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Tuning graphene for energy and environmental applications: Oxygen reduction reaction and greenhouse gas mitigation

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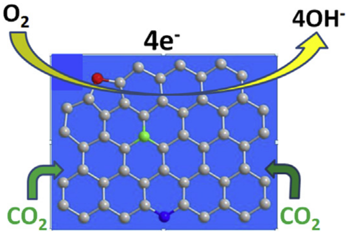
HIGHLIGHTS

- Tuning of solid precursor based nitrogen doped graphene for multiple applications.
- Nitrogen doping and thermal treatment enabled efficient carbon dioxide capture.
- Quaternary nitrogen enabled high efficiency oxygen reduction reaction.
- N-graphene electrode had superior stability and tolerance to crossover effect.

GRAPHICAL ABSTRACT



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ABSTRACT

Porous nitrogen-doped graphene samples were synthesized and tuned via pyrolysis of solid nitrogen precursor dimethyl-aminoterephthalate with graphene oxide as template. Our investigations show that the extent of thermal treatment, total concentration of nitrogen and the nature of nitrogen moieties play important roles in enhancing oxygen reduction reaction (ORR) and CO_2 uptake. N-doped graphene synthesized at 650 °C (NG-650) with specific BET surface area of 278 m^2/g, exhibits enhanced CO_2 sorption capacity of 4.43 mmol/g (at 298 K, 1 bar) with exceptional selectivity (CO_2:N_2 = 42) and cyclic regeneration stability. In contrast, nitrogen-doped graphene synthesized at 750 °C (NG-750) demonstrated excellent catalytic activity for ORR via favourable $4e^-$ transfer, performance stability with tests conducted up to 5000 cycles, and is unaffected by methanol cross-over effect. Thus, NG-750 shows potential to replace metal-based electrodes for fuel cell application. The comparative results for ORR with non-doped and nitrogen-doped graphene electrodes showed that graphitic nitrogen sites play vital role in enhancing catalytic activity.

1. Introduction

Energy generation and CO_2 capture are among the key challenges facing humanity [1]. On the one hand, the energy demand is on the rise, while environmental challenges from greenhouse gases remain unabated [1c]. The task of tackling both problems in the face of climate change is an important goal for industry [2]. Apart from atmospheric pollution, high concentrations of CO_2 are lethal in space-limited chambers such as submarines and space ships [3]. The selective capture and storage of CO_2 in a cost effective manner

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at the emission level are crucial in certain applications [4]. Zeolites [5], mesoporous silica [6], activated carbons [7], metal-organic frameworks (MOFs) [8], aqueous amines [9], carbon nanotubes [10] microporous polymers (MOPs) [11], and zeolitic imidazolate frameworks (ZIFs) [12] have been widely explored for CO_2 capture via absorption, adsorption and membrane separation [13]. However, the use of nitrogen doped graphene is yet to be reported.

In industry, chemisorptive formation of N—C bonded carbamate using ammonia solution and aqueous amine technologies are widely used for absorbing CO_2, however, they suffer from corrosion and high regeneration and recycling costs [9,14]. For efficient capture of CO_2 from flue gases, solid adsorbents [15] with their desirable characteristics of chemical inertness, high surface area and selectivity, and carbon based adsorbents in particular are promising for CO_2 capture [10,16]. In addition, the decorated basic N functionalities on carbon framework provide active basic centres and favourable surface chemistry for capturing acidic guest molecules such as CO_2 [17,18].

Zeolitic framework and microporous polymers synthesized with nitrogen containing organic compounds as crosslinkers have limitations of structural stability, selectivity and CO_2 sorption/desorption efficiency in the presence of water [19,94]. The main limitation of amine modified solids is loss of ammonia with thermal energy input during regeneration [20]. Similarly, amine impregnated or surface modified porous silica such as SBA-15 [21], MCM-48 [22], MCM-41 [23], and zeolite 13X fail to capture CO_2 effectively, and require high temperature and long regeneration times, while structural stability weakens considerably after multiple cycles [24]. In addition, post-synthetic incorporation of amine groups causes pore blockage [25], requiring costly, time consuming procedures with the use of corrosive, toxic reagents. Therefore, it is desirable to develop permanently doped porous carbon material for superior selective CO_2 uptake.

The dual challenges of a lack of renewable energy source and pollution caused by fossil fuels can potentially be overcome with fuel cells [26]. However, two major challenges need to be overcome. First, electrodes in conventional fuel cells contain Pt or Pt alloys as electrocatalysts [27] for oxygen reduction reaction (ORR); however, the scarcity, high cost and low stability limit their commercial viability [28,71]. Second, the poor efficiency of conventional ORR means just one of two redox (half) reactions occurs in fuel cells [29]. Metal-containing catalysts are not favourable with ORR for long term usage because in acidic and basic media, metals leach from electrode surfaces to the detriment of electrocatalytic activity and catalyst life [30]. Thus, the wider acceptance of fuel cells for large scale commercial applications requires not only the development of electrocatalysts based on abundant, non-precious and non-metallic electrocatalysts but also efficient, catalytically active and inexpensive materials having long term stability.

