



A facile approach to tailoring electrocatalytic activities of imine-rich nitrogen-doped graphene for oxygen reduction reaction



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ABSTRACT

We report efficient modulation of the electrocatalytic activity of imine-rich nitrogen-doped graphene nanosheets (IRnGs) in the oxygen reduction reaction (ORR) by chemical functionalization. IRnGs are prepared by a simple acid-catalyzed dehydration reaction between graphene oxide and aniline derivatives. Various electron-donating and electron-withdrawing substituents are introduced in the *para*-position of aniline to afford diverse IRnG electrocatalysts. Cyclic voltammetry and rotating ring disk electrode measurements show that the electrocatalytic activity of IRnGs for ORR is highly sensitive to the electronic characteristics of functionalities present in their chemical structures. Thus, the above ORR activities are significantly improved by increasing the electron-withdrawing capability of substituents, since this promotes the beneficial polarization of electrocatalytically active imine bond ($-\text{C}=\text{N}-$) in IRnGs. In addition, metal-free IRnGs electrocatalysts offer additional advantages of high selectivity, good long-term stability and excellent tolerance to methanol crossover for ORR in alkaline solution.

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1. Introduction

Owing to significant drawbacks of commercial platinum-based electrodes for the cathodic oxygen reduction reaction (ORR) in fuel cells, the development of alternative electrocatalysts is currently in the limelight [1–5]. Among various candidates, nitrogen-doped (N-doped) graphene is a promising metal-free electrocatalyst, exhibiting cost-effectiveness, high electrocatalytic activity, long-term operational stability, and good resistance to methanol crossover/carbon monoxide poisoning [6–9]. The incorporation of more electronegative nitrogen atoms (N , $\chi = 3.04$) into two-dimensional carbon (C , $\chi = 2.55$) networks can induce strong charge polarization [10], which can significantly enhance ORR activities. After being incorporated into graphitic networks, the

nitrogen atoms usually exhibit three different configurations, i.e., graphitic N (or quaternary N), pyridinic N and pyrrolic N [8]. However, their arrangements in N-doped graphene are not limited to these three types, other configurations such as imine ($-\text{C}=\text{N}-$) or pyrazine moieties can be also introduced by controlling applied chemistry used in the preparation steps [11]. Moreover, the ORR performance of N-doped graphene is highly sensitive to the type and concentration of the present nitrogen atoms [4,12,13]. Although some controversies still exist, it is believed that pyridinic N in N-doped graphene can efficiently improve ORR activity by facilitating O_2 adsorption and the four-electron pathway [14–17]. Similarly, the pyrazine moiety, being a symmetric aromatic heterocycle with two pyridinic nitrogens, exhibits superior ORR electrocatalytic properties, when presented in graphitic structures [18].

Interestingly, it has been recently reported that the ORR activities of N-doped carbon allotropes such as glassy carbon (GC) and carbon nanotubes (CNTs) can be tuned by chemical modification [19,20]. This tuning was achieved by introducing various electron-donating or electron-withdrawing substituents near vicinity of nitrogen atoms, which changed the electronic charge density distributions on nitrogen-mediated active sites. For example,

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significantly enhanced ORR activities were obtained by appending electron-withdrawing moieties at the edges of a phenylenediamine-modified GC electrode, due to increased electrophilicity of the catalytically active pyrazine units [19]. Similarly, the ORR activity of pyridine-modified CNTs was facilitated by optimizing atomic charges on N and adjacent carbon (C_α) atoms as well as by the resulting N- C_α bond polarization, which can be also achieved by introducing electron-donating or electron-withdrawing functionalities in the α -position of the pyridine ring [20]. Therefore, more attention should be paid to the deliberate control of the chemical environments of nitrogen atoms for obtaining high-performance N-doped carbon-based electrocatalysts.

Recently, we have reported that a solution-based acid-catalyzed dehydration reaction between monoketone or α -diketone moieties in graphene oxide (GO) and aromatic *ortho*-diamines is highly promising for producing high-quality N-doped graphene [11,21,22]. Owing to its effectiveness and versatility, the obtained N-doped graphene exhibits outstanding performance in *n*-type field-effect transistors (FETs), fuel cells, and supercapacitors. Herein, we synthesized imine-rich N-doped graphene nanosheets (IRnGs) via the aforementioned acid-catalyzed dehydration reaction of GO with aromatic monoamines such as aniline (Fig. 1). Contrary to *ortho*-diamines, which can produce both imine and pyrazine linkages, monoamines can only produce imine bonds after condensation with the ketone groups in GO. Although imines, usually referred as Schiff bases, can also exhibit strong charge polarization of the C=N double bonds, their utilization in N-doped graphene for ORR has so far been scarce [23]. In addition, various electron-donating and electron-withdrawing substituents were systematically incorporated into imine-rich N-doped graphene using *para*-substituted aniline derivatives. Therefore, the significant changes in the electronic charge density distribution and bond polarization of the imine linkage (*vide supra*) are expected to result in facile modulation of the ORR activities of IRnGs.

