Short communication

Insights into heterogeneous catalytic activation of peroxydisulfate by Pd/g-C₃N₄: The role of superoxide radical and singlet oxygen

Yanbin Wang^a, Di Cao^{a,b}, Man Liu^c, Xu Zhao^{a,b,*}^a Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China^b University of Chinese Academy of Sciences, Beijing 100049, PR China^c School of Civil Engineering and Transportation, Hebei University of Technology, Tianjin 300401, PR China

ARTICLE INFO

Keywords:

Pd nanoparticles

Graphitic carbon nitride

Peroxydisulfate

Singlet oxygen

ABSTRACT

Pd nanoparticles anchored on graphitic nitride carbon (Pd/g-C₃N₄) hybrid catalytic system was prepared by a simple KBH₄ reduction method. Pd/g-C₃N₄ was very active in the degradation of bisphenol A (BPA) by efficiently activating peroxydisulfate (PDS). Important influencing factors, such as catalyst dosage, PDS concentration, pH and reaction temperature for the BPA removal were investigated. Pd/g-C₃N₄-PDS demonstrated a wide effective pH range, namely 3.0–9.0. Radical quenching tests and electron spin resonance (ESR) analyses revealed that superoxide radical (O₂^{•−}) and singlet oxygen (¹O₂) instead of sulfate radical (SO₄^{•−}) and hydroxyl radicals (•OH) were the major oxidized species for the degradation of BPA.

1. Introduction

Advanced oxidation processes (AOPs) based on sulfate radical (SO₄^{•−}) have been increasingly recognized as alternative methods for degrading refractory organic contaminants [1]. SO₄^{•−} possesses high oxidation potential (SO₄^{•−}, 2.5–3.1 V vs. NHE), which is even higher than that of hydroxyl radical (•OH, 1.8–2.7 V vs. NHE). In general, SO₄^{•−} is generated from the activation of peroxydisulfate (PDS) or peroxydisulfate (PDS) by heating, UV irradiation [2], bases [3], and transition metals [4]. Without the need of energy input, PDS activation by transition metals (e.g., Co²⁺, Fe²⁺ and Mn²⁺) and their oxide counterparts (e.g., Co₃O₄ [5], CoFe₂O₄ [6], CuFe₂O₄ [7–9] and MnO₂ [10]) have attracted considerable attention. However, the inevitable metal leaching leads to secondary pollution. Recently, some carbonaceous materials, such as reduced graphene oxide [11], activated carbon [12] and carbon nanotubes [13] displayed high catalytic activity for the activation of PDS.

Generally, SO₄^{•−} and/or •OH generated from PMS/PDS activation are responsible for the degradation of organics. However, it was found that the inhibitory effect of ethanol/methanol (scavenger for both •OH and SO₄^{•−}) on the degradation of organics in heterogeneous activation of PMS/PDS was insignificant [14–17]. In these reports, SO₄^{•−} and/or •OH were not assigned to be the major oxidized species for the degradation of organics. Instead, non-radical oxidation mechanisms were proposed. For example, Zhang et al. [17] suggested that the outer-

sphere interaction between the CuO and PDS caused the electron rearrangement of PDS molecular, which subsequently increased the oxidizing power of PDS. Similar phenomena were also observed in the PDS activation by carbon nanotubes (CNTs) [16] and graphitized nanodiamond [18], in which process reactive complexes were formed due to the interplay of PDS and CNTs, where immediately decomposed upon reaction with the organic compounds. Ahn et al. [19] found that noble metals, such as Pt, Pd, Au and Ag also possess catalytic activity for the activation of PMS. The latter was believed to act as an oxidant that directly accepts electrons from the organic compound with the help of noble metal, and no radical is formed during reaction. Feng et al. [20] claimed that degradation of 1,4-dioxane is due to the surface-bound sulfate radical, which is generated from the activation of PMS on alumina-supported palladium (Pd/Al₂O₃). Therefore, more efforts still need to be made for further understanding the intrinsic catalytic mechanism of PMS activation by Pd.

