Persulfate enhanced photocatalytic degradation of bisphenol A by g-C₃N₄ nanosheets under visible light irradiation

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HIGHLIGHTS

- The g-C₃N₄ nanosheets presents better photocatalytic activity than bulk g-C₃N₄.
- Persulfate improved BPA degradation in g-C₃N₄ visible light photocatalysis system.
- Superoxide radicals are the dominant oxidizing species for bisphenol A degradation.

GRAPHICAL ABSTRACT

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ABSTRACT

The enhancement of g-C₃N₄ photocatalytic degradation of bisphenol A (BPA) via persulfate (PS) addition was investigated under visible light irradiation. The effects of various parameters on the BPA degradation were investigated, such as catalysts dosage, PS concentrations, initial pH value and BPA concentration. The results showed that g-C₃N₄ nanosheets exhibited superior photocatalytic activity toward BPA degradation as compared with bulk g-C₃N₄. The addition of PS can further improve the g-C₃N₄ photocatalytic performance for BPA degradation. With 5 mM PS, the degradation rate of BPA was increased from 72.5% to 100% at 90 min, and the corresponding first-order kinetic constants were increased from 0.0028 to 0.0140 min⁻¹. The removal efficiency of BPA increased with the decrease of solution pH value. The active radicals in the reaction system were tested by electron spin resonance (ESR) and radicals quenching experiments. Instead of persulfate radicals' oxidation, it was proposed that the main active radicals for BPA degradation were superoxide radicals and the photogenerated holes.

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1. Introduction

Bisphenol A (BPA) is a kind of alkylphenol compounds, which is one of the most important materials for the production of polycarbonate and epoxy resin in the plastics industry. Due to the rapid development of the industrialization, it has been widely distributed

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in industrial wastewaters, rivers, lakes, groundwater and other natural water bodies (Torres et al., 2016). BPA is an endocrine disrupting compound, which can induce endocrine disorders, hereditary diseases, cancer and infertility.

Due to the strong chemical resistance and stable characteristics of BPA, traditional treatment processes were limited for its removal. In recent years, advanced oxidation processes (AOPs) has received numerous attention for the degradation of refractory organics. There are several studies on the degradation of BPA by AOPs, such as ozonation (Garoma and Matsumoto, 2010), ultrasound irradiation (Torres et al., 2008), Fenton (Poerschmann et al., 2010), photo-Fenton (Zhan et al., 2006), electro-Fenton (Akbari et al., 2016), photoelectrocatalysis (Watanabe et al., 2003; Yan et al., 2015).

Over the past decades, heterogeneous photocatalysis has attracted a tremendous attention for the treatment of organic contaminants in aqueous system. Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$), a metal-free polymer semiconductor, has been regarded as a promising photocatalytic material due to its visible light response, robust stability and environmentally benign characteristics. Application of $g\text{-C}_3\text{N}_4$ in the photocatalytic degradation of organic compounds, such as phenol, Rhodamine B (RhB) dye, has been reported (Chen and Zhang, 2014; Liang and Zhu, 2016; Xu et al., 2014; Zhang et al., 2015a,b). The results indicated that $g\text{-C}_3\text{N}_4$ was limited for the efficient degradation of organic contaminants. Many studies have been devoted to improve the photocatalytic oxidation activity by modified $g\text{-C}_3\text{N}_4$ using copolymerization, metal and anion doping and applying bias voltage etc. (Han et al., 2014; Hu et al., 2014; Qi et al., 2016; Yan et al., 2014; Zhong et al., 2015).

Recently, persulfate (PS), a kind of oxidant agent, was used for *in situ* chemical oxidation in the remediation of organic pollutants in aqueous systems (Ahmad et al., 2013; Hazimea et al., 2013). A large number of studies showed that PS can be active by UV, heat, alkaline, transition metals to produce sulfate radicals ($\text{SO}_4^{\bullet-}$) and hydroxyl radicals ($\cdot\text{OH}$) (Chen and Huang, 2015; Hazimea et al., 2013; Waldemer et al., 2007; Zeng et al., 2016; Hu et al., 2016), which have high redox potential and can destroy most of organic compounds efficiently. Hu and tian investigated the $g\text{-C}_3\text{N}_4/\text{Fe(III)}/\text{PS}$ system which found that the phenol degradation efficiency can be significantly improved by combining photocatalysis and light Fenton interaction (Hu et al., 2016).

