Synergic mechanism of adsorption and metal-free catalysis for phenol degradation by N-doped graphene aerogel

Xiaohua Ren [a, b], Huanhuan Guo [a], Jinkui Feng [a], Pengchao Si [a], Lin Zhang [a, **], Lijie Ci [a, *]

[a] SDU & Rice Joint Center for Carbon Nanomaterials, Key Laboratory for Liquid-Solid Structural Evolution & Processing of Materials (Ministry of Education), School of Materials Science and Engineering, Shandong University, Jinan 250061, China
[b] Weifang University of Science and Technology, Weifang 262700, China

HIGHLIGHTS

- N-rGO aerogels exhibit promising catalytic performance for phenol.
- Adsorption has an important effect on phenol catalytic degradation.
- Both $SO_4^{\cdot-}$ and $\cdot OH$ are generated in the N-RGO-A/PS system, and $SO_4^{\cdot-}$ plays the dominant role.
- DFT calculations verify carbon atoms linked to graphitic N are most active.
- The activation mechanism of persulfate relies on electron-transfer to N-rGO.

ARTICLE INFO

ABSTRACT

3D porous N-doped reduced graphene oxide (N-rGO) aerogels were synthesized by a hydrothermal reduction of graphene oxide (GO) with urea and following freeze-drying process. N-rGO aerogels have a high BET surface of 499.70 m^2/g and a high N doping content (5.93—7.46 at%) including three kinds of N (graphitic, pyridinic and pyrrolic). Their high catalytic performance for phenol oxidation in aqueous solution was investigated by catalytic activation of persulfate (PS). We have demonstrated that N-rGO aerogels are promising metal-free catalysts for phenol removal. Kinetics studies indicate that phenol degradation follows first-order reaction kinetics with the reaction rate constant of 0.16799 min^{-1} for N-rGO-A(1:30). Interestingly, the comparison of direct catalytic oxidation with adsorption-catalytic oxidation experiments indicates that adsorption plays an important role in the catalytic oxidation of phenol by decreasing the phenol degradation time. Spin density and adsorption modeling demonstrates that graphitic N in N-rGO plays the most important role for the catalytic performance by inducing high positive charge densities to adjacent carbon atoms and facilitating phenol adsorption on these carbon sites. Furthermore, the activation mechanism of persulfate (PS) on N-rGO was first investigated by DFT method and PS can be activated to generate strongly oxidative radical ($SO_4 \cdot ^-$) by transferring electrons to N-rGO.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

One of the most serious issues in industrialization is the discharge of organic wastewater. Particularly, wastewater containing phenol or phenolic compounds can be produced in various fields, such as petrochemical, pesticide manufacture, dye and pharmaceutical industries (Liu et al., 2016b). The phenol or phenolic compounds are strongly harmful to aquatic life and human health due to their toxic and refractorily biodegradable properties. Therefore, various techniques (Abdelwahab et al., 2008; Babuponnusami and Muthukumar, 2012; Mukherjee and De, 2014; Long et al., 2015), including physical adsorption, chemical oxidation, photocatalytic and electro-fenton processes, have been widely developed. Among these technologies, advanced oxidation processes (AOPs) have been taken more attention because of the complete decomposition of organic contaminants.

Generally, hydroxyl radicals ($\cdot OH$) was generated to remove the refractory organic pollutants in AOPs. Recently, being an attractive

---

alternative to ·OH, catalytic oxidation by sulfate radicals (SO_4^-) generated by persulfate (PS) or peroxymonosulfate (PMS) activation has emerged as a promising method (Long et al., 2012; Indrawirawan et al., 2015a; Wang et al., 2015; Liu et al., 2016a). Moreover, SO_4^- has a comparable or even superior oxidative potential of 2.5–3.1 V compared to ·OH (2.7 V), and can be applicable to a wide pH range (Shukla et al., 2011; Sun et al., 2014). Homogeneous Co(II)/peroxymonosulfate (PMS) and heterogeneous catalysis with cobalt oxide or iron oxide have been proved to efficiently oxidize organic pollutants (George P. Anipsitakis et al., 2005; Anipsitakis et al., 2006; Ling et al., 2010; Gao et al., 2016). However, the barriers of these systems are the metal ions leaching, leading to secondary contamination to water body and causing environmental issues (Sun et al., 2014). Therefore, more and more attentions have been focused on metal-free catalysts, such as carbon nanomaterials, which are cheap and environmental friendly, and highly in need of green and sustainable development.

