Activation of peroxymonosulfate by carbonaceous oxygen groups: experimental and density functional theory calculations

Yuxian Wang [a,b], Zhimin Ao [c], Hongqi Sun [d,*], Xiaoguang Duan [a], Shaobin Wang [b,*]

[a] State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing, 18 Fuxue Road, Beijing, 102249, PR China
[b] Department of Chemical Engineering, Curtin University, GPO Box U1987, Perth, Western Australia, 6845, Australia
[c] Institute of Environmental Health and Pollution Control, School of Environmental Science and Engineering, Guangdong University of Technology, Guangzhou, 510006, PR China
[d] School of Engineering, Edith Cowan University, 270 Joondalup Drive, Joondalup, Western Australia 6027, Australia

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ABSTRACT

The active sites for metal-free carbocatalysis in environmental remediation are intricate compared to those for traditional metal-based catalysis. In this study, we report a facile fabrication of amorphous carbon spheres with varying oxygen functional groups by hydrothermal treatment of glucose solutions. With air/N_2 annealing and regeneration in the glucose solution of the as-synthesized carbon spheres, the concentrations of oxygen-containing groups were tailored on the amorphous carbon spheres in an Excess-On-Off-On manner. Accordingly, an Off-On-Off-On catalytic behavior in peroxymonosulfate (PMS) activation using these amorphous carbon spheres was observed. To uncover the mechanism of catalytic activity, electron spin resonance (EPR) spectra were recorded to investigate the variation of the generated $^{\bullet}$OH and $SO_4^{\bullet-}$ radicals. Moreover, density functional theory (DFT) studies were employed to identify the role of oxygen-containing groups on the amorphous carbon spheres in adsorptive O—O bond activation of PMS. Results revealed that ketone groups (C=O) are the dominant active sites for PMS activation among oxygen-containing functional groups. In order to simulate real wastewater treatment, influences of chloride anions and humic acid on PMS activation for phenol degradation were further evaluated. This study provides an in-depth insight to discovering the role of oxygen-containing functional groups as the active sites in metal-free carbocatalysis.

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1. Introduction

With the rapid development of industrialization and urbanization, environmental deterioration, especially water resource depletion, has posed great public concerns for pivoting this resources-lack world to a sustainable future. In the past years, considerable research efforts have been dedicated to water resource remediation, including physical adsorption, bio-degradation, membrane separation, chemical oxidation and flocculation [1–3]. However, most of these technologies are cost/energy intensive with incomplete remediation capabilities and/or low purification efficiencies, leading to further treatment still required [4]. In recent years, advanced oxidation processes (AOPs) utilizing reactive species have displayed their promising capabilities in effective water remediation owing to excellent degradation efficiency and complete mineralization of the toxic organic pollutants [5–7].

Among AOPs, peroxymonosulfate (PMS, commercially known as Oxone®) has become a favorable alternative to hydrogen peroxide (H_2O_2) for environmental catalysis to overcome the drawbacks of Fenton reactions, such as a low pH range, large amounts of sludge generation and cost-intensive storage and transportation of the oxidant [8,9]. Due to the high redox potentials, the produced sulfate radicals ($E_0 \approx 3.1$ V) and hydroxyl radicals ($E_0 \approx 2.7$ V) from PMS activation are responsible for non-selective oxidation of harmful organic compounds [10]. Homogenous PMS activation using Co(II), Mn(II), Fe(II), Ru(III), and Ag(I) ions [10–12] or heterogeneous activation by cobalt oxides [13], manganese oxides [14,15], or supported metal catalysts [16,17] demonstrated a superb degradation efficiency because of the variable chemical states and unoccupied orbitals of these metal-based catalysts, yet they experienced severe metal leaching which results in secondary contamination to water body [18]. Therefore, metal-free catalysis was recently suggested to be a green process for water remediation [19,20].

* Corresponding authors.
  E-mail addresses: h.sun@ecu.edu.au (H. Sun), shaobin.wang@curtin.edu.au, shaobin.wang@exchange.curtin.edu.au (S. Wang).

In terms of carbocatalysis, carbon-based materials such as graphene oxide (GO), graphene, carbon nanotubes (CNTs), and activated carbon have been demonstrated to be catalytically effective for energy and environmental applications [21–24]. In previous studies, we applied for the first time such carbon catalysts for heterogeneous PMS activation for decomposition of aqueous organic pollutants [25–27]. Chemically reduced graphene oxide (rGO) was firstly discovered for PMS activation to produce reactive radicals for decomposition of various organics in water [25]. With the rGO, sp^2 hybridized carbon, oxygen-containing functional groups and edge defects (zigzag or armchair) were suggested to be the catalytic active sites [25,28]. In a subsequent study [27], nitrogen doped rGO with chemically modified sp^2 carbon showed enhanced catalysis due to the N heteroatoms at defective sites, which demonstrated the contributions of both defective sites and nitrogen dopant to the catalytic activity. Then multiwall carbon nanotubes (MWCNTs) with minimized structural defects and oxygen functional groups were also tested for PMS activation [26]. However, in the above studies, a variety of active sites on nanocarbons were involved in PMS activation, due to the chemical nature of rGO or carbon nanotubes, such as sp^2 carbon, defective structure and oxygen-containing groups. The contribution of different types of active sites to the carbocatalysis is still not clear and conclusive. Moreover, to the best of our knowledge, there is no research focusing on switching on/off the catalytic activity of carbocatalysts by manipulating the specific active sites in environmental remediation.

