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Article

Mechanistic studies on peroxymonosulfate activation by g-C₃N₄ under visible light for enhanced oxidation of light-inert dimethyl phthalate

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ARTICLE INFO

Article history:

Received 19 April 2019

Accepted 5 July 2019

Published 5 February 2020

Keywords:

Graphitic carbon nitride

Visible light

Peroxymonosulfate

Dimethyl phthalate

Activation

Degradation

ABSTRACT

Excitation of metal-free graphitic carbon nitride (g-C₃N₄) under visible light can successfully achieve efficient activation of peroxymonosulfate (PMS). Synergistic effects and involved mechanism were systematically investigated using a light-inert endocrine disrupting compound, dimethyl phthalate (DMP), as the target pollutant. Under visible light irradiation, DMP could not be degraded by direct g-C₃N₄-mediated photocatalysis, while in the presence of PMS, the dominant radicals were converted from •O₂ to SO₄•⁻ and •OH, resulting in effective DMP degradation and mineralization. Results showed that higher dosage of PMS or g-C₃N₄ could increase the activation amount of PMS and corresponding DMP degradation efficiency, but the latter approach was more productive in terms of making the most of PMS. High DMP concentration hindered effective contact between PMS and g-C₃N₄, but could provide efficient use of PMS. Higher DMP degradation efficiency was achieved at pH lower than the point of zero charge (5.4). Based on intermediates identification, the DMP degradation was found mainly through radical attack (•OH and SO₄•⁻) of the benzene ring and oxidation of the aliphatic chains.

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1. Introduction

Advanced oxidation technologies (AOTs) are intensively investigated to degrade the emerging recalcitrant organic contaminants in water. Among various AOTs, the peroxymonosulfate (PMS)-based processes have attracted considerable attention in recent years [1]. PMS as an oxidant with the redox po-

tential of 1.82 V has been used as a chlorine-free sanitizer, bleaching agent in industrial field and some public amenities [2]. However, direct oxidation of refractory organic pollutants by PMS is too slow or even not able to occur so that activation is needed to generate radicals with stronger oxidizing capability.

Compared to other conventional radical-providing oxidants

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This work was supported by the Natural Science Foundation of Jiangsu Province (BK20160936, BK20160938), the National Natural Science Foundation of China (51708297), and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD). The advanced analysis and testing center of Nanjing Forestry University is also acknowledged.

DOI: S1872-2067(19)63447-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 41, No. 2, February 20204

(e.g., H_2O_2 and peroxydisulfate), PMS has the advantage that it is potentially non-toxic, cheap, more stable, easily soluble in water ($> 250 \text{ g}\cdot\text{L}^{-1}$ at 20°C), and more easily to be activated due to the unsymmetrical structure [2–4]. Both $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ are the frequently detected radicals in different PMS-activated AOTs. Compared to $\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$ has a higher redox potential ($E^0 = 2.5\text{--}3.1 \text{ V}$) [5], a better flexibility to a broad pH range [6] and also a longer half-life ($30\text{--}40 \mu\text{s}$) than that of $\bullet\text{OH}$ (20 ns) [7]. Many approaches can activate PMS, such as ultrasound [8], ultraviolet (UV) irradiation [9], heat [10], metal ions [11], metallic oxides [12] and metal-free catalysis [13]. Artificial energy input is necessary for many activation methods [14] and the metal-related activation approaches have aroused the concern of secondary environmental pollution due to metal leaching and the high cost.

Solar energy can be a promising energy source for activating PMS, while the solar light utilization is limited to UV region ($< 5\%$ of solar spectra) because PMS does not absorb visible light [3]. However, using visible-light-responsive photocatalysts is a promising approach to convert direct energy activation to conduction-band electron (e_{CB}^-) activation of PMS, which can successfully introduce visible light to PMS activation process. Many studies have been carried out to develop effective photocatalysts, such as the N-doped TiO_2 [3], noble-metal-based catalysts [15], mineral catalysts [16–18]. In view of environmental impact and high costs of metallic catalysts, it is necessary to develop metal-free catalysts, more preferably consisting of earth-abundant elements to activate PMS under visible light.

Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) as a polymeric semiconductor is composed of the Earth-abundant elements and attracts increasing interest owing to its metal-free nature, high degree of thermal stability ($< 600^\circ\text{C}$ in air) [19], facile preparation from cheap precursors and resistance to acid, alkaline and organic solvents [20,21]. In particular, $\text{g-C}_3\text{N}_4$ is a visible light reactive photocatalyst [22]. Most of the current studies focus on $\text{g-C}_3\text{N}_4$ -mediated direct photocatalytic degradation of organic pollutants (e.g., [23–25]), while the fast recombination of photo-generated carriers often leads to unsatisfactory efficiency. So far, very limited investigations concentrate on using pure $\text{g-C}_3\text{N}_4$ to activate PMS under visible light for the degradation of emerging contaminants. Tao et al. [26] reported the utilization of $\text{g-C}_3\text{N}_4$ to effectively activate PMS under visible light for dye degradation. However, the visible-light-absorption characteristic of dye may lead the obtained results not applicable for those transparent or light-inert organic pollutants since some photosensitizing phenomenon may get involved.

Dimethyl phthalate (DMP) is the simplest member of phthalate acid esters (PAEs), widely used as the plasticizer in industrial field [27], which is the most often detected PAEs in water environment due to its heavy use and higher water solubility ($4,000 \text{ mg}\cdot\text{L}^{-1}$ at 25°C). DMP is known as an endocrine disruptor and has been listed as one of the priority pollutants in some countries including China [28]. Particularly, DMP shows the minimum quantum yield among PAEs [29]. Until now, no studies have investigated the possibility of using the conduction-band electron to activate PMS for the degradation of PAEs.

