Effects of nitrogen-, boron-, and phosphorus-doping or codoping on metal-free graphene catalysis

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ABSTRACT

Graphene-based materials have been demonstrated as excellent alternatives to traditional metal-based catalysts in environmental remediation. The metal-free nature of the nanocarbons can completely prevent toxic metal leaching and the associated secondary contamination. In this study, nitrogen doped graphene (NG) at a doping level of 6.54 at.% was prepared at mild conditions. Moreover, B- and P-doping or codoping with N in graphene were also achieved by a simple route. The modified graphene can efficiently activate peroxymonosulfate (PMS) to produce sulfate radicals to oxidize phenol solutions. Kinetic studies indicated that initial phenol concentration, PMS dosage, and temperature presented significant influences on the degradation rates. Electron paramagnetic resonance (EPR) analysis provided further insights into the evolution of active radicals during the activation of PMS and $SO_4^{\bullet-}$ was believed to be the primary radicals in the oxidation reactions. This study demonstrated a metal-free material for green catalysis in environmental remediation.

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1. Introduction

Industrial processes have discharged a large amount of wastewater, in which hazardous components, such as phenolics, dyes, and pharmaceuticals, have posed great threats to the aquatic life, agriculture, and public health of human beings [1,2]. Meanwhile, the lack of clean water resources occurs worldwide. Effective remediation technologies for removal of organic pollutants from wastewater for water reuse are therefore highly in demand. Advanced oxidation processes (AOPs) have drawn intensive attention, as they can completely decompose organics into water, carbon dioxide and inorganic ions/acids/groups by the active radicals [3–5]. Among various AOPs, Fenton reaction, based on a $H_2O_2/Fe(II)$ homogeneous system, is mostly popular and has been widely applied due to the capability to destroy a wide range of contaminants [6]. However, Fenton reaction suffers from the drawbacks such as generation of excess sludge and low pH (∼3) requirement [7].

Recently, heterogeneous catalytic oxidation using peroxymonosulfate (PMS, commercially available as Oxone®) with cobalt catalysts has been employed for phenol oxidative decomposition [8–10]. Sulfate radicals ($SO_4^{\bullet-}$) produced from PMS are believed to possess a higher oxidation potential (2.5–3.1 V) than hydroxyl radicals (•OH, 2.7 V), then they not only present better oxidation towards phenol degradation, but are flexible to a broad range of pH solutions [11]. However, cobalt leaching has inevitably occurred, giving rise to the secondary contamination to water body and bringing out other health issues to human beings [12].

The emerging nanocarbons, such as graphene, carbon nanotubes (CNTs), carbon nanofiber (CNF), and nanodiamond, as metal-free catalysts, have attracted considerable research interests and been applied to various catalytic processes [13–16]. The unique characteristics such as large specific surface area (SSA), super capability of electron transfer, good thermal stability, and non-toxicity also make them promising alternatives for environmental remediation [17,18]. Sun et al. [17], for the first time, reported that a reduced graphene oxide (rGO) through a hydrothermal approach can demonstrate an excellent performance in PMS activation and provide 70% phenol removal in 180 min. Structural modification was found to be effective for improving the catalytic activity in phenol oxidation [19,20]. It was well known that chemical doping could offer an effective method to modulate the electron states of graphene and bring about new properties [21]. Nitrogen doping was demonstrated to significantly improve the catalytic activities of nanocarbons for PMS activation [22,23].

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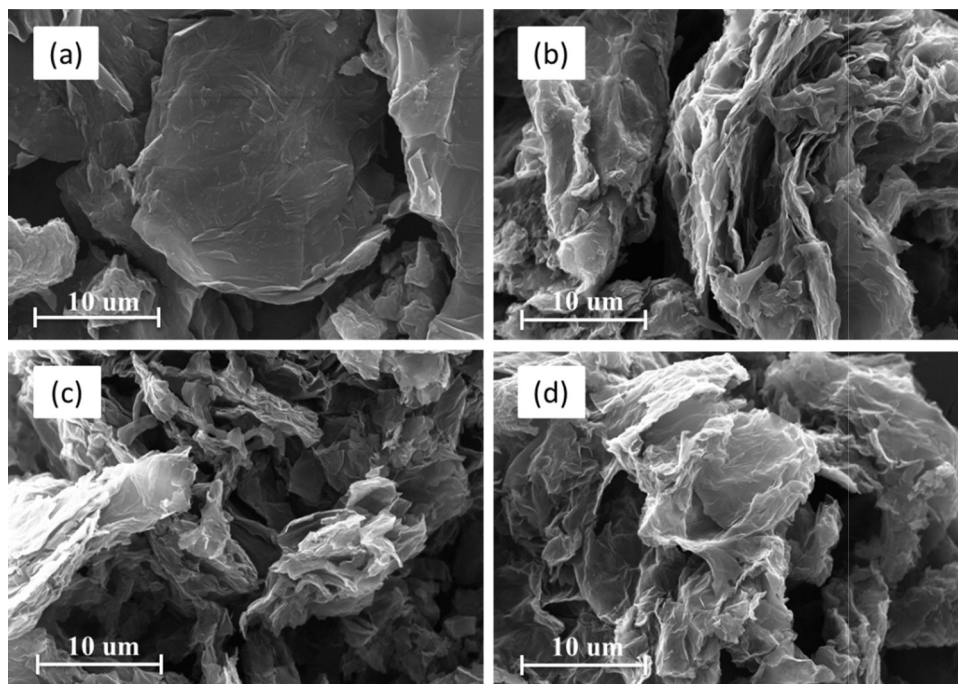
Fig. 1. SEM image of (a) GO, (b) NG350, (c) BNG 0.1% B_2O_3, and (d) PNG 0.1% P_2O_5.

