Enhanced heterogeneous activation of peroxydisulfate by S, N co-doped graphene via controlling S, N functionalization for the catalytic decolorization of dyes in water

Xiaohua Ren [a, b, **], Jinkui Feng [a], Pengchao Si [a], Lin Zhang [a], Jun Lou [a, c], 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] Shandong Peninsula Engineering Research Center of Comprehensive Brine Utilization, Weifang University of Science and Technology, Weifang 262700, China
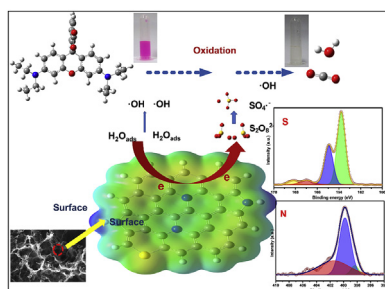[c] SDU& Rice Joint Center for Carbon Nanomaterials, Department of Materials Science and NanoEngineering, Rice University, Houston, TX 77005, USA

HIGHLIGHTS

- 3D porous graphene with regulable S N doping was fabricated by a one-pot process.
- S, N co-doping could synergistically enhance the catalytic performance.
- Low S and high N can induce more disturbances to the surface chemistry of graphene.
- $SO_4{\cdot}^-$ and $\cdot OH$ were the main radicals in oxidation decolorization of dye.
- S,N co-doped graphene catalyst shows great recyclability and stability.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

3D porous sulfur and nitrogen co-doped graphene aerogel has been fabricated by a facile one-pot process. Both experimental and theoretical studies have demonstrated that sulfur and nitrogen co-doping could synergistically enhance the catalytic performance for activating peroxydisulfate (PDS) compared to the original and N doped graphene aerogels. The ratio of sulfur/nitrogen in the aerogel can be controlled by regulating the additions of thiourea and urea sources, and the aerogel with the S/N ratio of about 1:2.5 shows a better catalytic effect due to more significant changes in the electrostatic potential and the surface charge distribution, as revealed by the theoretical simulations. The radical quenching tests indicated that both $SO_4{\cdot}^-$ and $\cdot OH$ radicals could be formed in the SN-rGO aerogel + PDS system and contribute most to RhB degradation.

* Corresponding author.
** Corresponding author. 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.
E-mail addresses: rxh2008@wfust.edu.cn (X. Ren), lci@sdu.edu.cn (L. Ci).

1. Introduction

Organic dye wastewater, mainly produced from the textile and dyestuff industries, has become a serious environmental issue without appropriate treatment (Hachem et al., 2001; Ji et al., 2015).

The conventional physical, chemical and biological technology could only transfer the pollutants from the liquid phase to the solid phase, and further treatment is inevitable and complicated (Zhu et al., 2013; Xiong et al., 2016; Zhang et al., 2016; Liu et al., 2017; Mady et al., 2017). Moreover, dye pollutants with low concentrations are difficult to remove by traditional methods (Xu et al., 2015). To address the problem, many advanced oxidation processes (AOPs) have been widely explored (Pelaez et al., 2012; Dong et al., 2015). Among various AOPs, catalytic oxidation based on sulfate radical ($SO_4\cdot^-$), a powerful oxidant, has become one of promising methods in the field of removing organic pollutants. Compared with $\cdot OH$ (2.7 V), SO_4^- has a comparable or superior redox potential of 2.5–3.1 V (Shukla et al., 2011; Sun et al., 2014), which is highly recommended to be the attractive alternative to $\cdot OH$. Commonly, $SO_4\cdot^-$ can be generated from catalyzing peroxydisulfate (PDS), peroxymonosulfate (PMS) and sulfite by transition metals or metallic oxidants (George P. Anipsitakis et al., 2005; Anipsitakis et al., 2006; Ling et al., 2010; Shi et al., 2012; Guo et al., 2013b; Zou et al., 2013; Gao et al., 2016; Jiang et al., 2016). However, the inevitable metal ions leaching, might further lead to a secondary contamination to water and limit their practical application (Muhammad et al., 2012; Sun et al., 2014; Duan et al., 2015a). Therefore, it is highly recommended to explore green and metal-free catalysts for wastewater treatment.