Graphitic carbon nitride (g-C₃N₄) with characteristic N-coordinating cavities has attracted increasing interest in the field of material and catalytic science [21]. It might be facilely produced at a large scale with low cost. In this work, g-C₃N₄ was prepared via one-step polymerization of urea, where Pd nanoparticles were anchored into the cavities of g-C₃N₄ to form Pd nanoparticles modified g-C₃N₄ hybrid system (Pd/g-C₃N₄). The latter was used as heterogeneous catalyst for the activation of PMS. Bisphenol A (BPA), an endocrine disrupting compound, is released from landfill leachates, paper and plastics plants [22]. It was

* Corresponding author at: Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China.

E-mail address: zhaoxu@rcees.ac.cn (X. Zhao).

<http://dx.doi.org/10.1016/j.catcom.2017.08.016>

Received 8 May 2017; Received in revised form 8 August 2017; Accepted 9 August 2017

Available online 10 August 2017

1566-7367/ © 2017 Elsevier B.V. All rights reserved.

selected as a target pollutant to evaluate the catalytic activity of Pd/g-C₃N₄. Compared with the current technologies (e.g., photo-Fenton [23], electro-Fenton [24] and photocatalysis [25]) for the degradation of BPA, Pd/g-C₃N₄-PMS system requires no energy input and leads to no secondary pollution. Important influencing factors for the BPA removal, such as PMS concentration, catalyst dosage, pH value and reaction temperature were investigated. A plausible mechanism was proposed based on X-ray photoelectron spectroscopy (XPS) and electron spin response (ESR) studies and radical quenching tests.

2. Experimental

2.1. Catalyst preparation

The g-C₃N₄ support material was prepared by heating urea at 600 °C with a ramp rate of 5 °C/min for 2 h in a closed alumina crucible placed in a muffle furnace. 2.5 g prepared g-C₃N₄ were dispersed in 250 mL deionized water and magnetically stirred in an ultrasonic bath for 1 h. Subsequently, 11.8 mL of a solution of PdCl₂ (0.01 M) and NaCl (0.04 M) were added, and the resulting suspension was further stirred in the ultrasonic bath for 1 h. Then, freshly prepared aqueous solution of KBH₄ (3.5 mL, 0.5 M) was added to this slurry and stirred for 24 h. The obtained Pd/g-C₃N₄ catalyst was separated by vacuum filtration, washed with deionized water, and vacuum dried overnight at 50 °C.

2.2. Catalyst characterization

Detailed information of chemicals and reagents, catalyst characterization studies, catalytic activity tests and analytical methods are provided in Supporting Information.

3. Results and discussion

3.1. Characterization of Pd/g-C₃N₄

Pd/g-C₃N₄ shows a similar X-ray diffraction (XRD) pattern with the pristine g-C₃N₄ (Fig. S1), suggesting that the crystal structure of g-C₃N₄ is not changed after the introduction of Pd nanoparticles. No diffraction peaks of Pd nanoparticles are observed in the XRD pattern of Pd/g-C₃N₄, which might be the result of Pd content below the detection limit of XRD and/or the peak broadening from the small size of Pd nanoparticles formed. Scanning electron microscope (SEM) images of g-C₃N₄ and Pd/g-C₃N₄ are shown in Fig. S2. It can be seen that Pd/g-C₃N₄ exhibits a layered structure and no obvious changes are observed compared with pristine g-C₃N₄. The bright regions in the scanning transmission electron microscope (STEM) image of Pd/g-C₃N₄ (Fig. 1a) point out the presence of Pd nanoparticles, which are highly dispersed on g-C₃N₄ with estimated size in the 2–4 nm range (inset in Fig. 1a).

The N₂ adsorption-desorption isotherms of g-C₃N₄ and Pd/g-C₃N₄ reveal that all the samples exhibit typical IV isotherms with H3-type hysteresis loop in the relative pressure range of 0.8–1.0 (Fig. S3). This indicates the existence of mesoporous structure originated from the stacking of g-C₃N₄ nanosheets. The BET specific surface area of g-C₃N₄ and Pd/g-C₃N₄ are 65 and 59 m²·g^{−1}, respectively, indicating that the existence of Pd nanoparticles only little might affect the structure of g-C₃N₄. The pore size distribution curves present two peaks at about 2 and 30 nm, which might be beneficial to mass transfer effects during the catalytic process.

