



Synthesis of boron and nitrogen co-doped graphene nano-platelets using a two-step solution process and catalytic properties for oxygen reduction reaction



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ABSTRACT

Chemically modified graphenes (CMGs) show great promise for various applications owing to the feasibility of their low-cost mass production and good solution processability. Recently, hetero-atom-doped CMGs have been suggested as good candidate materials for electrochemical catalysts in oxygen reduction reaction (ORR). In this study, we synthesized B, N co-doped graphene nano-platelets (BN-rG-O) using a two-step solution process with sequential reaction of graphene oxide with borane tetrahydrofuran and hydrazine monohydrate. In the ORR measured in a basic medium (0.1 M KOH), BN-rG-O exhibits an onset potential of 0.81 V (vs. reversible hydrogen electrode), follows near four electron pathway, and shows excellent stability against methanol poisoning and during durability tests.

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1. Introduction

Chemically modified graphene (CMG) nano-platelets have been intensively investigated in energy conversion and storage applications such as fuel cells [1], batteries [2,3], supercapacitors [4,5] and hydrogen storages [6] owing to their good electrical, mechanical, and thermal properties, large surface area, and excellent electrochemical activities [7–9]. Hetero-atom doping of the CMG systems has been a promising way to control their physical and chemical properties for such applications. Recently, graphene-based co-doping systems containing two different hetero-atoms have attracted interest [10,11]. In particular, a boron and nitrogen co-doped system, produced by gas phase processing under high temperature and high pressure, showed good performance as an electrode in a supercapacitor and as a catalyst for oxygen reduction reaction (ORR) [12,13]. Consequently, it is highly important to develop new methods for the production of co-doped graphene nano-platelets using solution processing at low temperatures for their mass production with low costs and good solution processability.

Graphite oxide (GO), which is obtained by the oxidation of graphite, has been frequently used to produce CMG materials using the solution process owing to its good processability as well as chemical reactivity of the oxygen functional groups of GO. N-doped graphene was generated by the reaction between graphene oxide (G-O), which is produced by sonication of GO, and N-containing chemicals such as hydrazine or ammonium hydroxide in liquid phase at a low temperature [14–16]. B-doping into graphene networks was achieved by the reaction of G-O with a borane adduct using the solution process [17,18]. However, the solution-based production of co-doping systems including B and N atoms has hardly been reported. Here, we present a synthesis of B, N co-doped graphene nano-platelets (BN-rG-O) using a two-step solution process involving sequential reactions of G-O, first with a borane adduct and then with hydrazine monohydrate, and describe their catalytic performances for the ORR application.

2. Experimental

2.1. Preparation of B-G-O and BN-rG-O

GO was prepared by oxidizing natural graphite (SP-1, Bay carbon, USA) using the modified Hummers method [19]. An aqueous

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colloidal suspension of G-O was generated by sonication of GO (3 mg for 1 mL of deionized (DI) water (18.2 M Ω , Millipore, Germany)). Borane-tetrahydrofuran (BH₃-THF, 3 μ L for 1 mg of GO, Sigma–Aldrich) was added to this suspension, and the mixture was stirred at 80 °C for 2 days. The resulting suspension containing B-G-O nano-platelets was filtered through a membrane filter (pore size 0.2 μ m, 47 mm in diameter, Whatman, Germany) and the filtrate was washed with DI water at least twenty times, providing B-G-O in a paper-like material. After drying under vacuum at room temperature for 12 h, the B-G-O paper was used for various characterizations. To make BN-rG-O materials, the B-G-O suspension was placed at room temperature for cooling. Then, hydrazine monohydrate (1 μ L for 3 mg of GO, 98%, Sigma–Aldrich) was added to the suspension. The mixture was stirred at 80 °C for 12 h, generating agglomerated particles. The black powder was filtered through a glass filter and washed with DI water at least twenty times. The resulting BN-rG-O powder was used for further characterization and ORR tests after drying under vacuum at room temperature for 12 h.

2.2. Electrochemical characterization

The electrochemical characterization of the catalysts was performed using an IviumStat electrochemical analyzer. The electrochemical experiments were performed at room temperature using a three-compartment electrochemical cell. A graphite rod counter electrode and an Hg/HgO reference electrode were used. In this study, all potentials were reported with respect to the reversible hydrogen electrode (RHE). The Hg/HgO reference electrode was calibrated with respect to the hydrogen reference electrode (Hydroflex[®], Gaskatel) before every measurement. The potential difference between hydrogen reference electrode and Hg/HgO electrode was obtained after 20 min of stabilization. A glassy-carbon rotating ring-disk electrode (RRDE) was used as the working electrode, which was polished first with a 1.0 mm alumina suspension and then a 0.3 mm alumina suspension on a polishing cloth to give it a mirror finish. To prepare a catalyst ink, 30 mg of catalyst, 100 μ L of DI water, 1.01 mL of absolute ethanol, and 75 μ L of Nafion[®] (5 wt% in isopropanol, Aldrich) were mixed [for Pt/C catalysts, 5 mg of 20 wt% Pt/C (Johnson & Matthey, HiSPEC 3000), 1.15 mL of absolute ethanol, and 40.0 μ L of Nafion[®] were mixed], and the slurry was sonicated for 30 min using an ultra-sonicator (Branson 3510). Three μ L of the ink was taken by a microsyringe and deposited onto the glassy carbon RRDE with a diameter of 4 mm, and the electrode was dried at room temperature for 5 min. Before the electrochemical measurements, the surface of the catalyst was cleaned by cycling the potential between 0.05 and 1.20 V (vs RHE) 50 times at a scan rate of 100 mV s⁻¹. Cyclic voltammetry (CV) was performed over a voltage range of 0.05–1.2 V (vs RHE) at a scan rate of 50 mV s⁻¹ using nitrogen-saturated 0.1 M KOH electrolyte solutions. The ORR activity of the catalysts was measured with linear sweep voltammetry (LSV) from 1.1 to 0.2 V (from 0.2 to 1.1 V for Pt/C catalyst) at a scan rate of 5 mV s⁻¹, at rotating speeds of 100, 400, 900, 1600, and 2500 rpm in an oxygen-saturated electrolyte with oxygen purging.