Recently, metal-free catalysts for PS and peroxymonosulfate (PMS) activating have become more and more popular because of their good chemical stability, inexpensive and none secondary pollution. Duan and Ao investigated the diverse nanocarbons in structure and dimensions to activate PMS and found that radical and nonradical oxidation could occur by different carbon catalysts depending on the carbon structure (Duan et al., 2016). Lee and jeong found that carbon nanotubes can activate PS into nonradical species in the present of phenol (Lee et al., 2015). Tao and Ni investigated the degradation of organic dyes by using $g\text{-C}_3\text{N}_4$ to activate PMS under visible light irradiation; it was exhibited that the $g\text{-C}_3\text{N}_4$ can effectively activate PMS to generate $\text{SO}_4^{\bullet-}$ and $\cdot\text{OH}$ (Tao et al., 2015). Previous studies showed that the exfoliated $g\text{-C}_3\text{N}_4$ can significantly improve the photocatalysis performance compared with bulk $g\text{-C}_3\text{N}_4$ (Xu et al., 2014; Lin et al., 2015). However, only few studies investigated the influence of $g\text{-C}_3\text{N}_4$ structure on the activation of PS to degrade refractory organics in water.

Herein, the effect of PS on the photocatalytic degradation of BPA at the bulk $g\text{-C}_3\text{N}_4$ and $g\text{-C}_3\text{N}_4$ nanosheets was investigated under visible light irradiation. The results showed that the as prepared $g\text{-C}_3\text{N}_4$ nanosheets exhibited a much higher photocatalytic activity compared with bulk $g\text{-C}_3\text{N}_4$. And the PS can further promote the $g\text{-C}_3\text{N}_4$ photocatalytic degradation of BPA. It was proposed that superoxide radical ($\text{O}_2^{\bullet-}$) and photogenerated holes were mainly

responsible for the BPA degradation rather than $\text{SO}_4^{\bullet-}$ and $\cdot\text{OH}$.

2. Materials and methods

2.1. Chemicals

Cyanuric acid (>98%, purity) and benzoguanamine (>98%, purity) were purchased from Tokyo Kasei Kogyo Co., Ltd. Bisphenol A ($\geq 99\%$) was purchased from Sigma Aldrich. Methanol (MeOH) was of HPLC grade and purchased from Fisher chemical. Benzoquinone, ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), ethanol were reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium persulfate (98%, purity) was purchased from ACROS organics. All the reagents were used without further purification.

2.2. Synthesis and exfoliation of $g\text{-C}_3\text{N}_4$

The synthesis of $g\text{-C}_3\text{N}_4$ was prepared by thermal condensation method (Xu et al., 2014), in a typical process, benzoguanamine and cyanuric acid (1:1 of molar ratio) was added to 90 mL deionized water and stirred for 6 h to equilibrate the suspension, after centrifugation the sediment was vacuum drying at 60 °C for 12 h, and then the as prepared precursor was heating in tube furnace in a nitrogen atmosphere. The heating program was as follows: heating for 500 °C at the rate of 5 °C/min and hold for 2 h.

The exfoliation method of $g\text{-C}_3\text{N}_4$ was according to that reported by Lin et al. (2015) and the specific process was as follows: the as prepared $g\text{-C}_3\text{N}_4$ (1 g) was mixed with 40 mL ethanol and 90 mL water in a 250 mL beaker and the mixture suspension was ultrasoundly treated for 10 h at room temperature. The resulting suspension was centrifuged for 10 min at 3000 rpm to remove any unexfoliated $g\text{-C}_3\text{N}_4$, and then the suspension was centrifuged for 5 min at 10 000 rpm to collect the exfoliated $g\text{-C}_3\text{N}_4$ nanosheets.

