



Enhanced activation of peroxymonosulfate by nitrogen doped porous carbon for effective removal of organic pollutants



Guanlong Wang, Shuo Chen, Xie Quan*, Hongtao Yu, Yaobin Zhang

Key Laboratory of Industrial Ecology and Environmental Engineering (Ministry of Education, China), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China

ARTICLE INFO

Article history:

Received 22 November 2016

Received in revised form

19 January 2017

Accepted 20 January 2017

Available online 24 January 2017

Keywords:

Peroxymonosulfate activation

Metal-organic frameworks

Nitrogen doped porous carbon

Graphitic N

Sulfate radical

ABSTRACT

Nitrogen doped nanocarbon materials have emerged as promising metal-free catalysts towards peroxymonosulfate (PMS) activation for environmental remediation. However, their catalytic efficiency for PMS activation still needs improvement. Moreover, the relationship between the catalytic efficiency and nitrogen content or species, which is important to clarify the catalytic mechanism, remains unclear. In this study, three nitrogen-rich metal-organic frameworks (ZIF-8, NH₂-MIL-53 and IRMOF-3) with nitrogen content of 24.7 wt%, 6.28 wt% and 5.16 wt% respectively were chosen to prepare the nitrogen doped porous carbons (NPCs) with different nitrogen content. Several carbonization temperatures were employed to obtain the NPCs with varying nitrogen species. The PMS catalytic performance of NPCs and its relationship with nitrogen content or species were investigated. The results showed all the NPCs exhibited enhanced PMS activation for phenol degradation compared with the nitrogen-free porous carbon (obtained from MOF-5), and was even superior to the most effective PMS activator of homogeneous Co²⁺. The ZIF-8 derived NPC carbonized at 1000 °C, with the highest graphitic N content, displayed best performance with the kinetic constant of phenol degradation 4 times higher than that on porous carbon. The graphitic N plays a critical role for activating PMS to produce sulfate radical and hydroxyl radical.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Advanced oxidation processes (AOPs) are believed to be efficient approaches for complete decomposition of organic pollutants. The hydroxyl radical ($\cdot\text{OH}$), generated from Fenton or Fenton like process, are highly reactive to nearly all organic compounds. However, Fenton process suffers from the disadvantages such as the requirement of acidic pH condition (around 3) and the accumulation of iron containing sludge, resulting in the secondary pollution and catalysts loss [1,2]. Heterogeneous Fenton process could avoid the generation of massive iron containing sludge, but it still exhibits low catalytic efficiency [3,4]. During the past decades, the sulfate radical ($\text{SO}_4^{\cdot-}$)-based AOPs have attracted increasing research interests in environmental remediation [5–8]. $\text{SO}_4^{\cdot-}$, with a redox potential of 2.5–3.1 V, could be a potential alternative to $\cdot\text{OH}$ due to its strong oxidizing capability, long life span (30–40 μs), wide pH adaptive range (2–8) and high selectivity to organics with

unsaturated bond and aromatic structure [9–11]. Generally, $\text{SO}_4^{\cdot-}$ is generated from activating peroxydisulfate (PDS) or peroxymonosulfate (PMS) by heating [12], UV irradiation [13] and transitional metal ions or metallic oxidants catalysis [14–16]. However, the high energy input of heating or UV irradiation method and the inevitable toxic metal leaching of transitional metal/PMS system limit their practical application [17,18]. Therefore, it is highly desirable to develop a green and metal-free catalyst with strong PMS activation capability for environmental remediation.

Recently, nanocarbon materials such as graphene and carbon nanotube have shown their catalytic activity in PMS activation to yield the $\text{SO}_4^{\cdot-}$ [19,20]. The large surface area, unique surface chemistry property and metal-free nature of nanocarbon materials make them promising alternative to metal-based catalysts in environmental remediation [21]. What's more, it has been reported that doping nitrogen atom into the carbon matrixes could greatly improve their catalytic performance towards PMS activation [22–24]. The doped nitrogen could not only increase the surface basicity which is favorable for PMS adsorption, but also facilitate electron transfer reaction with PMS by activating the neighboring

* Corresponding author.