Due to the efficient formation of imine linkages and the good structural restoration of graphitic structures during the reaction, the resulting IRnGs exhibit promising ORR electrocatalytic activities, showing good selectivity, excellent operational stability, and high tolerance to methanol crossover. Furthermore, it has been found that the changes in electronic charge density distribution and bond polarization of the electrocatalytically active imine linkages can significantly contribute to the overall ORR catalytic activities, e.g., onset potentials, limiting currents, and electron-transfer numbers. Therefore, this study offers important insights for the development of high-performance metal-free ORR electrocatalysts by fine-tuning the configuration and chemical environment of nitrogen atoms in N-doped graphene.

2. Experimental

2.1. Materials and instruments

Graphite nanopowder (450 nm APS, 99.9% purity) was obtained from Nanostructured and Amorphous Materials, Inc. *N,N*-dimethyl-*p*-phenylenediamine (D1), *p*-anisidine (D2), aniline (H), 4-(trifluoromethyl)aniline (A1), and 4-(trifluoromethylsulfonyl)aniline (A2) were purchased from Aldrich Chem., Inc., and used as received. GO was synthesized from graphite nanopowder using the modified Hummers' oxidation method [24]. To prepare IRnGs via an acid-catalyzed dehydration reaction, GO (700 mg) was dispersed in DMF (210 mL) under sonication for 1 h. Subsequently, catalytic amounts of acetic acid (7 mL) and the related aniline derivatives (3.76 mmol) were added, and the mixture was heated at 120 °C for 24 h under stirring. After cooling to room temperature, IRnGs were collected by filtration (PTFE membrane, 0.45 μm) and washed with a large amount of THF. Further purification was conducted by consecutive Soxhlet extraction with water, THF, and methanol. Finally, various IRnGs, denoted IRnG-D1, IRnG-D2, IRnG-H, IRnG-A1, and IRnG-A2 depending on the used aniline derivative, were obtained as black powders after vacuum-drying at 50 °C overnight. Elemental analysis (EA) was conducted using a Thermo Scientific Flash 2000 instrument. Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Scientific IS 10 spectrometer using KBr pellets. Thermogravimetric analysis (TGA) was carried out on a TA Q200 instrument (TA Instrument) in air at a heating rate of 10 °C min^{-1} . Raman spectra were recorded using a confocal Raman microscope (Alpha 300S, WITec) equipped with a 532-nm He-Ne laser, and X-ray diffraction (XRD) patterns were recorded using an X-ray diffractometer (X'pert-MPD, Philips) with Cu K α radiation. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo Fisher K-alpha spectrometer. Field emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM) imaging were carried out using JEOL JSM-6700F and JEOL JEM-2100F microscopes, respectively. Cyclic voltammetry (CV) analyses were conducted using a VersaSTAT3 potentiostat (Princeton Applied Research). Linear sweep voltammetry (LSV) measurements using a rotating ring disk electrode (RRDE, glassy carbon disk with a 4-mm diameter and a Pt ring with 5-mm/7-mm inner/outer diameters) were conducted at rotating speeds from 625 to 2500 revolutions per minutes (rpm) using an RRDE-3A electrode rotator (BAS Inc.) linked with a PARSTAT multichannel chassis potentiostat (Princeton Applied Research). CV and RRDE analyses were carried out using typical three-electrode cells, and electrodes coated with samples were used as working electrodes. Pt wire and Ag/AgCl were used as counter and reference electrodes, respectively. The sample loading level of the RRDE

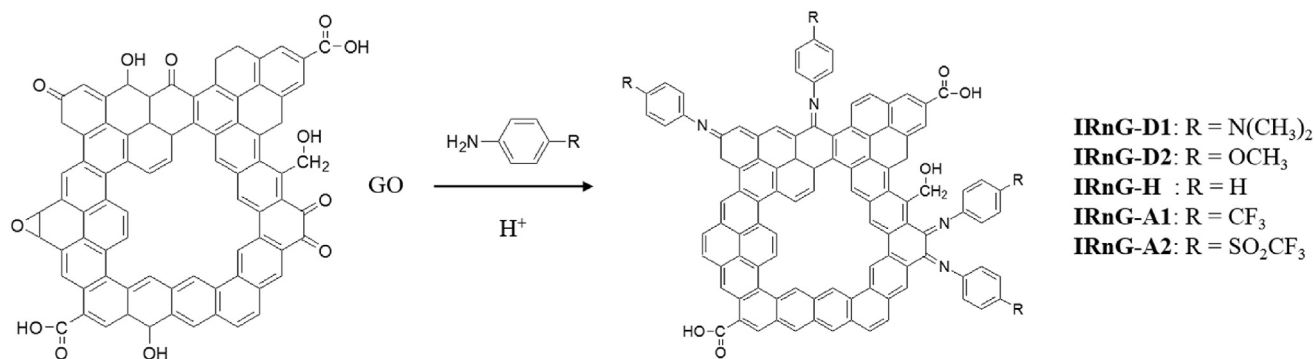


Fig. 1. Schematic representation of the acid-catalyzed dehydration reaction between GO and *para*-substituted anilines to produce IRnGs with various electron-donating ($\text{R} = \text{N}(\text{CH}_3)_2$ for IRnG-D1 or $\text{R} = \text{OCH}_3$ for IRnG-D2), neutral ($\text{R} = \text{H}$ for IRnG-H), and electron-accepting ($\text{R} = \text{CF}_3$ for IRnG-A1 or $\text{R} = \text{SO}_2\text{CF}_3$ for IRnG-A2) moieties.

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