The principal non-metallic electrodes under investigation for ORR are: porous carbon [31], carbon nanotubes [32], graphene [33,77] and graphite [34,97]. Recent substitution of carbon atoms in carbon structural materials with electronegative heteroatoms N, P, S and B have been attracting attention [35]. As the electronegativity of N (3.04) is greater than that of carbon (2.55), N-doping of carbon material is able to create positively charged sites which are more favourable towards oxygen adsorption for enhancing catalytic activity in ORR [36]. In general, tailoring the electronic arrangement of carbon-based material is a viable option to design and fabricate heteroatom-doped catalysts for improving electrocatalytic activity towards ORR. Graphene, a two dimensional single-layer nanostructure of sp^2-hybridized conjugated carbon [37,38], is a suitable electrode material due to its superior electrical, mechanical and thermal properties [38–40] as well as its high surface area, chemical stability and low cost [41–48,51]. Nitrogen doping of graphene has the potential of tuning its local electronic structure [49] and enhance electron mobility [50] for superior performance.

N-graphene is typically synthesized by chemical vapour deposition (CVD) [52], thermal conversion with nitrogen precursors [42,43,53,54,65], hydrothermal treatment [55], plasma [56,82], electrical arc discharge [57], and flame [58]. However, most of these techniques use gaseous or liquid sources of nitrogen to synthesize N-graphene, which suffers from contamination due to metal deposition and toxicity of precursors. For example, doping graphene via CVD with N-precursors is slow, tedious and expensive [48,51,59]. Further, toxic precursors use special devices or severe conditions that limit the scale-up of N-doped graphene via annealing with NH_3 [60,77], electric arc discharge [61] or nitrogen plasma [62]. Thus, new non-toxic, cost-effective methods are required to synthesize N-graphene for commercial applications [63,65].

Direct co-pyrolysis of graphene oxide with solid nitrogen source is attractive because the method can be scaled without using any catalyst or other potential contaminant [64]. A few solid nitrogen precursors reported include melamine [65], cyanamide [66], urea [67] sugar [67] aminoterephthalic acid [42], and methylimidazole [43]. In this work, we report a facile and scalable synthesis step using a solid nitrogen precursor dimethyl-amino-terephthalate with graphene oxide via pyrolysis to produce porous N-doped graphene that exhibits not only superior CO_2 adsorbance due to the presence of basic N-sites but also excellent ORR catalytic activities. The facile tuning of N-graphene via doping and thermal treatment and the mechanism of CO_2 capture and ORR activity for targeted applications are discussed.

2. Experimental

2.1. Synthesis of graphene oxide (GO)

Graphene oxide (GO) was synthesized [42,43,68] to obtain thermally expanded graphite; graphite flakes (Asbury Carbons, Grade: 3772, carbon content: 99%) on a ceramic boat were placed in a tube furnace at 1050 °C for 15 s. Then 500 ± 2 mg of expandable graphite and 200 ± 4 mL of H_2SO_4 (98%, Sigma Aldrich) were mixed in a three neck round bottom flask and stirred for 24 h at room temperature. Next, 5 ± 0.02 g of $KMnO_4$ (99%, Sigma Aldrich) was added gradually and was kept under continuous agitation for 24 h. The mixture was cooled in an ice bath.

A solution of 200 ± 3 mL deionized water and 50 ± 2 mL of H_2O_2 (30%, Sigma Aldrich) was prepared and added dropwise to GO under agitation making a slurry. The resulting mixture changed colour from dark to a light brown colour. Finally, the GO dispersion was washed five times with HCl solution ($9H_2O$:1HCl vol%) and subjected to centrifugation at 5000 rpm. The GO precipitate was washed 10 times with water till a pH of about 6 was obtained. Subsequently, GO was collected and dried at 80 °C in a vacuum oven for 24 h.

2.2. Synthesis of N-doped graphene

To prepare pristine graphene (PG), 30 mg GO was placed on a quartz boat inside a tube furnace (OTF-1200X), and heated to 750 °C for 2 h under argon flow. N-doped graphene samples were synthesized from GO-dimethyl-aminoterephthalate composite materials. In preparation of this composite, 30 ± 2 mg GO and 30 ± 3 mg 2-methylimidazole (99%, Sigma-Aldrich) were mixed in 50 ± 2 mL H_2O, and dispersed in a sonication bath (Soniclean 80T, 60 W) for 1 h. The mixture was subsequently heated to 90 °C and stirred for 12 h while removing water. The resulting solid composite (GO-dimethylterephthalate) was taken in a ceramic boat and