In this study, systematic investigations were carried out us-

ing $\text{g-C}_3\text{N}_4$ to activate PMS mostly under visible light to degrade DMP. Synergistic effects were comprehensively analyzed under different conditions. The mechanisms were studied based on identifying the major radicals and DMP degradation intermediates.

2. Experimental

2.1. Chemicals and reagents

DMP ($\geq 99\%$), PMS (Oxone®: KHSO_5 , 0.5KHSO_4 , $0.5\text{K}_2\text{SO}_4$) and melamine (99%) were all purchased from Sigma-Aldrich. The 5,5-Dimethyl-1-pyrroline N-oxide (DMPPO) ($\geq 97\%$) and ABTS [$=2,2'$ -Azinobis(3-ethylbenzothiazoline-6-sulfonic Acid Ammonium Salt)] were purchased from Shanghai Aladdin Biochemical Co., Ltd. Reagents included methanol (LCMS grade), ethanol (EtOH , $\geq 99.8\%$, Aldrich) and tert butyl alcohol (TBA, $\geq 99.5\%$, Aldrich). Solutions of 0.1 M sulfuric acid and 0.1 M sodium hydroxide were used for pH adjustment. Deionized-distilled water was used exclusively.

2.2. Preparation of $\text{g-C}_3\text{N}_4$ catalyst

The photocatalyst of $\text{g-C}_3\text{N}_4$ was prepared by a method of thermal decomposition of melamine [30]. Briefly, melamine was contained in a covered alumina crucible and heated to 550°C at a heating rate of $7^\circ\text{C}\cdot\text{min}^{-1}$. The reaction was further maintained at 550°C for another 2 h in a muffle furnace. The sample was then cooled to ambient temperature. Light yellow products were obtained after grinding.

2.3. Characterization

See text S1 in Supporting Information (SI).

2.4. Photocatalytic degradation experiment

The photochemical reactions were conducted using a photo-reactor tailor made by Ning Bo Scientz Biotechnology Co., China. Monochromatic mercury lamps with four different wavelengths (254 , 300 , 350 and 420 nm) were purchased from Rayonet®. org and the emission spectra are provided in Fig. S1. Commercial light emitting diode (LED) lamp provides continuous emission spectra ranging from 400 nm to 630 nm (Fig. S1). Ten tubes were used for each wavelength and the incident photon intensity approximates to be $1.71 \times 10^{-5} \text{ Einstein}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ (254 nm), $6.92 \times 10^{-6} \text{ Einstein}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ (300 nm) and $5.2 \times 10^{-5} \text{ Einstein}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ (350 nm) determined by chemical actinometer, potassium ferrioxalate. The radiation intensities of the 420 nm visible light and LED were 3810 and $3696 \mu\text{W}\cdot\text{cm}^{-2}$, respectively, as measured at the surface position of the reaction solution via the 420 nm channel by Beijing Normal University Illuminometer.

All experiments were carried out in 100 mL quartz beakers at room temperature of $22 \pm 1^\circ\text{C}$. A dark adsorption period of 20 min was allowed for each reaction involving $\text{g-C}_3\text{N}_4$, and certain amount of PMS was added afterwards. Light was turned

on to initiate the reaction and magnetic stirrer was used to ensure a thorough mixing. Samples were withdrawn at pre-determined time intervals and filtered by 0.45 μm membranes to remove particles for subsequent quantification analysis. The addition of PMS led to significant decrease of initial solution pH. To evaluate solution pH effect, the solution pH was adjusted after PMS addition, and neither further adjustment nor buffer was applied throughout. The initial concentration of DMP was 0.01 mM and the g-C₃N₄ dosage was 0.5 g·L⁻¹ in most cases unless otherwise stated. Conditions applied for intermediates identification and TOC measurement are: 1.5 g·L⁻¹ g-C₃N₄, 5.0 mM PMS and 0.01 mM DMP. Since there is minor dissolution of g-C₃N₄, the TOC decrease of DMP was calculated by deducting the dissolution amount at the same reaction period. For the recycling experiments, the catalyst was reused without any regeneration treatment after each reaction, and the next cycle was started by adding fresh DMP and PMS after collecting the catalyst by centrifugation.

2.5. Analytical methods

See text S2.

3. Results and discussion

3.1. Characterization of the g-C₃N₄ catalyst

Characterization of the as-prepared g-C₃N₄ was conducted and results are given in Fig. S3. The XRD spectra are shown in Fig. S3(a). Two characteristic peaks located at 27° and 13° are clearly observed, which can be assigned to the interlayer stacking (002) and in-plane structural packing (001) of the conjugated aromatic complex, respectively [5]. Fig. S3(b) presents the FT-IR spectra of g-C₃N₄. The broad absorption band around 3000–3300 cm⁻¹ is resulting from the stretching of NH₂ and NH groups and their intermolecular hydrogen bonding interactions [31]. The weak band at 2160 cm⁻¹ is due to the stretching vibration of -CN [32]. Strong absorption is observed at the range of 1240–1650 cm⁻¹, which corresponds to the characteristic breathing modes of aromatic carbon nitride het-

erocycles [33]. The strong absorption at 808 cm⁻¹ and weak absorption at 893 cm⁻¹ are ascribed to the ring breathing vibration of tri-s-triazine and the cross-linked deformation mode of N-H, respectively [5].