E-mail address: quanxie@dlut.edu.cn (X. Quan).

sp² carbon atoms, thus resulting in the improved catalytic efficiency [25–27]. Besides the nitrogen doping level, the nitrogen species may also influence the catalytic activity of nitrogen doped carbon [26,28]. Despite the above progress, the catalytic efficiency of nitrogen doped carbon for PMS activation still needs to be improved. Moreover, the relationship between the catalytic capability of nitrogen doped carbon and nitrogen content or species is still unclear. Thus, more efforts still need to be made for further enhancing the PMS catalytic performance of nitrogen doped carbon materials and gaining better understanding of their intrinsic catalytic mechanism.

The porous carbon synthesized from carbonization of metal-organic frameworks (MOFs) has attracted extensive attention due to its unique properties such as high specific surface area and hierarchically porous structure (micro-, meso-, or even macropores) [29–32]. Such properties endow the porous carbon with abundant exposed active sites and shortened diffusion pathways for reactant [33–35], which may give rise to the enhanced efficiency for PMS activation. Since the organic ligands of MOFs contain various atoms including C, N, O, P or S, different types of heteroatom doped porous carbon could be simply obtained through directly carbonizing the corresponding MOFs. Especially, the MOFs rich in nitrogen are ideal precursors to produce the porous carbon with uniform nitrogen doping [36–38]. More importantly, the nitrogen content and species related to the intrinsic catalytic activity could be easily tuned by rationally choosing MOF precursors or changing the carbonization temperature, thus making it easier to study their relation with the catalytic activity of nitrogen doped porous carbons (NPCs) and obtain the highly active NPC catalysts. Taking these advantages into account, constructing the NPCs from nitrogen-rich MOFs may provide a promising method for PMS activation.

In this study, three nitrogen-rich MOFs (ZIF-8, NH₂-MIL-53 and IRMOF-3) with nitrogen content of 24.7 wt%, 6.28 wt% and 5.16 wt% respectively were chosen to prepare the NPCs with varying nitrogen content. Different carbonization temperatures were used to synthesize the NPCs with varying nitrogen species. These NPCs were employed as catalysts for PMS activation to study the relationship between the catalytic activity of NPCs and nitrogen content or species. Several ubiquitous pollutants including the phenol, bisphenol A, methyl orange and rhodamine B were selected to evaluate the catalytic performance of NPCs for PMS activation. Furthermore, the catalytic mechanism of PMS activation on NPC was explored and analyzed.

2. Experimental

2.1. Preparation of nitrogen doped porous carbon (NPC)

ZIF-8 with high nitrogen content (24.7 wt%) was chosen as the precursor and it was synthesized according to the method reported previously [39]. Briefly, 10 mL Zn(NO₃)₂·6H₂O solution (74.4 g L⁻¹) was added into 90 mL imidazole derivative (2-methylimidazole) solution (137 g L⁻¹) at room temperature. The mixture, which immediately turned into a turbid liquid, was stirred with a magnetic bar for 24 h, and the milky colloidal dispersion was then centrifuged at 8000 rpm for 10 min. The deposited particles were washed with methanol three times and dried at 40 °C for 48 h to obtain ZIF-8. Finally, the synthesized ZIF-8 crystals were carbonized at 800, 900, 1000 and 1100 °C, respectively under Ar atmosphere for 5 h. The ZIF-8 derived NPC carbonized at X °C is denoted as the NPC_{ZIF-8-X}. The effect of carbonization temperature on catalytic performance of NPC_{ZIF-8} was initially evaluated (details in Text S1 and Fig. S1) and the results showed that the NPC_{ZIF-8} carbonized at 1000 °C displayed best catalytic performance. Thus, the NPC_{ZIF-8-1000} was used for the following experiments unless otherwise

