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Facile synthesis of nitrogen-doped graphene via low-temperature pyrolysis: The effects of precursors and annealing ambience on metal-free catalytic oxidation

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ABSTRACT

A green and facile protocol of thermal treatment of graphene oxide (GO) with urea was adopted to synthesize nitrogen-doped graphene (NG-Urea-air) at a low temperature (350 °C) in the static air. The resulting sample exhibited outstanding catalytic performance to activate peroxymonosulfate (PMS) toward organic degradation. The NG-Urea-air induced 49.7- and 11.5-fold enhancement over GO and pristine reduced graphene oxide (rGO-air). Moreover, the influences of nitrogen precursors including organic chemicals (urea, cyanamide, and melamine) and inorganic salts (ammonium nitrate and ammonium chloride) were investigated, and urea was demonstrated to be the best precursor for synthesizing N-doped graphene with a relative high doping level (18.7 at.%). The classical radical quenching and advanced *in situ* electron paramagnetic resonance (EPR) technology revealed that the outstanding oxidative effectiveness of PMS/NG-Urea-air system was originated from the nonradical oxidation pathway, in which PMS was activated by the positively charged carbon domains next to nitrogen atoms and the phenol was oxidized simultaneously on the carbon network via rapid charge transfer. Meanwhile, singlet oxygen and radicals may also partially contribute to the complete phenol degradation. This study facilitates a fundamental investigation of heteroatom doping progress during thermal treatment and sheds light on the insights into carbocatalysis in environmental remediation.

1. Introduction

Since A.K. Geim uncovered the existence of single-layered graphite, namely graphene, with carbon atoms perfectly packed into the honeycomb lattice in a uniform sp^2-hybridized configuration, graphene-based materials have opened up a new avenue to the world of materials science, nanotechnology, and chemical/energy conversions [1,2]. Versatile approaches, including chemical vapor deposition [3], epitaxial growth [4], and exfoliation of graphite [5], have been developed to synthesize graphene with desired physicochemical and electronic properties for wide applications. The exfoliation of graphite, the stacked layers of graphene, has attracted extensive interests because of the cheap and abundant carbon source and mild synthesis conditions. Several protocols of exfoliation have been developed such as micromechanical exfoliation [6], electrochemical exfoliation [7], and chemical exfoliation [8,9]. Among these methods, the Hummers' approach was most widely adopted to synthesize single or few-layered chemically exfoliated graphene oxide (GO), followed by post-processing with thermal-treatment or chemical reduction to achieve a better reductive degree of graphene, also known as reduced graphene oxide (rGO) [10–12]. Moreover, GO with sufficient oxygen functional groups, smaller particle sizes, and massive exposed edging sites offers a promising matrix for surface modification, especially for heteroatom doping.

Introducing heteroatoms (B, N, O, P, S, and so forth) into the carbon lattice can effectively disorientate the homogeneously conjugated electron network and modulate the surface properties

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by tweaking the charge distribution and spinning culture of the doped domains [13,14]. Nitrogen-doped graphene has been intensively investigated in recent years for metal-free catalysis. Nitrogen is adjacent to carbon in the periodic table of elements. Nitrogen atom pocesses a similar atomic radius (0.70 Å) as carbon (0.77 Å) and a more negative electronegativity ($\chi_N = 3.04$) than C ($\chi_C = 2.55$), making it easier to incorporate into the carbon basal plane via substitutional doping. N can reach a considerable doping level, meanwhile intrinsically altering the electron states of the graphene. Therefore, N-doping has been demonstrated to be able to endow pristine graphene with impressively enhanced activity toward chemical reactions and catalysis [15–17]. Various N-rich substances such as ammonia, ammonium salts, and organic matters have been utilized as the nitrogen precursors. However, very little attention has been paid to the effects of different precursors and the mechanism of N-doping process. Understanding the impacts of diverse precursors and the doping procedure will provide fundamental knowledge for the rational design of efficient carbocatalysts via elaborate nano-engineering.

In this study, we applied a facile strategy by direct treatment of GO and urea at a moderate temperature (350 °C). This protocol utilized cheap and green nitrogen precursors under mild conditions for synthesis of N-doped graphene without intensive energy input and rigorous reaction requirements for the aforementioned micromechanical/electrochemical exfoliation and chemical vapor deposition (CVD) approaches. The derived carbocatalysts were utilized to activate peroxymonosulfate (PMS) for catalytic oxidation. The chemically modified graphene exhibited significantly improved activity than the pristine graphene. Moreover, the N-doping procedure was investigated by exploring the effects of carbon matrix (oxygen-rich/deficient carbon precursors), N-doping precursors (organic/inorganic nitrogen-containing substances), and annealing conditions (oxidative or non-oxidative ambience). The green and efficient carbocatalysts have demonstrated extraordinary potentials for activating various superoxides (e.g. peroxymonosulfate, persulfate, hydrogen peroxide, and ozone) for the oxidative removal of toxic pollutants in wastewater without any secondary contamination [18–21]. However, due to the complicated structure and surface chemistry of nanocarbons, the mechanism of carbocatalysis in metal-free oxidation remains ambiguous, leaving more blanks for mechanistic study. This investigation facilitates an in-depth study of PMS activation on graphene-based materials with the occurrence of the nonradical mechanism and evolution of singlet oxygen besides the traditional radical pathway. The findings of this study would unveil the principles of achieving desirable N-doping in graphene-based materials and will definitely contribute to carbon-based materials science, green environmental remediation, and metal-free catalysis technologies.