The PL spectrum (Fig. S3(c)) of pure g-C₃N₄ solid powder was recorded. The strong emission peak at 412–535 nm can be ascribed to the recombination of electron-hole pairs [34,35]. The relatively strong PL intensity indicates a low quantum yield of the photocatalytic efficiency of g-C₃N₄ due to the easy recombination of photo-generated carriers. Moreover, Raman spectra analysis was performed to further demonstrate the structure (Fig. S3(d)). The most intense peak at 675 cm⁻¹ is assigned to the breathing 2 mode of the triazine ring, and the peak shown at 980 cm⁻¹ is due to the breathing 1 mode of the triazine ring [36], which turns weaker as the triazine ring combine to form more tri-s-triazine units. The characteristic peaks shown in the broad range of 1300–2200 cm⁻¹ are also attributed to the breathing modes of the s-triazine ring in the CN network [37].

In order to examine the optical property of g-C₃N₄, DRS spectrum was measured (Fig. S3(e)) and the Tauc plot is shown in the inset figure. The g-C₃N₄ catalyst shows an absorption edge at around 500 nm and the band gap energy is determined as 2.7 eV. The above characterization results agree with the reference report, indicating that the g-C₃N₄ was synthesized successfully. The production of photogenerated electrons by g-C₃N₄ under visible light (420 nm) was also tested by carrying out photocurrent-time profiles using the g-C₃N₄ electrode (Fig. S3(f)). The as-prepared electrode demonstrated a sensitive photocurrent response for each on-off run, indicating the capability of g-C₃N₄ to provide photoelectrons under visible light irradiation.

The morphological features of g-C₃N₄ were studied by TEM (Fig. S4). As can be seen, the obtained g-C₃N₄ exhibited layered-structure with flat-sheet morphology. The N₂ adsorption-desorption isotherms and pore size distribution curves for g-C₃N₄ is given in Fig. 1(a). Type IV adsorption-desorption isotherms with H3 type hysteresis loops can be clearly seen, which indicates a typical mesoporous structure (average pore diameter = 18.3 nm). The g-C₃N₄ has a relatively small surface area of

Fig. 1. (a) N₂ adsorption-desorption isotherms and pore size distribution of the as-prepared g-C₃N₄; (b) Mott-Schottky plots for n-type g-C₃N₄ according to impedance measurements.

10.3 m² g⁻¹. The flat-band position of n-type g-C₃N₄ obtained from Mott-Schottky plot was measured as -1.18 V vs. Ag/AgCl electrode (-0.98 V vs. normal hydrogen electrode, NHE) (Fig. 1(b)). The conduction band (CB) minimum is about 0.1 V higher than the flat potential for n-type semiconductor [38]. Thus, the VB position of g-C₃N₄ was determined as -1.08 V. The position of conduction band (CB) for g-C₃N₄ is 1.62 V.

3.2. Effect of different incident light on DMP degradation

Since both g-C₃N₄ and PMS have photoactivities, the DMP degradation performance in light+g-C₃N₄+PMS and related constituent processes (i.e., light, light+PMS and light+g-C₃N₄) was examined under the irradiation of different light conditions, and results are shown in Fig. 2(a–d). Direct oxidation of DMP by PMS alone and activation of PMS by g-C₃N₄ in dark were precluded by control experiments (data not shown). It was found in Fig. 2(a, b) that, in the absence of g-C₃N₄, only UV light could lead to DMP degradation. In particular, direct photolysis of DMP was only achieved at the irradiation of 254 and 300 nm (Fig. 2(a)). Generally all of the groups of PAEs show low quantum yields during photolysis and DMP with the shortest chain exhibits the highest stability [29,39]. DMP removal of 70% and 13.5% within 2 h was achieved by photolysis at 254 and 300 nm UV light, respectively. The kinetics of direct photolysis of organic compounds was reported to be pseudo-first order in many other studies (e.g., [3]), which was, however, not applicable for DMP photolysis at UV_{254nm} irradiation in the present study. Hydroxyl radical (•OH) was identified during DMP photolysis at 254 nm based on ESR detection (Fig. S5), which may lead to the deviation of pseudo-first order kinetics. Since water does not absorb significantly at λ > 200 nm, the formation of •OH from H₂O decomposition is assumed to be unlikely. The mechanism proposed by Ryu et al. [40] may ex-

plain the origin of •OH under 254 nm UV irradiation. Superoxide radicals (O₂•⁻) may form from dissolved oxygen by accepting the electrons from excited DMP molecules (Reaction (1)). H₂O₂ can form through Reactions (2)–(4) [40], and then undergoes photo-decomposition at λ = 254 nm to provide •OH (Reactions (2)–(5)) [41]. Fig. S6 presents the generation profiles of H₂O₂ during the photolysis of DMP solution and pure water. It can be clearly seen that no H₂O₂ was produced in pure water while more H₂O₂ was detected at higher concentrations of DMP, providing strong support for the above hypothesis.

Fig. 2(b) shows DMP degradation performance in light+PMS processes. Highly efficient DMP degradation was achieved under 300 and 254 nm UV conditions with nearly complete DMP degradation within 15 min, suggesting the effectiveness of PMS activation by UVC and UVB light (Reaction (6)). The UVA (350 nm) light was found much less efficient for PMS activation and only 30% DMP was degraded within 2 h. Hardly any DMP degradation was observed by using both 420 nm monochromatic light and LED, indicating that PMS could hardly be directly activated by visible light.