The surface composition and chemical oxidation states of Pd/g-C₃N₄ were determined by XPS (Fig. S4). The elements of C, N, O and Pd are observed in the survey spectrum. The N 1s spectrum was fitted into four peaks at 397.5, 398.3, 399.9 and 403.4 eV, which can be assigned to the sp²-hybridized nitrogen (C–N=C), tertiary nitrogen (N–(C)₃), amino functional groups (C–N–H) and the charging effects, respectively [26]. The XPS spectra of Pd 3d before and after reaction are presented in Fig. 1b, in which the peaks at 342.6 and 337.2 eV are assigned to Pd^{II},

while the peaks at 340.6 and 335.3 eV to Pd⁰ [27]. After the degradation reaction, the Pd⁰/Pd^{II} ratio decreases from 2.02 to 1.19, illustrating that part of Pd⁰ changed to Pd^{II} during the PMS activation catalytic process.

3.2. The catalytic performance of Pd/g-C₃N₄

The adsorption ability of Pd/g-C₃N₄ toward BPA was investigated first and the removal of BPA by adsorption was found to be insignificant (Fig. 2a). Meanwhile, the degradation of BPA by PMS was negligible due to the low oxidative capacity of PMS. The g-C₃N₄ presented poor catalytic activity for activation of PMS, which is consistent with the previous report [28]. However, degradation efficiency of BPA was achieved using the Pd/g-C₃N₄-PMS catalytic system. It was found that 91% of BPA (20 mg·L^{−1}) can be removed in 60 min with 0.1 g·L^{−1} of catalyst loading and 1.0 mM of PMS, which indicates the good catalytic performance of Pd/g-C₃N₄ for the activation of PMS.

To comprehensively evaluate the catalytic performance of Pd/g-C₃N₄-PMS, the influence of PMS concentration, catalyst loading, pH value and reaction temperature were systematically investigated. As shown in Fig. S5a, the removal efficiency of BPA increases from 74% to 91% in 60 min when the PMS concentration increases from 0.2 to 1.0 mM. However, only 5% enhancement is achieved when PMS concentration further increased to 1.5 and 2.0 mM. It is inferred that the active sites were almost occupied by PMS (1.0 mM). Fig. S5b indicates that catalyst loading has a great influence on the BPA removal rate. The degradation rate constant of BPA increases from 0.038 to 0.463 min^{−1} with catalyst loading increasing from 0.1 to 0.4 g·L^{−1}. One reasonable explanation might be that more active sites are present for the activation of PMS at higher catalyst loadings. To investigate the influence of pH on the BPA removal rate, the pH of the suspension was maintained at a certain pH value (± 0.2) after adjustment with 0.1 M H₂SO₄ and 0.1 M NaOH at all times. As illustrated in Fig. S5c, the catalytic ability of Pd/g-C₃N₄ is greatly influenced by the pH of solution. With the pH increasing from 3.0 to 9.0, the degradation rate of BPA increases from 0.034 to 0.114 min^{−1}. However, when the pH is further increased to 11.0, the degradation rate of BPA decreases to 0.023 min^{−1}. The pK_a value of PMS is 9.4 [29], thus the SO₅^{2−} is the dominant species when the pH of solution is higher than 9.4. As reported elsewhere [30], the redox potential of SO₅^{2−} (1.22 V vs. NHE) is lower than HSO₅[−] (1.75 V vs. NHE). In addition, SO₅^{2−} is much more difficult to react than HSO₅[−] [31].

The effect of reaction temperature (25, 35 and 45 °C) on the BPA removal rate is shown in Fig. 2b. The degradation rate constants of BPA were estimated and found to be 0.0367, 0.0629 and 0.0969 min^{−1} at 25, 35 and 45 °C, respectively. According to the Van't Hoff's equation, the negative slope (inset in Fig. 2b) indicates that the catalytic reaction process is endothermic and the activation energy (*E*_a) for degradation of BPA was estimated to be 38.6 kJ·mol^{−1} (*R*² = 0.989).