2.3. Experimental procedure

The photocatalysis experiments were conducted in the quartz reactor with magnetic stirring under visible light irradiation by using a 150 W Xenon lamp (Zolix instruments Co. China) as light source with a 400 nm cutoff filter. In a typical experiment, 50 mg of $g\text{-C}_3\text{N}_4$ and 5 mM persulfate were dispersed into 100 mL BPA aqueous solution (5 mg/L). Before the light irradiation, the suspension was stirred for 5 min. Then the light was turned on and a 0.8 mL aliquot was sampled at certain time and added to the centrifuge tube which contained the same volume of methanol then was filtered with a 0.22 μm organic phase filter. H_2SO_4 (0.1 M) and NaOH (0.1 M) were used to adjusted initial pH of the solution.

2.4. Analytical techniques

The change of BPA concentration was detected by HPLC (Shimadzu, DGU-20A3R(C), Japan) with a C18 column and a UV detector. The mobile phase was methanol: water (60:40), and flow rate was 1 mL/min, a C18 separation column was used as the chromatographic column and the temperature was 30 °C, the detection wavelength was set as 230 nm.

The morphologies of bulk $g\text{-C}_3\text{N}_4$ and $g\text{-C}_3\text{N}_4$ nanosheets were examined by scanning electron microscopy (SEM, SU8000, Hitachi Ltd., Japan). X-ray diffraction (XRD) patterns were collected on an X'pert PRO MPD PC system, utilizing Cu K α radiation at a scan rate (2 θ) of 0.5° s⁻¹. The photoluminescence (PL) spectra were surveyed by an Edinburgh FLSP920 spectrophotometer with an excitation wave-length at 400 nm. The Mott-Schottky plots were examined by electrochemical workstation (Shanghai Chen Hua CHI660C,

Chinese). The Zeta potential of g-C₃N₄ examined by nanoparticle size and Zeta potential analyzer (ZS90, Malvern Ltd., UK).

3. Results and discussion

3.1. Catalyst characterization

The morphology and microstructure of the bulk g-C₃N₄ and g-C₃N₄ nanosheets were first characterized by SEM. Fig. 1 illustrates an obvious morphology difference of the bulk g-C₃N₄ and g-C₃N₄ nanosheets. The bulk g-C₃N₄ shows a typical flat layer structures, and the morphology of g-C₃N₄ nanosheets sample are loose and irregular tissue-like nanosheets, which indicates that the exfoliated treatment can significantly change the g-C₃N₄ form and structure (Lin et al., 2015).

The XRD patterns of bulk g-C₃N₄ and g-C₃N₄ nanosheets were shown in Fig. 2a. It can be seen that two characteristic peaks at 13.6° assigned to (100) diffraction and 27.4° originated from (002) diffraction can be observed, which were consistent with previous studies (Zhu et al., 2015; Wang et al., 2009). And those characteristic diffraction peaks are corresponding to 0.681 and 0.326 nm interlayer spacing and the accumulation of conjugated aromatic systems. An intensity decrease in the peak of g-C₃N₄ nanosheets indicates that g-C₃N₄ has been exfoliated into nanostructure. The PL spectra can check the separation and recombination of photo-generated carriers. As shown in Fig. 2b, the PL peaks of g-C₃N₄ and g-C₃N₄ nanosheets both appear at 500 nm, indicating that the π -conjugated system of g-C₃N₄ nanosheets does not change and the peaks intensity of g-C₃N₄ nanosheets is lower than that of bulk g-C₃N₄, suggesting that the recombination of photogenerated carriers can be suppressed by exfoliating g-C₃N₄ into ultrathin nanosheets efficiently (Wang and Wang, 2012). The Mott-Schottky plots were conducted to investigate the electronic structures of the layered g-C₃N₄ and g-C₃N₄ nanosheets. Fig. 2c shows that the flat-band potentials derived from Mott-Schottky plots are changed from about −0.6 to −0.9 V after being exfoliated. These results indicate that the conduction and valence band edges of bulk g-C₃N₄ shifted in opposite directions after the exfoliation treatment, which are

attributed to the quantum effect of a few-layer structure of g-C₃N₄ nanosheets (Zhang et al., 2015a,b).