As is known that g-C₃N₄ is a visible light responsive photocatalyst, the photocatalytic degradation of DMP was also examined without PMS (Fig. 2(c)). However, no measurable DMP degradation was detected except for 254 nm UV condition, in which only 22% of DMP was removed after 2 h photocatalytic treatment. Under 254 nm UV condition, DMP degradation with the presence of g-C₃N₄ turned to even slower compared to direct photolysis (Fig. 2(a)). These results are mainly due to two reasons, which will be discussed later in details. In brief, the dominant reactive oxygen species (ROS) in g-C₃N₄ mediated photocatalytic process was found to be O₂•⁻, which cannot react with DMP. In addition, the presence of g-C₃N₄ also could compete light with DMP molecules and the H₂O₂ formed in UV_{254nm} condition, leading to difficulties in producing •OH to enhance DMP degradation as is shown in Fig. 2(a).

It was found in Fig. 2(d) that, when combining g-C₃N₄ with PMS, DMP could be degraded effectively under all light conditions. However, the introduction of g-C₃N₄ inhibited DMP degradation under the irradiation of 254 nm and 300 nm light (Fig. 2(b) vs. 2(d)). This was mainly due to three reasons: (1) g-C₃N₄ could impede direct photolysis of DMP as discussed above (see Fig. 2(a) and 2(c)); (2) the presence of g-C₃N₄ could decrease the UV intensity by "inner filter" effect; (3) the photo-electron activation of PMS was less efficient under 254 and 300 nm conditions than UV activation. Whereas, DMP could be decomposed efficiently under UVA (350 nm) and visible light irradiation (420 nm and LED), and the removal rate was 78%, 65% and 90%, respectively. Based on the results obtained by control experiments (Figs. 2(a)–(c)), this substantial improvement was ascribed to the interactions between PMS and g-C₃N₄ under UVA and visible light conditions, which could generate effective

Fig. 2. Effects of incident light on DMP degradation in different related processes. (a) under light irradiation only; (b) light+PMS; (c) light+g-C₃N₄; (d) light+g-C₃N₄+PMS. Reaction conditions: [DMP]₀ = 0.01 mM, [PMS]₀ = 2.0 mM, g-C₃N₄ dosage 0.5 g·L⁻¹, pH₀ = 6.5 ± 0.1 without PMS, pH₀ = 3.0 ± 0.05 with PMS.

ROS to degrade DMP. In order to investigate the involved mechanisms in depth, 420 nm light source was selected for further study since DMP was inert in all related processes under 420 nm visible light irradiation except for the g-C₃N₄+PMS+Vis₄₂₀ system.

3.3. Effect of reagents' dosage

Since significant synergistic effect was observed by combining g-C₃N₄ and PMS under visible light irradiation, the respective role of g-C₃N₄ and PMS was investigated by examining the influence of their concentrations on DMP degradation (Fig. 3). It was found in Figs. 3(a) and (b) that, DMP degradation was enhanced by increasing [PMS]₀, and the pseudo first-order rate constant (*k*) increased from 0.0012 to 0.0113 min⁻¹ as [PMS]₀ varied from 0.05 to 7.0 mM. However, the relationship between *k* and [PMS]₀ showed an obvious two-stage trend. A faster improvement stage was obtained with 0.05 mM ≤ [PMS]₀ ≤ 0.5 mM and a milder improvement was observed with 0.5 mM ≤ [PMS]₀ ≤ 7.0 mM. To further examine the role of PMS, the consumption of PMS was determined at different PMS dosages (Fig. 4(a)). As can be seen, more PMS was activated at higher [PMS]₀ to improve the generation of ROS, and thereupon higher DMP degradation efficiency could be obtained. Whereas, by calculating the ratio of ΔPMS/ΔDMP (Fig. 4(b)), it was found that higher [PMS]₀ resulted in a higher value of ΔPMS/ΔDMP, which implied that the increase of PMS concentration also led to its unproductive consumption most likely due to the scav-

enging role of HSO₅⁻ (Reactions (7) and (8)) [3]. Therefore, PMS plays a dual role of both the radical provider and consumer in the g-C₃N₄+PMS+Vis₄₂₀ system. In order to ensure the concentration of PMS not being the limiting factor in producing radicals, relatively higher [PMS]₀ of 5.0 mM was applied for further investigation.

Figs. 3(c and d) show DMP degradation with different g-C₃N₄ dosages (0.1~1.5 g·L⁻¹). Generally, more g-C₃N₄ loading corresponded to higher DMP degradation rate, which can be attributed to the stronger capability in producing photoelectrons and more active sites on g-C₃N₄ surface for PMS contact to generate more active radicals. Similarly, the improvement can also be divided into two stages, a faster acceleration and a milder enhancement before and after 0.5 g·L⁻¹ g-C₃N₄, respectively. Fig. 4(c) shows clearly that more PMS could be activated at higher g-C₃N₄ loading, confirming that the improvement of DMP degradation is primarily due to more efficient activation of PMS. The ratio of ΔPMS/ΔDMP as shown in Fig. 4(d) obtained at varied g-C₃N₄ dosages shows relatively gentle change compared with that obtained by increasing PMS concentration. This implies that DMP degradation promoted by increasing g-C₃N₄ dosage can make PMS activation more productive than that by increasing PMS dosage. However, the increase of g-C₃N₄ also strengthened the "inner filter" effect of incident light and weakened the photon density for unit mass of g-C₃N₄, which may lead to the much milder increase of *k* at higher g-C₃N₄

Fig. 3. Influence of different parameters on DMP degradation in the process of g-C₃N₄+PMS+Vis₄₂₀: (a) PMS initial concentration ([PMS]₀); (b) relationship between pseudo-first order rate constants (*k*) and [PMS]₀; (c) g-C₃N₄ dosage; (d) relationship between *k* and g-C₃N₄ dosage; (e) initial concentration of DMP ([DMP]₀); (f) relationship between *k* and [DMP]₀. Reaction conditions: (a,b) g-C₃N₄ dosage 0.5 g·L⁻¹, [DMP]₀ = 0.01 mM, pH₀ = 2.4~3.9 for varied PMS concentration; (c,d) [PMS]₀ = 5.0 mM, [DMP]₀ = 0.01 mM, pH₀ = 2.5 ± 0.1; (e,f) g-C₃N₄ dosage 0.5 g·L⁻¹, [PMS]₀ = 5.0 mM, pH₀ = 2.5 ± 0.1.