3.3. The plausible mechanism in Pd/g-C₃N₄-PMS

3.3.1. Radical quenching tests

To identify the reactive oxygen species (ROS) generated in the Pd/g-C₃N₄-PMS system, radical quenching tests were conducted at 0.1 g·L^{−1} catalyst loading and 1 mM PMS concentration with different scavengers added at room temperature. Methanol (MeOH) can scavenge both ·OH (*k*_{MeOH·OH} = 9.7 × 10⁸ M^{−1}·s^{−1}) and SO₄·[−] (*k*_{MeOH·SO₄·} = 2.5 × 10⁷ M^{−1}·s^{−1}), whereas *tert*-butyl alcohol (TBA) only scavenge ·OH since it reacts with SO₄·[−] over 1000-fold slower than with ·OH (*k*_{TBA·OH} = 3.8–7.6 × 10⁸ M^{−1}·s^{−1}; *k*_{TBA·SO₄·} = 4.0–9.1 × 10⁵ M^{−1}·s^{−1}). To guarantee complete quenching of free radicals, the degradation experiments of BPA with different molar ratios between scavenger and PMS were carried out (Fig. S6). The degradation of BPA is not significantly inhibited by TBA/MeOH even using 1000:1 molar ratio of TBA/MeOH:PMS (Fig. S7). Compared with the control experiment, the degradation rate constant of BPA decreased by 3% and 10% with TBA and MeOH as scavengers, respectively

Fig. 1. (a) STEM image of Pd/g-C₃N₄ and the Pd nanoparticle size distribution (inset); (b) high-resolution XPS spectra of Pd 3d before and after reaction.

Fig. 2. (a) BPA removal at different systems; (b) the influence of reaction temperature on BPA removal in Pd/g-C₃N₄-PMS and Arrhenius plot (inset). Reaction conditions: [BPA]₀ = 20 mg·L⁻¹, [PMS] = 1 mM, [Pd/g-C₃N₄] = 0.1 g·L⁻¹.

Fig. 3. The pseudo-first-order kinetic rate constant of BPA degradation in the presence of different scavengers. Reaction conditions: [BPA]₀ = 20 mg·L⁻¹, [PMS] = 1 mM, [Pd/g-C₃N₄] = 0.1 g·L⁻¹, [MeOH] = [TBA] = 1000 mM, [p-BQ] = [L-histidine] = 12 mM.

(Fig. 3). Therefore, it can be concluded that $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ are not the major oxidizing species for the degradation of BPA. Other ROS might be involved in the case of Pd/g-C₃N₄-PMS system. As shown in Fig. 3, the degradation rate of BPA is greatly reduced in the presence of *p*-benzoquinone (*p*-BQ), which is a scavenger of superoxide radical ($\text{O}_2^{\cdot-}$) with a rate constant of $0.9\text{--}1.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ [32]. The BPA degradation is almost completely quenched with the addition of L-histidine, which is a

scavenger of singlet oxygen ($^1\text{O}_2$) [18]. These results demonstrate that $\text{O}_2^{\cdot-}$ and $^1\text{O}_2$ play a key role for the degradation of BPA in the Pd/g-C₃N₄-PMS system. It can be concluded that $\text{O}_2^{\cdot-}$ and $^1\text{O}_2$ instead of $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ are the major oxidizing species in the Pd/g-C₃N₄-PMS system and the experimental conditions applied.

3.3.2. ESR analysis

To further confirm the kind of ROS involved in the Pd/g-C₃N₄-PMS system, ESR studies were carried out. Neither DMPO-OH nor DMPO-SO₄ signals were observed (Fig. 4a), which is consistent with the radical quenching tests. 2,2,6,6-Tetramethyl-4-piperidone (4-oxo-TEMPO) was used to trap $^1\text{O}_2$ with the formation of 2,2,6,6-tetramethyl-4-oxo-piperidin-1-oxyl (4-oxo-TEMPO) [33]. As shown in Fig. 4b, the characteristic triplet of 4-oxo-TEMPO ($a_N = 16.9 \text{ G}$, $g = 2.0054$) was observed, indicating the existence of $^1\text{O}_2$ in the Pd/g-C₃N₄-PMS system. In addition, the intensity of 4-oxo-TEMPO remained after 60 min, although it decayed with reaction time.