In this study, graphene oxide (GO) was synthesized by a modified Hummers method [24] and N-doped graphene was prepared by annealing GO with ammonium nitrate as a N precursor in mild preparation conditions. The effects of N-, P-, and B-doping or codoping in GO on physicochemical properties of graphene were also investigated. The obtained catalysts were applied to activate PMS for catalytically oxidative removal of phenol in aqueous solutions. Kinetic studies and stability tests of the nanocarbons were systematically carried out. The degradation mechanism was also investigated and discussed.

2. Experimental

2.1. Synthesis of nanocarbon catalysts

Graphene oxide (GO) was synthesized by oxidation of natural graphite powders with condensed sulphuric acid and potassium permanganate reported elsewhere [24]. For synthesis of nitrogen doped materials, GO (1.0 g) was dispersed in ethanol (50 mL), stirred for 1 h and sonicated for 30 min. Then ammonium nitrate (1.0 g) was added into the solution as the nitrogen precursor. The mixture was stirred and heated on a hotplate at 60 °C to evaporate ethanol. The dried mixture was finely grinded and transferred into a muffle furnace and calcined at 350 °C for 1 h and the resulted sample was denoted as NG350. For a comparison, an undoped rGO350 sample was prepared via GO thermal reduction at 350 °C in N_2.

Additional boron and phosphorus doped graphene samples were synthesized following the same procedure of nitrogen-doped sample using certain amounts of ammonium pentaborate octahydrate ($H_8B_{10}N_2O_{16}\cdot 8H_2O$) and ammonium phosphate monobasic ($NH_4H_2PO_4$) as the boron (B_2O_3), and phosphorus (P_2O_5) precursors, respectively. The samples were denoted as B-rGO and P-rGO, respectively. To prepare B- (or P-) and N- co-doped graphene, the ammonium pentaborate octahydrate (or ammonium phosphate monobasic) and ammonium nitrate were added simultaneously into the GO suspension after sonication. The samples were referred as BNG and PNG, respectively.

2.2. Characterization of nanocarbons

Scanning electron microscopy (SEM, Zeiss Neon 40EsB FIB-SEM) was performed to obtain the surface morphology of the catalysts. X-ray photoelectron spectroscopy (XPS, Thermal Escalab 250) was conducted with an Al Kα source. X-ray diffraction (XRD) patterns were acquired from a Bruker D8-Advanecd X-ray diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å). Raman spectra were conducted on an ISA dispersive Raman spectrometer. The Brunauer–Emmett–Teller (BET) specific surface area, pore volume and pore distribution analyses were conducted on a Micrometrics Tristar 3000 in liquid nitrogen (−196 °C) with the BET and Barrett–Joyner–Halenda (BJH) method. Fourier-transform infrared (FT-IR) spectra were obtained from a Perkin-Elmer Spectroscopy 100. Thermal analysis of nanocarbons was performed on a Mettler-Toledo Star system with thermal gravimetric analysis-differential scanning calorimetry (TGA-DSC) under air heating from 35 to 900 °C at a rate of 10 °C/min.

2.3. Catalytic oxidation of phenol solutions

Degradation reactions were carried out in a batch reactor containing 250 mL of phenol solution. Reaction temperature was kept at 25 °C by a temperature controller set in a water bath. A certain amount of catalyst was added into the solution, which was mechanically stirred at a speed of 400 rpm to form a well-mixed heterogeneous system before and after the addition of Oxone® ($2KHSO_5\cdot KHSO_4\cdot K_2SO_4$, Sigma–Aldrich). During each interval time, 1 mL of the solution was withdrawn and filtered with 0.45 μm membrane, and then injected into a HPLC vial mixed with 0.5 mL methanol as the quenching agent. The sample was analyzed by a High Performance Liquid Chromatography (HPLC) from Varian Instrument with a C18 column and a UV detector set at 270 nm. Electron paramagnetic resonance (EPR) spectra were obtained on a Bruker EMS-plus equipment to identify and quantify the active radicals produced from PMS activation (centre field: 3516 G; sweep width: 100 G; microwave frequency: 9.87 GHz; power: 18.75 mW).