Fig. 4. Influence of different parameters on PMS activation in the process of g-C₃N₄+PMS+Vis420: (a) [PMS]₀; (b) relationship between $\Delta\text{PMS}/\Delta\text{DMP}$ and [PMS]₀; (c) g-C₃N₄ dosage; (d) relationship between $\Delta\text{PMS}/\Delta\text{DMP}$ and g-C₃N₄ dosage; (e) [DMP]₀; (f) relationship between $\Delta\text{PMS}/\Delta\text{DMP}$ and [DMP]₀. Reaction conditions: (a,b) g-C₃N₄ dosage 0.5 g·L⁻¹, [DMP]₀ = 0.01 mM, pH₀ = 2.4~3.9 for varied PMS concentrations; (c,d) [PMS]₀ = 5.0 mM, [DMP]₀ = 0.01 mM, pH₀ = 2.5 ± 0.1; (e,f) g-C₃N₄ dosage 0.5 g·L⁻¹, [PMS]₀ = 5.0 mM, pH₀ = 2.5 ± 0.1.

dosages.

The influence of initial concentration of DMP on its degradation is presented in Figs. 3(e and f). As expected, faster degradation was observed at lower [DMP]₀, which was due to the relatively abundant radicals prevailing compared to the radical consumers. Similar results were also obtained from studies using other PMS activation approaches [42]. Inverse relationship between k and [DMP]₀ was observed (Fig. 3(f)). By measuring the consumption profile of PMS, it was found that lower [DMP]₀ corresponded to more decomposition of PMS (Fig. 4(e)). It is probably because the intense competition between DMP and PMS for the active sites on g-C₃N₄ surface at higher [DMP]₀ hindered the effective contact between PMS and g-C₃N₄. However, the higher concentration of DMP resulted in much lower value of $\Delta\text{PMS}/\Delta\text{DMP}$, indicating a high efficiency of PMS utilization (Fig. 4(f)).

3.4. Effect of environment conditions

Influence of initial solution pH on the heterogeneous g-C₃N₄+PMS+Vis420 process was examined in a wide range of 2.5~10.15; results are presented in Fig. 5(a). It was found that DMP degradation was affected significantly by initial solution pH. In general, DMP degradation rate decreased gradually as pH₀ increased. However, two stage variation can be observed, i.e., a much slow k decrease as pH₀ increased from 2.5 to 5.5 and a sharp deceleration of DMP degradation when pH₀ was

further increased to 10.15. Since DMP is a non-dissociating compound, solution pH is not able to influence the state of DMP. The PZC of the as-prepared g-C₃N₄ was measured to be around 5.4 (Fig. S7), which indicates that the g-C₃N₄ surface is positively charged at pH < 5.4 and negatively charged at pH > 5.4. Therefore, the worse DMP degradation performance at pH > 5.5 was most likely due to the increasing electrostatic repulsion between negatively charged g-C₃N₄ surface and HSO₅⁻, leading to much less effective activation of PMS. Moreover, the degradation decrease at strong alkaline conditions was also due to the reaction of SO₄^{•-} with OH⁻ to form •OH and followed by the conversion of •OH into its conjugate base •O⁻ (Reactions 9 and 10), a much weak radical [43].

At acidic conditions, apart from the electrostatic attraction between the positively charged g-C₃N₄ and HSO₅⁻, the H⁺ on the surface of the protonated g-C₃N₄ easily forms hydrogen bond with the peroxide bond (O-O) of PMS, which favors the contact between PMS and g-C₃N₄. Since DMP degradation in g-C₃N₄+PMS+Vis420 process is ascribed to PMS activation (Fig. 2), the pH influence on the contact between PMS and g-C₃N₄ can play important role on DMP degradation. Unlike some metal ion activated methods (e.g., [44]) that showed difficulties of PMS activation at pH < 3, the g-C₃N₄+PMS+Vis420 process maintained the highest DMP degradation efficiency at pH₀ = 2.5. It should be noted that, the pH₀ = 2.5 was achieved by add-

Fig. 5. Influence of environment conditions on DMP degradation in the process of g-C₃N₄+PMS+Vis420. (a) initial solution pH; (b) incident light intensity. Reaction conditions: g-C₃N₄ dosage 0.5 g·L⁻¹, [PMS]₀ = 5.0 mM, [DMP]₀ = 0.01 mM, pH₀ = 2.5 ± 0.1 for Figure (b).

ing 5.0 mM oxone to the reaction solution without any further adjustment. This implies that the acidic environment induced by oxone alone could create a good pH condition for DMP degradation in g-C₃N₄+PMS+Vis420 process.

The influence of light intensity on DMP degradation was examined by varying the applied number of light tubes. As shown in Fig. 5(b), it was found that DMP degradation was accelerated with the increasing number of lamps, but the increase diminished at higher light intensities (more than 7 lamps) with the *k* reaching a maximum. The results suggest that the visible light intensity is not a rate-limiting factor in the process and the DMP removal rate becomes less-dependent on light intensity.