Previously, reduced graphene oxide (rGO) was first reported to be effective in activating PMS to generate sulfate radicals (SO_4^-), and the adsorptive and catalytic performances of rGO were improved with increasing specific surface area and oxygen containing groups (Peng et al., 2013). More recently, rGO was found to be an effective metal-free catalyst to activate PS by weakening the O–O band at the active sites and working as an excellent electron bridge (Duan et al., 2015d). Additionally, annealed nanodiamond (Duan et al., 2016), cubic mesoporous carbon (Duan et al., 2017) and CNT (Jian et al., 2016) were also reported to have the ability to activate PS and degrade organic pollutants. Furthermore, the catalytic performances of carbon nanomaterials were reported to be enhanced by doping with other elements such as N, B and S (Long et al., 2012; Kong et al., 2013; Sun et al., 2013; Duan et al., 2014; Indrawirawan et al., 2015a), and several activation and phenol oxidation mechanisms were proposed based on the experimental results and DFT calculations (Duan et al., 2014, 2015a, 2015b; Indrawirawan et al., 2015a, 2015b). However, it is not sufficient to understand the detailed catalytic and reactive mechanisms due to the limitations of in situ characterization methods. Furthermore, the catalytic performance and activity origins of N-rGO as electrocatalysts for oxygen reduction reaction (ORR) have been investigated a lot (Zheng et al., 2012; Tian et al., 2014; Wang and Su, 2014; Shui et al., 2015; Yang et al., 2016), but it is still confusing and controversial for the essential active sites and detailed mechanism. For example, on the one hand, Geng et al. (2011). proposed that the graphitic-type N in N-doped graphene probably has the most important effect on ORR activity. Yang et al. (2016). first demonstrated experimentally that quaternary N sites as the electron donor were responsible for ORR activity. On the other hand, recent reports (Ding et al., 2015; Liu and Dai, 2016) expected that the active site should be the pyridinic N with a lone electron pair, which could enhance the electron-donating capability and weaken the O–O bond. Guo et al. (2016). presented that the ORR active sites of N-doped carbon materials originate from the carbon atoms with Lewis basicity next to pyridinic N. Similarly, the confusion of the active sites and catalytic mechanism for N-doped carbon nanomaterials could remain in the catalytic oxidation of organic pollutants, and the crucial active sites and reaction mechanism for catalytic oxidation of phenol by N-rGO have never been studied with theoretical simulation.

Additionally, most reported N-rGO catalysts are in powder form, which makes the separation after reaction time-consuming and costly, hindering the practical application of these promising metal-free catalysts. Therefore, in this study, N-rGO aerogels were synthesized with a simple hydrothermal and freeze-drying method, and its adsorption and catalytic performances on phenol solution were further investigated. More importantly, the active

sites of N-rGO for phenol adsorption and PS activation mechanism by N-rGO were first studied with theoretical simulation.

2. Experiment and simulation

2.1. Materials and chemicals

Expandable graphite was purchased from Henglide Graphite Company (Qingdao, China). NaCl, concentrated H_2SO_4, $NaNO_3$, $KMnO_7$, H_2O_2, urea and HCl were all purchased from Sinopharm Chemical Reagent Co., Ltd., China. All these chemicals were of analytical grade purity and used without further purification. Phenol and 5,5-dimethylpyrroline-oxide (DMPO) were obtained from Aladdin, and sodium persulfate was purchased from Sigma-Aldrich.

2.2. Preparation of N-doped reduced graphene oxide aerogel (N-rGO aerogel)

Graphene oxide (GO) was prepared with a modified Hummers method (Hummers and Offeman, 1958; Choi et al., 2010) and used as the carbon precursor for N-doped reduced graphene oxide aerogel (N-rGO aerogel). The N-rGO aerogel (N-rGO-A) was synthesized by the hydrothermal reduction of GO with urea as the N precursor and following freezy-drying method. Briefly, a mount of urea was dissolved in 40 mL of 2 mg/mL GO water solution, and the mixture was transferred into a 50 mL Teflon-lined autoclave, and maintained at 180 °C for 12 h. Then, the formed N-rGO hydrogel was immersed in deionized water for 72 h to remove the residual agents. Finally, the N-rGO-A was achieved by vacuum freeze-drying for 48 h. N-rGO aerogels were prepared with four mass ratios of GO and urea (1:10, 1:20, 1:30 and 1:40), and denoted as N-rGO-A (1:10), N-rGO-A (1:20), N-rGO-A (1:30) and N-rGO-A (1:40) respectively. For comparison, rGO aerogel (rGO-A) was prepared by the same method without introducing urea.

2.3. Characterizations

The morphology of the as-synthesized materials was characterized by field emission scanning electron microscope (FE-SEM, Hitachi SU-70, Japan). The structural characterization was analyzed with Raman spectroscopy (Renishaw InVia Reflex) and X-ray diffraction (XRD, Miniflex 600). The surface functional groups were determined with Fourier transform infrared spectroscopy (FT-IR, Bruker Tensor 37) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250, ThermoFisher SCIENTIFIC). The Brunauer-Emmett-Teller (BET, ASAP 2020, Micromeritics) specific surface area was evaluated from the N_2 adsorption isotherm. Thermogravimetric analysis (TGA, METTLER TOLEDO) was carried out by heating the samples in air atmosphere at a 10 °C/min heating rate. Electron paramagnetic resonance (EPR) spectrum of active radicals trapped by DMPO was recorded at room temperature on a JES-X320 spectrometer and the settings were as follows: center field, 3256 G; microwave frequency, 9.15 GHz; microwave power, 3 mW; modulation frequency, 100 KHz; sweep width, 100 G; time constant, 0.03 s; sweep time, 30 s.

2.4. Adsorption and catalytic oxidation of phenol

The adsorption of phenol was carried out in a 500 mL conical flask with phenol concentration of 20 mg/L and N-rGO-A (or rGO-A) of 0.2 g/L in a temperature-controlled water bath with the temperature of 25 °C. The catalytic oxidation of phenol was carried out in the same condition except that PS (2.0 g/L) was added. At each time interval, 2 mL solution was taken out by a syringe, filtered