According to the radical quenching process, ESR/XPS analyses and the previous reports, a plausible mechanism could be inferred. For the Pd/g-C₃N₄-PMS system, H_2O_2 generated from the reaction between HSO_5^- and H_2O (Eq. (1)[3]) is catalyzed by Pd^0 to form Pd^0OH (Eq. (2)). Then, $^1\text{O}_2$ is generated according to Eqs. (3)–(4). As it is well known, PMS is easily activated via hemolytic cleavage to simultaneously produce $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ owing to its asymmetric structure. Therefore, PMS could be catalyzed by Pd^0 to form surface-bound radical

Fig. 4. ESR spectra obtained in Pd/g-C₃N₄-PMS using DMPO (a) and 4-oxo-TEMP (b) as spin-trapping agents.

intermediates $\cdot\text{OHPd}^0\text{SO}_4^-$ (Eq. (5)) [20], which finally decompose to Pd^{II} , SO_4^{2-} and H^+ (Eq. (6)). $\text{Pd}^0\cdot\text{OH}$ reacts also with H_2O_2 to generate $\cdot\text{OOH}$ (Eq. (7)).

4. Conclusions

Pd/g-C₃N₄ was prepared via a simple KBH₄ reduction method and Pd nanoparticles (d ~ 2–4 nm) were highly dispersed on g-C₃N₄. Pd/g-C₃N₄ exhibited high heterogeneous catalytic activity for the activation of PMS. At the conditions of catalyst loading of 0.1 g L⁻¹ and PMS concentration of 1.0 mM, 91% BPA with initial concentration of 20 mg L⁻¹ can be degraded in 60 min. The activation energy for BPA oxidation in Pd/g-C₃N₄-PMS was found to be 38.6 kJ mol⁻¹. The ROSS involved in Pd/g-C₃N₄-PMS system were identified and the results showed that $\text{O}_2^{\cdot-}$ and ${}^1\text{O}_2$ instead of $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ were the major oxidative species for the degradation of BPA.

Acknowledgements

This work was supported by the National Nature Science Foundation of China (grant nos. 21377148, 51438011), the Chinese Academy of Sciences (QYZDB-SSW-DQC018) and China Postdoctoral Science Foundation funded project (grant no. 2017M611022). We appreciate the anonymous reviewers' valuable revision suggestions.

Appendix A. Supplementary data

Including experimental, XRD patterns, SEM images, N₂ adsorption-desorption isotherms, XPS spectra and the BPA degradation curves at different experimental conditions. Supplementary data associated with this article can be found in the online version, at <http://dx.doi.org/10.1016/j.catcom.2017.08.016>.