It was suggested that amorphous carbon with oxygen functional groups can be obtained by hydrothermal carbonization of carbohydrates [29]. In this study, amorphous carbon spheres were fabricated via a facile one-step hydrothermal method (**Excess** mode). By such an elaborate design, we ruled out the contribution of sp^2 hybridized carbon atoms and edge defects to the catalytic activity (as well as doped nitrogen), and exclusively focused on oxygen-containing groups. Meanwhile, concentrations of the surface oxygen-functional groups were successfully manipulated by air annealing (**On**[1] mode), N_2 annealing (**Off** mode) and regeneration in a glucose solution (**On**[2] mode). We evaluated the contribution of oxygen functional groups to PMS activation by testing the catalytic activities of these amorphous carbon spheres with different modes toward phenol degradation. Moreover, to provide theoretically insights into the role of oxygen functional groups on the carbons in catalysis, we further employed density functional theory (DFT) calculations by constructing molecular amorphous carbon models containing −OH, −C=O, −COOH and three adjacent −C=O groups. We dedicate this research to developing novel green catalysts for environmental remediation and revealing the contribution of oxygen functional groups to carbocatalysis.

2. Experimental

2.1. Materials and chemicals

D-glucose (99.8%) and Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, PMS) were obtained from Sigma-Aldrich. Phenol (99.8%) was purchased from Ajax Finechem. 5,5-Dimethyl-1-pyrroline (DMPO, >99.0%) was obtained from Fluka. Multi-walled carbon nanotubes (MWCNTs, >99.5%) were purchased from Chengdu Organic Chemical, China. All chemicals were used as received without further purification.

2.2. Preparation of carbon materials

Fresh carbon nanospheres (CS, **Excess** model of oxygen groups) were prepared by hydrothermal carbonization of glucose at 180 °C for 18 h. For tailoring the oxygen-functional groups, CS-AIR (**On**[1]

model of oxygen groups) was prepared by annealing the CS in air at 350 °C for 1 h; CS-N_2 (**Off** model of oxygen groups) was fabricated by annealing the CS in nitrogen 400 °C for 1 h; and CS-REG (**On**[2] model of oxygen groups) was obtained by hydrothermal treatment of CS-N_2 in a glucose solution at 180 °C for 3 h. Detailed synthesis routes for tailoring oxygen-functional groups could be found in the Supplementary Data.

2.3. Characterization

Structure and morphology of the materials were observed on a ZEISS NEON 40EsB scanning electron microscope (SEM). XRD (X-ray diffraction) patterns were performed on a Bruker D8 diffractometer (Bruker-AXS, Karlsruhe, Germany) using filtered Cu Kα radiation (λ = 1.5418 Å) with an accelerating voltage of 40 kV and a current of 30 mA. The Brunauer–Emmett–Teller (BET) specific surface area and the pore size distribution of the samples were measured by N_2 adsorption/desorption using a Micromeritics Tristar 3000. Prior to measurement, the samples were degassed at 150 °C overnight under vacuum condition. Fourier transform infrared spectra (FTIR) were obtained from a Bruker instrument with an ATR correction mode. Raman study was measured on an ISA dispersive Raman spectrometer using argon ion lasers (514 nm). X-ray photoelectron microscopy (XPS) was acquired on a Kratos AXIS Ultra DLD system under UHV condition with Al-Kα X-ray. Spectra were fitted with Kratos Vision and CasaXPS software.

2.4. PMS activation and catalytic oxidation

The catalytic oxidation of phenol was carried out in a 500 mL conical flask containing 20 ppm of phenol solution with a constant stirring at 300 rpm. The reactor was attached to a stand and dipped into a water bath with a temperature controller. Unless specifically stated, the reaction temperature was maintained at 25 °C. In a typical test, 0.1 g catalyst was firstly added into the phenol solution for 30 min to achieve adsorption-desorption equilibrium, and then 2 g/L PMS was added into the solution. At certain intervals, 1 mL aqueous sample was withdrawn by a syringe and filtered into a HPLC vial, which was prior injected by 0.5 mL of methanol to quench the reaction. The concentration of phenol was analyzed using a Varian HPLC with a UV detector at wavelength of 270 nm. A C-18 column was used to separate the organics while the mobile phase with a flow rate of 1 mL/min was made of 30% CH_3CN and 70% water. Total organic carbon (TOC) was measured on a Shimadzu TOC-vcph analyzer at fixed time intervals during the reaction. For the recycle tests of the catalyst, after each run, the catalyst was obtained by vacuum filtration and washed with ultrapure water for 3 times. Then the washed catalyst was dried in an oven at 60 °C for 12 h. For catalytic phenol degradation, experiments were repeated three times in order to obtain error bars on the plots. The electron paramagnetic resonance (EPR) from a Bruker EMS-plus was employed to detect the radicals generated during activation of PMS, operating at following conditions: center field: 3517 G; sweep width: 100 G; sweep time 30 s; microwave frequency: 9.87 GHz; power setting: 18.75 mW.

2.5. Computational models and methodology

The spin-polarized density functional theory (DFT) calculations in this work were executed using the DMOL[3] module [30]. The local density approximation (LDA) with Perdew-Wang correlation (PWC) function was utilized as the exchange-correlation function. A double numerical plus polarization (DNP) was used as the basis set, while the All Electron core treatment was utilized to include relativistic effects. The convergence tolerance of the energy was set to 10^{-5} Ha (1 Ha = 27.21 eV), and the maximum allowed force