3.2. Degradation of BPA under different systems

Fig. 3a and b compare the degradation of BPA under different systems by using bulk g-C₃N₄ and g-C₃N₄ nanosheets as catalysts, respectively. Negligible removal of BPA was found in the g-C₃N₄ with the addition of PS system (g-C₃N₄/PS) without light irradiation, and 29.4% BPA was degraded after 90 min in the presence of PS under visible light irradiation (PS/Vis) system, which indicates that the adsorption removal of BPA was slight and the addition of PS promotes the photocatalytic degradation of BPA. It was observed that the marked influence of structure between bulk g-C₃N₄ and exfoliated g-C₃N₄ nanosheets on their photocatalytic performance for BPA degradation under the g-C₃N₄/Vis systems. The removal rate of BPA was 22% for bulk g-C₃N₄ and 72.5% for g-C₃N₄ nanosheets after 90 min, and the first order kinetic constants were 0.0028 and 0.0140 min^{−1}, respectively.

This result indicated that g-C₃N₄ nanosheets exhibited an improved photocatalytic activity toward BPA degradation than that of bulk g-C₃N₄. In comparison, the degradation rates of BPA over both g-C₃N₄ photocatalysts were significantly improved with the addition of PS into the photocatalytic system. The degradation rate of BPA were 77% on bulk g-C₃N₄, and almost complete removal was observed after 90 min by using g-C₃N₄ nanosheets as catalyst. The reaction first-order kinetic constants of BPA over bulk g-C₃N₄ and g-C₃N₄ nanosheets were 0.0150 and 0.0469 min^{−1}, respectively. The performance of g-C₃N₄ nanosheets/PS/Vis system was compared with previous reports and the results were listed in Table 1. It can be seen that g-C₃N₄ nanosheets/PS/Vis system showed excellent performance for the degradation of persistent organic pollutants.

3.3. Effect of g-C₃N₄ dosages

Fig. 4 showed the effect of bulk g-C₃N₄ and g-C₃N₄ nanosheets dosage on the degradation of BPA. The effect of bulk g-C₃N₄ dosage on the BPA degradation is slight. The degradation rate of BPA is

Fig. 1. SEM images of (a–b) g-C₃N₄ nanosheets and (c–d) Bulk g-C₃N₄.

Fig. 2. (a) XRD patterns, (b) Photoluminescence spectra and (c) Mott-Schottky plots of bulk $g\text{-C}_3\text{N}_4$ and $g\text{-C}_3\text{N}_4$ nanosheets.

63%–70% when the dosages were 0.25–0.75 g/L and the reaction rate of BPA remains nearly constant. An enhancement of BPA degradation is observed by increasing the $g\text{-C}_3\text{N}_4$ nanosheets amounts. When the dosage of $g\text{-C}_3\text{N}_4$ nanosheets is 0.25 g/L, the BPA removal efficiency is 82.2% after 90 min. When the dosage is increased to be 0.5 g/L, the BPA is nearly completely removed. Correspondingly, the first-order reaction rate constants of BPA are increased from 0.0187 to 0.0614 min^{-1} . Furthermore, there is only a slight increase of BPA degradation rate when the $g\text{-C}_3\text{N}_4$ nanosheets amounts are increased to be 0.75 g/L.

The bulk $g\text{-C}_3\text{N}_4$ has a large particle size and cannot be evenly

dispersed in the solution. The catalyst dosage increase may improve the competition of the active sites of the catalyst and decrease the transparency of the solution, which may affect the BPA degradation (Tao et al., 2015). By contrast, the $g\text{-C}_3\text{N}_4$ nanosheets possess a large specific surface area and more active sites and can be easily dispersed in the solution, which promotes the degradation of BPA (Lin et al., 2015). But the degradation rate of BPA was slowed down due to the deterioration of the light transmittance at relatively high $g\text{-C}_3\text{N}_4$ concentration. Therefore, in the subsequent experiment, $g\text{-C}_3\text{N}_4$ dosage was set as 0.5 g/L.