References

- [1] W.D. Oh, Z.L. Dong, T.T. Lim, *Appl. Catal. B Environ.* 194 (2016) 169–201.
- [2] Y.H. Guan, J. Ma, X.C. Li, J.Y. Fang, L.W. Chen, *Environ. Sci. Technol.* 45 (2011) 9308–9314.
- [3] C.D. Qi, X.T. Liu, J. Ma, C.Y. Lin, X.W. Li, H.J. Zhang, *Chemosphere* 151 (2016) 280–288.
- [4] G.P. Anipsitakis, D.D. Dionysiou, *Environ. Sci. Technol.* 38 (2004) 3705–3712.
- [5] G.P. Anipsitakis, E. Stathatos, D.D. Dionysiou, *J. Phys. Chem. B* 109 (2005) 13052–13055.
- [6] J. Deng, Y.S. Shao, N.Y. Gao, C.Q. Tan, S.Q. Zhou, X.H. Hu, *J. Hazard. Mater.* 262 (2013) 836–844.
- [7] Y.B. Ding, L.H. Zhu, N. Wang, H.Q. Tang, *Appl. Catal. B Environ.* 129 (2013) 153–162.
- [8] Y.H. Guan, J. Ma, Y.M. Ren, Y.L. Liu, J.Y. Xiao, L.Q. Lin, C. Zhang, *Water Res.* 47 (2013) 5431–5438.
- [9] T. Zhang, H.B. Zhu, J.P. Croue, *Environ. Sci. Technol.* 47 (2013) 2784–2791.
- [10] E. Saputra, S. Muhammad, H.Q. Sun, H.M. Ang, M.O. Tade, S.B. Wang, *Environ. Sci. Technol.* 47 (2013) 5882–5887.
- [11] H.Q. Sun, S.Z. Liu, G.L. Zhou, H.M. Ang, M.O. Tade, S.B. Wang, *ACS Appl. Mater. Interfaces* 4 (2012) 5466–5471.
- [12] E. Saputra, S. Muhammad, H.Q. Sun, S.B. Wang, *RSC Adv.* 3 (2013) 21905–21910.
- [13] H.Q. Sun, C. Kwan, A. Suvorova, H.M. Ang, M.O. Tade, S.B. Wang, *Appl. Catal. B Environ.* 154 (2014) 134–141.
- [14] X.G. Duan, H.Q. Sun, Y.X. Wang, J. Kang, S.B. Wang, *ACS Catal.* 5 (2015) 553–559.
- [15] X.G. Duan, Z.M. Ao, H.Q. Sun, L. Zhou, G.X. Wang, S.B. Wang, *Chem. Commun.* 51 (2015) 15249–15252.
- [16] H. Lee, H.J. Lee, J. Jeong, J. Lee, N.B. Park, C. Lee, *Chem. Eng. J.* 266 (2015) 28–33.
- [17] T. Zhang, Y. Chen, Y. Wang, J. Le Roux, Y. Yang, J.P. Croue, *Environ. Sci. Technol.* 48 (2014) 5868–5875.
- [18] H. Lee, H.I. Kim, S. Weon, W. Choi, Y.S. Hwang, J. Seo, C. Lee, J.H. Kim, *Environ. Sci. Technol.* 50 (2016) 10134–10142.
- [19] Y.Y. Ahn, E.T. Yun, J.W. Seo, C. Lee, S.H. Kim, J.H. Kim, J. Lee, *Environ. Sci. Technol.* 50 (2016) 10187–10197.
- [20] Y. Feng, P.H. Lee, D. Wu, K. Shih, *Water Res.* 120 (2017) 12–21.
- [21] Z.W. Zhao, Y.J. Sun, F. Dong, *Nano* 7 (2015) 15–37.
- [22] R.A. Torres, J.I. Nieto, E. Combet, C. Petrier, C. Pulgarin, *Appl. Catal. B Environ.* 80 (2008) 168–175.
- [23] M. Perez-Moya, T. Kaisto, M. Navarro, L.J. del Valle, *Environ. Sci. Pollut. R.* 24 (2017) 6241–6251.
- [24] A. Chmayssem, S. Taha, D. Hauchard, *Electrochim. Acta* 225 (2017) 435–442.
- [25] C.F. Mu, Y. Zhang, W.Q. Cui, Y.H. Liang, Y.F. Zhu, *Appl. Catal. B Environ.* 212 (2017) 41–49.
- [26] B.H. Long, J.L. Lin, X.C. Wang, *J. Mater. Chem. A* 2 (2014) 2942–2951.
- [27] X.Y. Su, A. Vinu, S.S. Aldeyab, L. Zhong, *Catal. Lett.* 145 (2015) 1388–1395.
- [28] Y.F. Tao, Q. Ni, M.Y. Wei, D.S. Xia, X.X. Li, A.H. Xu, *RSC Adv.* 5 (2015) 44128–44136.
- [29] D.L. Ball, J.O. Edwards, *J. Am. Chem. Soc.* 78 (1956) 1125–1129.
- [30] M. Spiro, *Electrochim. Acta* 24 (1979) 313–314.
- [31] G. Lente, J. Kalmar, Z. Baranyai, A. Kun, I. Kek, D. Bajusz, M. Takacs, L. Veres, I. Fabian, *Inorg. Chem.* 48 (2009) 1763–1773.
- [32] P.S. Rao, E. Hayon, *J. Phys. Chem.* 79 (1975) 397–402.
- [33] J. Moan, E. Wold, *Nature* 279 (1979) 450–451.