specified. As references, two other nitrogen-containing MOFs (IRMOF-3 and NH₂-MIL-53 with nitrogen content of 6.28 wt% and 5.16 wt%, respectively) and the nitrogen-free MOF (MOF-5) were also prepared and carbonized under 1000 °C to obtain the NPC_{IR-MOF-3}, NPC_{NH₂-MIL-53} and PC_{MOF-5} respectively, and their detailed synthesis procedure could be found in the Text S3 of the supporting information. Before tests, the resultant materials were washed thoroughly in 5% HF to remove residual metal species. Subsequently, the obtained powders were further washed three times in ultrapure water (resistivity >18 MΩ cm), and then dried under vacuum conditions for 24 h at 40 °C.

2.2. Characterizations

The morphologies and structures of catalysts were observed by field emission scanning electron microscope (FE-SEM, HitachiS-4800). The crystal structure of the catalyst was characterized using X-ray diffraction (XRD, Shimadzu LabXRD-6000). The carbonization degree of catalyst was evaluated via Raman spectrum (Renishaw Micro-Raman system 2000 spectrometer with He–Ne laser excitation (wavelength 623.8 nm). The element composition was characterized by X-ray photoelectron spectroscopy (XPS) got from a VG ESCALAB 250 spectrometer using a non monochromatized Al Kα X-ray source (1486.6 eV) with the pass energy high resolution scan at 30 eV and survey scan at 100 eV. Spectra were analyzed with XPSPEAK41 software. Component fitting for each element was based on Gaussian-Lorentzian product function with a 20% Lorentzian-Gaussian value using Shirley background. The C 1s at 284.5 eV was used as the reference for charge correction. The BET specific surface area, pore size distribution and pore volume were determined through N₂ adsorption-desorption isotherms at 77 K with a Quadrasorb instrument. To probe the electron transfer resistance at different interface of NPC/PMS, electrochemical impedance spectroscopy (EIS) was performed with an electrochemical station (CHI660D, Shanghai Chenhua Ltd., China) in a conventional three-electrode system with the NPC as a working electrode, Pt as a counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The electrolyte was composed of 0.01 M Na₂SO₄ and 1.6 mM PMS.

2.3. Evaluation of catalytic performance

The catalytic performance tests were carried out in a 100 mL beaker at 25 °C. NPC (0.2 g L⁻¹) was dispersed in 50 mL solution of 20 mg L⁻¹ phenol and stirred for 40 min to establish the adsorption-desorption equilibrium, followed by adding PMS (1.6 mM) to initiate the reaction. During each time interval, 1 mL solution was withdrawn by a syringe and filtered through a 0.22 μm Millipore film. Then 0.1 mL methanol was injected into the reaction solution as a quenching reagent. The concentration of phenol and total organic carbon (TOC) in the samples were then tested. Sodium nitrite was added in the TOC samples as quenching reagent. The experiments were conducted in triplicates, and the average values with standard deviations were presented. The effects of NPC dosage, PMS loading, temperature, pH, phenol concentration and inorganic ions on degradation efficiency of phenol were evaluated. The pH of solution was adjusted by adding 0.1 M HCl or NaOH. In the reusability test of NPC, the used NPCs were collected via vacuum filtration and washed with ultrapure water (resistivity >18 MΩ cm).

Three other kinds of organic compounds including rhodamine B (RhB), methyl orange (MO) and bisphenol A (BPA) were also taken as target pollutants to evaluate the catalytic performance under the same reaction conditions of phenol. To ascertain the radical species formed in the catalytic system, two sets of quenching tests were

Download English Version:

<https://daneshyari.com/en/article/5432320>

Download Persian Version:

<https://daneshyari.com/article/5432320>

[Daneshyari.com](https://daneshyari.com)