3.5. Analysis of reactive oxygen species

The photo-induced carriers and the derived ROS may be involved in the degradation of DMP. Competitive radical experiments were carried out to identify the contribution of each ROS. It was found in Fig. 6(a) that, different inhibition degrees were obtained by applying EtOH and TBA at different concen-

trations. EtOH was used to scavenge both •OH (1.2~2.8 × 10⁹ M⁻¹·s⁻¹) and SO₄^{•-} (1.6~7.7 × 10⁷ M⁻¹·s⁻¹) at high rates, while TBA is effective to quench •OH (3.8~7.6 × 10⁸ M⁻¹·s⁻¹) and much less competent for SO₄^{•-} quenching (4.0~9.1 × 10⁵ M⁻¹·s⁻¹) [6,45]. Overall, the application of EtOH resulted in greater extent of inhibition. Application of 0.5 and 1.0 mM EtOH could almost fully quench DMP degradation compared to 57% and 60% inhibition of DMP degradation with the application of 0.5 TBA and 1.0 mM TBA, respectively. When applying 0.1 mM scavengers, 43% and 28% inhibition were obtained by EtOH and TBA, respectively. The difference of the quenching effects between two scavengers suggests that both •OH and SO₄^{•-} are the contributors to the degradation of DMP.

The possible ROS present in g-C₃N₄+Vis420 process was also investigated using bisphenol A as a target compound since DMP was totally inert toward g-C₃N₄+Vis420 process (Fig. 6(b)). It can be seen, unlike DMP, approximately 72% of BPA could be degraded within 90 min in g-C₃N₄+Vis420 process. Different scavengers were also applied. In addition to TBA, disodium ethylenediaminetetraacetate (EDTA-2Na) and *p*-benzoquinone (*p*-BQ) were applied as hole (h_{VB}⁺) and •O₂⁻

Fig. 6. Inhibiting effect of different scavengers on DMP degradation in the process of g-C₃N₄+PMS+Vis420 (a) and on BPA degradation in g-C₃N₄+Vis420 process (b). Reaction conditions: g-C₃N₄ dosage 0.5 g·L⁻¹, [PMS]₀ = 5.0 mM for figure a, [DMP]₀ = 0.01 mM, [BPA]₀ = 0.01 mM for figure b, pH₀ = 2.5 ± 0.1.

scavengers, respectively. The addition of TBA and EDTA-2Na showed negligible influence on BPA degradation. However, the presence of *p*-BQ nearly completely inhibited BPA degradation. These results indicate that $\bullet\text{O}_2^-$ is the major ROS contributing to BPA degradation in $\text{g-C}_3\text{N}_4/\text{Vis420}$ process, while the role of $\bullet\text{OH}$ and $h\nu_{\text{VB}}^+$ is limited. Since $\bullet\text{O}_2^-$ has moderate oxidizing power (i.e., $E^0(\text{HO}_2\bullet/\text{H}_2\text{O}_2) = 1.44 \text{ V}_{\text{NHE}}$ or $E^0(\bullet\text{O}_2^-/\text{HO}_2^-) = 1.03 \text{ V}_{\text{NHE}}$) [46], it is possible to use it for oxidizing some metal ions or very labile organic compounds. Liu et al. [47] showed that superoxide radicals are incapable of degrading DMP, which agrees with the results of the present study that DMP is not able to be degraded in $\bullet\text{O}_2^-$ -dominated $\text{g-C}_3\text{N}_4/\text{Vis420}$ process.

The active radicals generated in both $\text{g-C}_3\text{N}_4/\text{Vis420}$ and $\text{g-C}_3\text{N}_4/\text{PMS}/\text{Vis420}$ processes were further analyzed using ESR (Fig. 7). Different concentrations of DMPO were applied to elucidate the possible interference caused by DMPO addition to the original systems. In the $\text{g-C}_3\text{N}_4/\text{Vis420}$ process (Fig. 7(i)), very weak signals assigned to $\text{DMPO}\cdot\bullet\text{O}_2^-$ could be detected using 2 mM DMPO (d) and strong signals could be obtained (b) when 80 mM DMPO was applied. This implies that $\bullet\text{O}_2^-$ is formed in $\text{g-C}_3\text{N}_4/\text{Vis420}$ process, which agrees with the quenching results shown in Fig. 6(b). Higher concentration of DMPO increases the opportunity for $\bullet\text{O}_2^-$ capture. In addition, in accordance with expectations that no peaks assigned to $\text{DMPO}\cdot\bullet\text{OH}$ could be found with the addition of 2 mM DMPO (c). However, four peaks of $\text{DMPO}\cdot\bullet\text{OH}$ with intensity ratio of 1:2:2:1 were detected with 80 mM DMPO (a). The three peaks marked with orange symbols were resulting from the reaction between DMPO and O_2 . Due to the lower valance band (1.62 V vs. NHE) compared with the potential of $\bullet\text{OH}/\text{H}_2\text{O}$ (2.68 V vs. NHE) and $\bullet\text{OH}/\text{OH}^-$ (1.99 V vs. NHE), $\bullet\text{OH}$ is assumed not to be produced by h^+ [48]. The detected $\bullet\text{OH}$ is assumed to be related to dissolved oxygen (Reactions (2)~(4), (11)~(12)). In view of the incapable degradation of DMP in the $\text{g-C}_3\text{N}_4/\text{Vis420}$ process (Fig. 2(c)) and the quenching results shown in Fig. 6(b), it was assumed that the $\bullet\text{OH}$ formation was most likely enhanced

by the presence of high concentration of DMPO. The reactivity of DMPO may interfere of recombination of electron-hole pairs, and thereby facilitates Reaction (12) to enhance the production of $\bullet\text{OH}$ in ESR detection.