The number of electrons transferred (n) was calculated from the slopes of Koutecky–Levich plots. The kinetic parameters were analyzed on the basis of the Koutecky–Levich equations:

$$\frac{1}{i} = \frac{1}{i_l} + \frac{1}{i_k} = \frac{1}{B\omega^{1/2}} + \frac{1}{i_k}$$

$$B = 0.62nFC_0D_0^{2/3}\nu^{-1/6}$$

here, i is the measured current density, i_k and i_l are the kinetic- and diffusion-limiting current densities, ω is the angular velocity of the disk ($\omega = 2\pi N$, N is the linear rotation speed), n is the overall number of electrons transferred in ORR, F is the Faraday constant (96485 C mol⁻¹), C_0 is the bulk concentration of O₂ in 0.1 M KOH (1.2 $\times 10^{-6}$ mol cm⁻³), D_0 is the diffusion coefficient of O₂ in 0.1 M KOH (1.9 $\times 10^{-5}$ cm² s⁻¹) and ν is the kinematic viscosity of the electrolyte (1.01 $\times 10^{-2}$ cm² s⁻¹).

To explore the long-term durability of the catalysts, the chronoamperometric response was obtained by applying 0.75 V (vs. RHE) in an oxygen-saturated 0.1 M KOH solution with a rotation rate of 1600 rpm for 10,000 s. The measured current was normalized with respect to its initial current. To assess the methanol-tolerance of the catalysts, 3.0 M methanol was added during the aforementioned test.

2.3. Instruments

Elemental analysis was performed with a FLASH EA1112 instrument (Thermo Electron, Italia) under helium atmosphere to determine C, N, O, and H contents. X-ray photoelectron spectroscopy (XPS) measurements were performed on an Angle-Resolved X-ray Photoelectron Spectrometer (Theta probe, Thermo electron cooperation, UK). Fourier transform infrared (FT-IR) spectra were collected using KBr pellets containing powder samples on a FT-IR Vacuum Spectrometer (Bruker VERTEX 80V, Bruker, Germany). Each spectrum, which was recorded as the average of 16 scans with a resolution of 4 cm⁻¹, was collected from 4000 cm⁻¹ to 400 cm⁻¹. Scanning electron microscopy (SEM) images were obtained with a field emission gun scanning electron microscope (S-4300, Hitach, Japan). Brunauer–Emmett–Teller (BET) surface area measurements (Full automatic physisorption analyzer, Micromeritics, Japan) were performed using adsorption of nitrogen.

3. Results and discussion

GO has a wide range of reactive oxygen functional groups on the basal planes and at the edges [20]. We used this chemically reactive material to introduce boron and nitrogen atoms into graphene-based networks. It was reported that hydrazine treatment of G-O leads to nitrogen incorporation in pyrazole form at the edges [21] and BH₃-THF treatment produces B-doped graphene materials separately [5]. Based on these results, we carried out sequential treatment of G-O using the stated chemicals, first BH₃-THF then hydrazine, to produce co-doped materials (BN-rG-O) as shown in Fig. 1a.

An aqueous solution of BH₃-THF was added into an aqueous suspension of GO at room temperature. After 2 days of reaction at 80 °C, a stable brown suspension containing B-G-O nano-platelets was resulted without any visible particles (Fig. 1). Reaction of hydrazine monohydrate with the B-G-O suspension generated agglomerated black particles (BN-rG-O). As shown in Fig. 1b, an SEM image shows that agglomerated BN-rG-O powder has crumpled morphology. A BET specific surface area of BN-rG-O powder was as high as 275 m²/g.

Chemical structures of the material were characterized using FT-IR spectroscopy, XPS, and combustion-based elemental analysis. A C1s XPS spectrum of GO (Fig. 2a) shows several components at 284.6 eV, 287 eV, and at around 289 eV, corresponding to graphitic carbon, C–O moieties such as hydroxyl and epoxy groups, and C/O moieties such as ketone and carboxyl groups, respectively [14,19,21–23]. After the reaction with BH₃-THF at 80 °C for 2 days, the XPS spectra of B-G-O show that the oxygen concentration was slightly reduced relative to that of GO. On the other hand, that of BN-rG-O shows significant decrease in the intensity of oxygen containing groups, indicating that GO was successfully reduced. C/

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