3.4. Effect of persulfate concentrations

Fig. 5 illustrates the influence of the PS concentration on the degradation of BPA. With the PS concentration increases from 0.5 to 5.0 mM, the degradation efficiency is increased from 70% to 100% after 90 min, and the apparent first-order kinetic constants are increased from 0.0135 to 0.0469 min^{-1} . At the higher concentration of 8.0 mM, the kinetic constant is increased to be 0.0644 min^{-1} . This may due to the increase of photogenerated electron capture agent, thus decreasing the recombination of photogenerated carriers and leading to the increase of the photocatalytic performance.

3.5. Effect of initial pH

Fig. 6a shows the influence of initial pH value on the degradation of BPA. It can be found that a slight decrease of the BPA removal efficiency at acidic and weak alkaline conditions. At pH 3, nearly complete degradation of BPA is observed at 60 min, and the reaction rate constant is 0.0795 min^{-1} . At pH 9, the degradation of BPA is decreased to 91.7%, and the reaction rate constant is 0.0297 min^{-1} . While a tremendous inhibition on BPA degradation is observed at the initial pH of 10, the removal efficiency is decreased to 41.6%, and the reaction rate of BPA is significantly reduced by almost 93%. Fig. 6b shows the zeta potential of the $g\text{-C}_3\text{N}_4$ and $g\text{-C}_3\text{N}_4/\text{PS}$ systems under different pH values, which implied that the presence of PS can reduce the zeta potential of the $g\text{-C}_3\text{N}_4$ particles through compressing the thickness of the electric double layer (Zhang et al., 2014; Zhang and Croué, 2014). The changes of pH during the reaction were also detected; under acidic conditions, a slight change of pH value was observed. By contrast, at neutral and weak alkaline conditions, the pH values are rapidly decreased, and final pH values are all below 5. However, when initial pH was 10, the decrease of pH value becomes slight.

This phenomenon may be attributed to the electrostatic interactions between catalysts, PS and BPA in aqueous solution. As shown in Fig. 6b, the point of zero charge (PZC) of $g\text{-C}_3\text{N}_4$ was approximately 5, which coincided with the previous studies (Zhu et al., 2015; Yang et al., 2017; Hernández-Urestia et al., 2016; Zhang et al., 2015a,b). The pK_a value of BPA is 9.6–10.2 (Bautista-Toledo et al., 2005). At $\text{pH} < \text{pH}_{(\text{PZC})}$, the $g\text{-C}_3\text{N}_4$ surface is positively charged. The negatively charged $\text{S}_2\text{O}_8^{2-}$ in the solution was favorable to be adsorbed on the $g\text{-C}_3\text{N}_4$ surface. Under visible light irradiation, the photogenerated electrons were rapidly captured by PS, which promoted the separation of photogenerated hole and electron pairs, thus improving the degradation efficiency of BPA. As the pH value decreased, more $\text{S}_2\text{O}_8^{2-}$ ions were adsorbed on the surface of $g\text{-C}_3\text{N}_4$, which facilitated the degradation of BPA. When pH was higher than $\text{pH}_{(\text{PZC})}$, the surface of $g\text{-C}_3\text{N}_4$ was negatively charged, the $\text{S}_2\text{O}_8^{2-}$ adsorbed on the catalyst surface decreased with the pH value increase, thus decreasing the degradation of BPA. While during the reaction the pH values of the solution were gradually decreased to be less than the $\text{pH}_{(\text{PZC})}$, thus promoting the degradation of BPA. At pH 10, the reduction of the solution pH value becomes very slow; the BPA degradation will be dramatically

Fig. 3. BPA degradation with different systems by using (a) bulk $g\text{-C}_3\text{N}_4$ and (b) $g\text{-C}_3\text{N}_4$ nanosheets ($g\text{-C}_3\text{N}_4$ NS) and corresponding kinetic fitted curves (c, d). Conditions: $g\text{-C}_3\text{N}_4$: 0.5 g L^{-1} , PS: 5 mM , BPA: 5 ppm .