With the presence of PMS (Fig. 7(ii)), no signals assigned to $\text{SO}_4^{\bullet-}$ were detected. Weak signals indicating $\text{DMPO}\cdot\bullet\text{OH}$ could be observed with 80 mM DMPO and 2 mM PMS (g), the intensity of which was lower than that obtained in $\text{g-C}_3\text{N}_4/\text{Vis420}$ process (a), most likely due to the consumption of $\bullet\text{OH}$ by PMS (Reaction (7)). At the same DMPO concentration of 80 mM, increasing [PMS] to 10 mM gave rise to the formation of 5,5-dimethyl-2-pyrrolidone-N-oxyl (DMPOX) (h) with a characteristic seven-line spectra. Although the reason for DMPOX formation was controversial, in view of the results of quenching experiments, the formation of DMPOX was likely ascribed to the interaction between DMPO and the strong oxidizing species produced by PMS activation. To further elucidate this, lower [DMPO] of 2 mM and [PMS] of 7 mM were applied, and however the intensity of DMPOX signals increased significantly. It revealed that over high [DMPO] impeded the efficient activation of PMS; large amount of ROS could be generated to oxidize DMPO. As we know, the $\text{DMPO}\cdot\text{SO}_4^{\bullet-}$ adduct is difficult to detect because of its low sensitivity and short life-time [49]. Thus, the DMPOX signal can be originated from $\text{DMPO}\cdot\text{SO}_4^{\bullet-}$ [15]. At the same conditions ([DMPO] = 2 mM, [PMS] = 7 mM), no $\text{DMPO}\cdot\bullet\text{O}_2^-$ signals could be detected, suggesting that the intensity of $\text{SO}_4^{\bullet-}$ should be much stronger than that of $\bullet\text{O}_2^-$ when PMS was present. Similarly, when increasing DMPO concentration to 80 mM, the $\text{DMPO}\cdot\bullet\text{O}_2^-$ signals could be observed clearly. Based on the above analysis, the mechanisms for DMP degradation in $\text{g-C}_3\text{N}_4/\text{PMS}/\text{Vis420}$ process are illustrated in Fig. 10.

3.6. Reusability of $\text{g-C}_3\text{N}_4$ catalyst

The reusability of $\text{g-C}_3\text{N}_4$ was examined by evaluating its catalytic performance for four cycles and results are shown in Fig. 8. It was found that after three consecutive cycling runs, DMP degradation percentage within 120 min decreased from 72% to 59%. It should be noted that the weight loss of catalyst reached approximately 14% after two runs of recovery (centrifugation), which is assumed to be the primary reason for the decrease of the catalytic efficiency. Before the start of the fourth round, catalyst of $\text{g-C}_3\text{N}_4$ was replenished to maintain an equal loading ($0.5 \text{ g}\cdot\text{L}^{-1}$). It was observed that, DMP degradation ratio achieved 73%, similar with that obtained in the first run. This gives a hint that if the $\text{g-C}_3\text{N}_4$ can be immobilized properly in practical application to minimize catalyst leaching, stable catalytic performance can be obtained.

3.7. Identification of DMP degradation products

The primary intermediates of DMP degradation were identified to further interpret the mechanisms involved in $\text{g-C}_3\text{N}_4/\text{PMS}/\text{Vis420}$ process. The identified intermediates can

Fig. 7. ESR spectra obtained from two processes. (a) $\text{g-C}_3\text{N}_4/\text{Vis420}$; (b) $\text{g-C}_3\text{N}_4/\text{PMS}/\text{Vis420}$. Reaction conditions: $\text{g-C}_3\text{N}_4$ dosage $0.5 \text{ g}\cdot\text{L}^{-1}$, methanol solvent for $\text{O}_2^{\bullet-}$ detection, water solvent for the others.

Fig. 8. The reuse performance of the g-C₃N₄ catalysis. Reaction conditions: g-C₃N₄ dosage 0.5 g·L⁻¹, [PMS]₀ = 5.0 mM, [DMP]₀ = 0.01 mM.

be divided into three categories, the hydroxy intermediates (molecule weight (mw) = 210.18, 226.18, 248.21), the sulfoxy intermediates (mw = 290.25, 322.25) and the side chain oxidized intermediates (mw = 180.16, 166.13). The detected primary intermediates indicate three reaction pathways initiating the degradation of DMP as shown in Fig. 9: (a) hydroxylation of the aromatic ring, (b) sulfate radical attack of the aromatic ring, and (c) oxidation of the aliphatic chain. This also agrees with the results obtained from the quenching experiments and ESR detection that DMP degradation in g-C₃N₄+PMS+Vis420 process is mainly due to the oxidation by •OH and SO₄•-. An et al. [50] also reported the (a) and (c) pathways as the dominant reaction processes for DMP degradation in •OH-mediated AOTs

Fig. 9. The proposed degradation pathways of DMP in g-C₃N₄+PMS+Vis420 process.

based on theoretical calculation. In our previous study investigating PMS activation by Co-based catalyst, intermediates produced by pathway (b) were also detected [44], indicating similar reaction mechanisms for DMP degradation by Co-activation and photo electron activation of PMS.