2. Experimental

2.1. Materials preparation

The chemicals in this study were purchased from Sigma-Aldrich, Australia with a reagent grade and used as received without further purification. Firstly, graphene oxide (GO) was prepared via a chemical exfoliation approach based-on a modified Hummers' method, and the detailed procedures can be found in a previous study [18]. The nitrogen doped graphene (NG) was synthesized by a facile pyrolysis of GO with nitrogen precursors. Briefly, GO (0.5 g) and urea (0.60 g) were dissolved in 30 mL ethanol and treated in an ultrasonic bath for 30 min to form a homogeneous solution. Then the mixture was heated on a hotplate at 60 °C to evaporate the solvent whilst keeping stirred. The obtained black mixture was ground finely, transferred to the muffle furnace in a crucible, and heated at 350 °C for 30 min in a static air with a heating rate of 5 °C/min. The obtained furry black powder was then washed with ethanol and deionized water several times and then dried in an oven at 60 °C overnight for further use. The products were ground and denoted as NG-Urea-air. Reduced graphene oxide (rGO-air) was prepared by the same procedure without the addition of nitrogen precursors. To investigate the effect of carbon sources, the GO was substituted by rGO-air in the aforementioned process and the product was marked as N-rGO-air. To investigated the effect of annealing environment, similar nanocarbon materials were prepared by treating the GO (or rGO)/urea mixture in a tubular furnace under N_2 (60 mL/min), and the resulting products were named as rGO-N_2, NG-Urea-N_2, and N-rGO-N_2. Besides, different N-precursors were also investigated with other organic precursors such as melamine, cyanamide, and inorganic salts such as ammonium nitrate (NH_4NO_3) and ammonium chloride (NH_4Cl). The dosage of the precursors was calculated based on the containing of 0.02 mol nitrogen atoms in all the precursors. The N-doped graphene from different N-precursors were prepared in the same procedure as NG-Urea-air, and the products were denoted as NG-Melamine, NG-Cyanamide, NG-NH_4NO_3, and NG-NH_4Cl, respectively.

2.2. Characterization of nanocarbons

The structure and morphology of the nanocarbons was revealed by a Zeiss Neon FIBSEM. The elemental distribution of nitrogen-doped graphene from different precursors was monitored by the EDS elemental mapping in Figs. S1–S5. FTIR spectra were acquired from a Bruker spectrometer. The BET surface area, nitrogen sorption isotherms, and pore diameter distributions were measured at −196 °C on a TriStar II apparatus. The surface elemental information was probed with a Kratos X-ray photoelectron spectroscopy (XPS) instrument equipped with a monochromated Al Kα X-ray gun.

2.3. Catalytic oxidation procedure

The catalytic performance of the nanocarbon catalysts was evaluated by PMS activation and oxidation of toxic organic contaminants. The aqueous reactions were carried out in a batch reactor with the organics, PMS, and carbocatalysts at the usage of 20 ppm organic chemicals, 6.5 mM PMS, and 0.4 g/L carbocatalysts at 25 °C. The solution was withdrawn at set intervals and filtered to remove the solid catalyst, quenched by methanol, and analyzed on an ultra-high performance liquid chromatography (UHPLC, ThermoFisher Scientific) with an UltiMate™ 3000 RSLCnano system. The generated singlet oxygen was captured by 2,2,6,6-tetramethyl-4-piperidone (TMP) and tested on a Bruker electron paramagnetic resonance (EPR) instrument with the settings at following parameters: center field 3515 G, sweep width 100.0 G, power 20.0 mW, sweeping time 30 s, and scan number 2.

3. Results and discussion

3.1. Characterization of samples

The SEM and TEM images in Figs. 1 and 2 display the morphologies of the nanocarbon catalysts. Different from the smooth lamellar and severe stacked layers of GO (Figs. 1 and 2a), the obviously expanded and corrugated thin layers were spotted for rGO-air (Figs. 1 and 2b). The N-doped graphene presents an obviously curled structure as shown in Fig. 1c, which is further reflected in the TEM image of Fig. 2c in the crinkled sheets, due to the distortion of carbon lattice induced by the simultaneous reduction and N-doping processes [22,23]. However, the partially aggregated