Table 1
Degradation of various organics by visible photocatalytic activated PMS/PS.

System	Pollutants	Pollutants conc. mg L^{-1}	Catalyst dosage/ g L^{-1}	PS/PMS conc./ g L^{-1}	Reaction temp./ $^{\circ}\text{C}$	Removal efficiency	Time/min	Ref.
$g\text{-C}_3\text{N}_4/\text{Fe(III)}/\text{PS}$	Phenol	10	1.9	PS 0.3	26	33%	120	(Hu et al., 2016)
$g\text{-C}_3\text{N}_4/\text{PMS}$	AO7	20	0.4	PMS 0.4	25	86%	30	(Tao et al., 2015)
$g\text{-C}_3\text{N}_4\text{-550}/\text{PMS}$	AO7	20	0.4	PMS 0.2	25	96.3%	30	(Jiang et al., 2017)
S-doped $g\text{-C}_3\text{N}_4/\text{PMS}$	BPA	50	0.3	PMS 0.3	40	80%	120	(Lin and Zhang, 2017)
$\text{Fe}_2\text{O}_3/g\text{-C}_3\text{N}_4/\text{PMS}$	AO7	20	0.4	PMS 0.2	20	98.5%	20	(Li et al., 2017)
$\text{Ag}/\text{mpg}\text{-C}_3\text{N}_4/\text{PMS}$	BPA	20	0.1	PMS 0.3	25	98%	60	(Wang et al., 2017)
$g\text{-C}_3\text{N}_4$ nanosheets/PS	BPA	5	0.5	PS 1.2	25	100%	90	This work

Fig. 4. Effect of bulk $g\text{-C}_3\text{N}_4$ (open symbols) and $g\text{-C}_3\text{N}_4$ nanosheets (solid symbols) amounts on the degradation of BPA. Conditions: PS: 5 mM , BPA: 5 ppm .

Fig. 5. Effect of PS concentration on the degradation of BPA. Conditions: catalyst: 0.5 g L^{-1} , BPA: 5 ppm .

Fig. 6. (a) Effect of initial pH on the degradation of BPA. (b) Zeta potential of bulk $g-C_3N_4$ and $g-C_3N_4$ nanosheets. Conditions: $g-C_3N_4$: 0.5 g L^{-1} , BPA: 5 ppm.

inhibited due to the electrostatic repulsion between catalysts and the deprotonated form of BPA (Zhu et al., 2015; Zhang et al., 2014; Zhang and Croué, 2014).

3.6. Effect of initial concentration of BPA

Fig. S1 depicts the effect of initial concentration on degradation of BPA. It is clearly shown that the degradation efficiency and degradation rate of BPA are gradually decreased with the increase of initial concentration of BPA. The reason for this phenomenon may be that the system produces a certain amount of active sites, and BPA with a high concentration may compete with the active sites, leading to the decrease of the BPA degradation rate.

3.7. A proposed enhancement mechanism

To identify reactive oxygen species involved in $g-C_3N_4$ /PS/Vis system, radicals quenching experiments were conducted first. As we known, MeOH can scavenge both $\cdot OH$ and $SO_4\cdot^-$, while BuOH only can quench $\cdot OH$ (Matzek and Carter, 2016). Assuming that $\cdot OH$ and $SO_4\cdot^-$ are the major oxide species, the degradation of BPA will be greatly inhibited in the presence of MeOH or BuOH. However, negligible effect of MeOH and BuOH on the degradation of BPA were observed in Fig. 7a, suggesting $\cdot OH$ and $SO_4\cdot^-$ are not responsible for the removal of BPA $g-C_3N_4$ /PS/Vis system. In contrast, the BPA removal efficiency is reduced to 55.6% and 12.0% in the presence of EDTA-2Na (a scavenger of hole) and

Fig. 7. (a) The effect of different scavengers on the degradation of BPA and (b) ESR spectra obtained in $g-C_3N_4$ /PS/Vis system.

