination treatment (N\(_2\)-g-C\(_3\)N\(_4\)), O-g-C\(_3\)N\(_4\) photocatalyst combined with H\(_2\)O\(_2\) treatment and calcination shows higher photocatalytic performance in photocatalytic BPA degradation. The species trapping experiments show that the superoxide ion (-\(\text{O}_2^-\)) dominates in the visible light photocatalytic degradation of BPA.
REFERENCES


Ho, W., Zhang, Z., Lin, W., Huang, S., Zhang, X., Wang, X. & Huang, Y. 2015 Copolymerization with 2,4,6-trimaminopyrimidine for the rolling-up the layer structure, tunable electronic properties, and photocatalysis of g-C3N4, *ACS Applied Materials & Interfaces* 7, 5497–5505.


Jaafarzadeh, N., Barzegar, G. & Ghanbari, F. 2017 Photo assisted electro-peroxone to degrade 2,4-D herbicide: the effects of supporting electrolytes and determining mechanism. *Process Safety and Environmental Protection* 111, 520–528.


Ong, W., Tan, L., Ng, Y., Yong, S. & Chai, S. 2016 Graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4})-based photocatalysts for artificial photosynthesis and environmental remediation: are we a step closer to achieving sustainability? Chemical Reviews 116, 7159–7329.


Yan, S., Li, Z. & Zou, Z. 2012 Photodegradation of rhodamine B and methyl orange over boron-doped g-C\textsubscript{3}N\textsubscript{4} under visible light irradiation. Langmuir 26, 3894–3901.


Zhang, Z., Huang, J., Zhang, M., Yuan, Q. & Dong, B. 2015 Ultrathin hexagonal Sn\textsubscript{2}S\textsubscript{3} nanosheets coupled with g-C\textsubscript{3}N\textsubscript{4} nanosheets as 2D/2D heterojunction photocatalysts toward high photocatalytic activity. Applied Catalysis B: Environmental 163, 298–305.


First received 21 March 2018; accepted in revised form 6 August 2018. Available online 20 August 2018.