Since reduced graphene oxide (rGO) was first reported to be a catalyst to activate PMS to yield SO_4^- (Peng et al., 2013), many nanocarbon materials have been developed to activate PDS or PMS, and their catalytic performances have been enhanced by doping with other elements such as N, S and B (Long et al., 2012; Kong et al., 2013; Sun et al., 2013; Duan et al., 2014; Indrawirawan et al., 2015; Ren et al., 2018). Wang's group (Indrawirawan et al., 2015) employed a low-temperature heat method to prepare N-doped graphene and found that it had efficient catalytic activation of PMS for phenol degradation. Our previous study (Ren et al., 2018) revealed that N-doped graphene aerogel synthesized by a hydrothermal process showed a significant catalysis for activating PDS to generate radicals to oxidative phenol. It was found that the doped nitrogen with lone-pair electrons (pyridinic and pyrrolic N) and the graphitic N could positively charge the adjacent C atoms and disturb the chemical inertness of the graphene framework (Deng et al., 2011; Ren et al., 2018). Moreover, graphene co-doped by elements with different electronegativity could give synergistic effects by producing a unique electronic structure (Kong et al., 2014). It was reported that great improvements occur in ORR by co-doping other nonmetallic elements (B, P, S or I) with N atom (Choi et al., 2012; Paraknowitsch and Thomas, 2013). Especially, sulfur and nitrogen dual-doped graphene exhibits a synergistic effect on promoting the electrocatalytic activity in ORR due to the redistribution of charge densities and more new active sites (Liang et al., 2012; Wohlgemuth et al., 2012; Xu et al., 2013).

Significant enhancements in ORR by co-doping inspire us to investigate the metal-free catalytic performance of co-doping heteroatoms into graphene sheets on the removal of organic pollutants. Sulfur and nitrogen co-doping was reported to give a synergistic effect for improving catalytic activation of PMS for phenol degradation through changing the electronic density of the adjacent carbons (Duan et al., 2015b). The reported sulfur and nitrogen co-doped graphene is general in fine powder form, which might make the separation after reaction more difficult and costly. Additionally, the effects of S/N doping ratios and doping types on the catalytic degradation should be further clarified. Therefore, graphene aerogel with tunable S/N doping ratio was successfully synthesized and exhibited an excellent catalytic activity for PDS to decolorize cationic and anionic dyes. Scheme 1 shows the preparation process that S, N co-doped graphene aerogel (SN-rGO-A) was facilely synthesized by a hydrothermal method using thiourea and/or urea as the S and N precursors, followed by a freeze-drying process. It is worth mentioning that the S/N ratio could be controlled by adjusting the mass ratio of thiourea and urea.

2. Experiment and simulation

2.1. Materials and chemicals

Expandable graphite powder was bought from Henglide Graphite Company (Qingdao, China). Thiourea and urea were obtained from Sinopharm Chemical Reagent Co., Ltd., China. Rhodamine B (RhB), methylene blue (MB), methyl orange (MO) and sodium persulfate were purchased from Sigma-Aldrich. The spin trapping reagent 5,5-dimethyl-pyrroline-oxide (DPMO) was purchased from Aladdin.

2.2. Synthesis of rGO-A, N-rGO-A and SN-rGO-A

Graphene oxide (GO) was prepared by a modified Hummers method (Hummers and Offeman, 1958; Choi et al., 2010). SN-rGO-A was synthesized as following steps: 2.4 g thiourea was added to 40 mL of 2 mg/mL GO water solution. After ultrasonic dispersion for 15 min, the mixture was transferred and sealed in a 50 mL Teflon-lined autoclave. Subsequently, the autoclave was heated and kept at 180 °C for 12 h. The S, N co-doped graphene hydrogel was obtained and then washed by deionized water for several times. Finally, S, N co-doped graphene aerogel (SN-rGO-A) was achieved by a freeze-drying process for 48 h. In contrast, rGO-A and N-rGO-A was synthesized with the same process as SN-rGO-A, without introducing any other chemical and with introducing urea replacing thiourea. Additionally, the S/N ratio could be controlled by adjusting the mass ratio of thiourea and urea, and five kinds of aerogels SN-rGO-A (1:5:10), SN-rGO-A(1:10:10), SN-rGO-A(1:10:20), SN-rGO-A(1:20:20) and SN-rGO-A(1:30) were prepared. For example, SN-rGO-A(1:5:10) means that the aerogel was synthesized with GO, thiourea and urea as precursors with a mass ratio of 1:5:10.

2.3. Characterizations

The morphologies of the aerogels were observed by field emission scanning electron microscope (FE-SEM, Hitachi SU-70, Japan). The N_2 adsorption and desorption isotherms were measured by the Micromeritics ASAP-2020 sorption analyzer. Raman spectra were analyzed with a Renishaw InVia-Reflex Raman Microscopy. X-ray diffraction (XRD) was obtained by a Miniflex 600 diffractometer. FT-IR (Bruker Tensor 37) and XPS (ESCALAB 250, ThermoFisher SCIENTIFIC) were measured to determine the surface functional groups.

2.4. Catalytic decolorization of dyes

The catalytic experiments were carried out in a 250 mL conical flask with dye concentration of 50 mg/L. First, the catalyst (1.0 g/L) was added and magnetically stirred for 30 min. Then, the oxidant PDS with the concentration of 5 mM was added. Finally, 2 mL solution was drawn out at every time interval, filtered by a filter paper, and measured immediately with a UV spectroscopy (Evolution 220, Thermo Fisher Scientific). To identify the radical species generated in the catalytic system, two set of radical quenching experiments were performed by using methanol (MA) and tert-butyl alcohol (TBA) as the radical scavengers.