The TOC measurement result showed that for 81% of DMP degradation within 2 h, about 19% of TOC was decreased. The least carbon-containing intermediates detected in this study can only remove 2 of 10 carbons (20% TOC decrease) at the DMP molecules (mw = 166.13 and 248.21). In view of the incomplete degradation of DMP within 2 h, the 19% decrease of TOC was resulted from further decomposition of the detected primary intermediates although they cannot be identified due to the limitation of LC/MS for strong polar and small molecular compounds.

4. Conclusions

The melamine-derived g-C₃N₄ showed visible light activity with the determined band energy of 2.7 eV. However, the major ROS produced in Vis/g-C₃N₄ process was •O₂•-, which could not oxidize DMP but could degrade BPA efficiently. Although PMS is not able to be directly activated by visible light, it can be activated effectively by the photoelectrons excited from g-C₃N₄ under visible light irradiation and the dominant ROS were found to be •OH and SO₄•- leading to DMP degradation and mineralization. In addition, increase of PMS and g-C₃N₄ dosage could accelerate DMP degradation in g-C₃N₄+PMS+Vis420 process via activating larger amount of PMS, whereas the latter approach is much more productive in terms of making the most of PMS. Higher DMP degradation efficiency was obtained at lower pH and the pH condition created by Oxone salts was beneficial to effect contact between g-C₃N₄ and PMS. The as-prepared g-C₃N₄ demonstrated stable catalytic performance but immobilization is suggested to prevent catalyst leaching. DMP degradation in the g-C₃N₄+PMS+Vis420 process was found mainly through three pathways, i.e., radical attack (•OH and SO₄•-) of the benzene ring and the oxidation of the aliphatic chains.

Fig. 10. Proposed mechanisms for DMP degradation in g-C₃N₄+PMS+Vis420 process.

Acknowledgment

This work was supported by the Natural Science Foundation of Jiangsu Province (BK20160936, BK20160938), the National Natural Science Foundation of China (51708297), and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD). The advanced analysis and testing center of Nanjing Forestry University is also acknowledged.

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Graphical Abstract

Chin. J. Catal., 2020, 41: 322–332 doi: S1872-2067(19)63447-9

Mechanistic studies on peroxymonosulfate activation by g-C₃N₄ under visible light for enhanced oxidation of light-inert dimethyl phthalate

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Synergistic effects were obtained by combining g-C₃N₄ with PMS under visible light. The dominant radicals were converted from •O₂⁻ to SO₄^{•-} and •OH. Increase of g-C₃N₄ dosage was more productive than increase of PMS.

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石墨相氮化碳可见光下活化过一硫酸盐氧化降解光惰性邻苯二甲酸二甲酯的机理研究

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摘要: 近几年过一硫酸盐(PMS)活化技术备受关注, 其中利用太阳能活化PMS具有可持续和环保的优势, 但PMS本身不吸收可见光。因此, 本文提出利用具有可见光响应的石墨相氮化碳(g-C₃N₄)激发产生光电子进而活化PMS。首先利用三聚氰胺前驱体通过热缩聚法制备g-C₃N₄, 通过X射线衍射(XRD)、傅里叶变换红外光谱(FT-IR)、紫外-可见光漫反射(UV-Vis)、荧光光谱(PL)、透射电镜(TEM)、N₂吸附脱附测试(BET)、电化学等一系列方法对g-C₃N₄进行表征, 研究其表面性质及光学性能。结果显示, g-C₃N₄具有典型的片层结构和可见光活性, 禁带宽度为2.7 eV。本文选取光惰性的内分泌干扰物邻苯二甲酸二甲酯(DMP)为目标污染物, 系统地研究了其降解动力学和降解机理。研究发现, 在短波紫外光(254和300nm)照射下, 直接光解和·OH参与的反应机理能实现DMP的光降解, 而在可见光照射下g-C₃N₄介导的光催化过程不能使DMP分解; 但当添加PMS时, 体系主导自由基由·O₂⁻转化为SO₄·⁻和·OH, 从而实现DMP的有效降解和矿化。研究还发现, 高浓度的PMS和高剂量的g-C₃N₄均可以提高PMS的活化量和相应的DMP降解效率, 但提高催化剂剂量的方式能更充分的利用PMS。尽管高浓度的DMP阻碍了PMS和光催化剂g-C₃N₄的有效接触, 但可以提高PMS的利用率。当pH低于零电荷点(5.4)时, DMP的降解效率较高。此外, 使用两种淬灭剂(乙醇和叔丁醇)与DMP进行竞争性实验, 结合电子自旋共振检测, 表明SO₄·⁻和·OH都是体系主要的自由基。此外, 还对g-C₃N₄的可持续性性能进行考察, 四次循环实验结果显示, 该催化剂具有良好的可重复利用性。对DMP降解进行总有机碳测定, 发现降低了19%。最后, 利用液相色谱质谱联用对DMP降解产物进行定性定量分析, 发现DMP主要通过SO₄·⁻和·OH对苯环的攻击以及脂肪族链的氧化断键这两种途径进行降解。综上所述, 利用可见光激发g-C₃N₄产生的光电子能有效活化PMS降解顽固型有机污染物, 可为实现太阳能活化PMS技术提供有力的技术参考。

关键词: 石墨相氮化碳; 可见光; 过一硫酸盐; 邻苯二甲酸二甲酯; 活化; 降解

收稿日期: 2019-04-19. 接受日期: 2019-07-05. 出版日期: 2020-02-05.

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基金来源: 江苏省自然科学基金青年基金(BK20160936, BK20160938); 国家自然科学基金青年基金(51708297); 江苏省优势学科建设项目.

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