benzoquinone (a scavenger of superoxide radical, $O_2\cdot^-$), respectively. These results indicate that photogenerated hole and $O_2\cdot^-$ play a key role for BPA degradation. To further verify the involved active radicals in $g-C_3N_4$ /PS/Vis systems, ESR was carried out using BMPO as spin trapping agent. ESR spectra of BMPO- $O_2\cdot^-$ adducts ($a_N = 9.56 \text{ G}$, $a_{H\beta} = 13.46 \text{ G}$) (Twahir et al., 2015) were observed in Fig. 7b, and their intensity present gradual increased then decreased after 20 min. However, neither BMPO- $\cdot OH$ ($a_N = 13.54 \text{ G}$, $a_{H\beta} = 12.3 \text{ G}$, $a_{H\gamma} = 0.66 \text{ G}$) (Chang et al., 2016) nor BMPO- $SO_4\cdot^-$ adducts signals were observed. All in all, $O_2\cdot^-$ instead of $\cdot OH$ and $SO_4\cdot^-$ are the major oxide species in $g-C_3N_4$ /PS/Vis systems.

Based on the above results and previous report (Yan et al., 2015), a plausible mechanism of BPA degradation was proposed:

As depicted in Fig.S2, the photogenerated electrons (e^-) and holes (h^+) were produced in the conduction band (CB) and valence band (VB) of $\text{g-C}_3\text{N}_4$ under visible light irradiation (Eq. (1)). The photogenerated e^- can induce the adsorbed O_2 into $\cdot\text{O}_2^-$ (Eq. (2)) because of its sufficient reductive ability. Meanwhile, PS (an electron acceptor) capture photogenerated electrons and then reduce O_2 into $\cdot\text{O}_2^-$ (Eqs. (3) and (4)), which inhibits the recombination of photogenerated e^- and h^+ pairs. The generated $\cdot\text{O}_2^-$ and photo-generated h^+ oxidize BPA to CO_2 and H_2O (Eqs. (5) and (6)).

3.8. Performance of $\text{g-C}_3\text{N}_4/\text{PS}/\text{Vis}$ and its stability

In order to evaluate the enhanced performance of $\text{g-C}_3\text{N}_4/\text{PS}/\text{Vis}$ system, the degradation of various organic contaminants including 2,4-dichlorophenol (2,4-DCP), phenol (PhoH) and ibuprofen (Ibu) were examined, respectively. As shown in Fig.S3, all of these pollutants are efficiently degraded after 90 min. These results indicate that it is an effective way by coupling $\text{g-C}_3\text{N}_4$ nanosheets with PS for organic compounds' degradation under visible light irradiation.

The stability of catalyst is one of the important indexes to evaluate the performance of the catalyst. Therefore, recycle experiments were conducted to test the stability of $\text{g-C}_3\text{N}_4$ nanosheets. As depicted in Fig. S4, It can be seen that there is only a slight decrease in the BPA degradation rate with the repeated use of the $\text{g-C}_3\text{N}_4$ nanosheets, which indicates the robust stability of $\text{g-C}_3\text{N}_4$ nanosheets.

4. Conclusions

In this work, the as prepared $\text{g-C}_3\text{N}_4$ nanosheets showed an improved photocatalytic activity toward BPA degradation in compared with the bulk $\text{g-C}_3\text{N}_4$. The photocatalytic performance of the $\text{g-C}_3\text{N}_4$ nanosheets can be significantly enhanced with the addition of persulfate under visible light irradiation. The first-order rate constants of BPA degradation were improved from 0.0133 to 0.0469 min^{-1} . Increase of the catalyst dosage and PS concentration can improve the photocatalytic activity of $\text{g-C}_3\text{N}_4$ nanosheets toward BPA degradation, whereas the photocatalytic efficiency decreased with the pH increase. Superoxide radical and photo-generated holes are main oxidative species for the BPA degradation. PS can act as an electron capture agent and boosted the separation of photogenerated hole electron pairs, which can remarkably improve the photocatalytic activity of $\text{g-C}_3\text{N}_4$ nanosheets. The $\text{g-C}_3\text{N}_4$ nanosheets also exhibited a good stability and can be used as a robust photocatalyst for the removal of refractory organic pollutants.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2017.08.169>.

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