One-step codoping of reduced graphene oxide using boric and nitric acid mixture and its use in metal-free electrocatalyst

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ABSTRACT

In this study, the preparation of a highly efficient metal-free electrocatalyst, boron and nitrogen codoped reduced graphene oxide (BN-rGO), with an excellent durability is reported. The BN-rGO were prepared in one step using boric and nitric acid mixture, exhibiting highly improved oxygen reduction reaction (ORR) activity than those of the pristine GO and single doped rGOs. The electrocatalyst also showed the excellent long-term durability and CO tolerance than those of the commercial Pt/C catalysts.

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1. Introduction

In recent years, cost-effective nonprecious metal and metal-free catalysts have been widely studied for alkaline anion exchange membrane fuel cells (AAEMFCs) [1,2]. The AAEMFCs offer several advantages over the proton exchange membrane fuel cells such as faster kinetic at electrodes for the oxygen reduction reaction and fuel oxidation in the alkaline environment and a lower cost by using metal free or nonprecious metal catalysts [3,4].

Reduced graphene oxide (rGO) exhibits both advanced chemical and physical adsorption capability owing to the abundant functional groups and high electrical conductivity of its well-developed sp^2 networks, enabling it as an alternative to the Pt/C catalysts in the fuel cell applications [5,6]. However, the zero band gap of graphene weakens its catalytic activity and limits its applications when it is used without metal components. The chemical doping of graphene or GO with heteroatoms is considered as an effective strategy to enhance the catalytic activity by tailoring its electronic environment [1,7–9].

In this study, we report the B and N codoped rGOs (BN-rGOs) synthesized by a simple one-step codoping process using mixed organic acids [10]. The lower and higher electronegativities of boron and nitrogen than that of carbon is believed to effectively modify the electronic structure of carbon to be more reactive toward oxygen. The BN-rGO fabricated using the mixture of boric and nitric acid exhibited excellent electrochemical performances

such as high ORR activity and CO tolerance when used as a metal-free catalyst in the alkaline media.

2. Experimental

GO was prepared according to the Hummers method as described in our previous report [10]. To prepare B-rGO, the N-rGO, and BN-rGO, GO were mixed with 0.1 M boric acid, nitric acid, and a mixture of boric and nitric acid in N-Methyl-2-pyrrolidone (NMP) and maintained at 180 °C for 1 h. Then, all the samples were annealed at 800 °C in argon atmosphere for 1 h after washing and drying. rGO was obtained by the thermal reduction of GO at same condition.

The catalyst suspensions in isopropanol ($10 \, mg \, mL^{-1}$) were prepared by introducing a predetermined amount of sample powder in the pure solvent under sonication followed by dropping 10 μL of Nafion solution (0.5 wt% in isopropanol) as the binder.

3. Results and discussion

The XPS survey spectra of the BN-rGO shown in Fig. 1(a) confirm the incorporation of B and N atoms to GO, indicating successful B and N doping on the GO. In addition, the higher binding energy of both B1s main peak (191.7 eV) and shoulder peak (190.4 eV) than that of the pure boron (187 eV) indicates the bonding of B with N and C atoms [11]. The N1s peak located at 398.3 and 400.4 eV indicates that the N atoms were incorporated to pyridinic-N and pyrrolic-N, respectively, also indicating the successful doping of N

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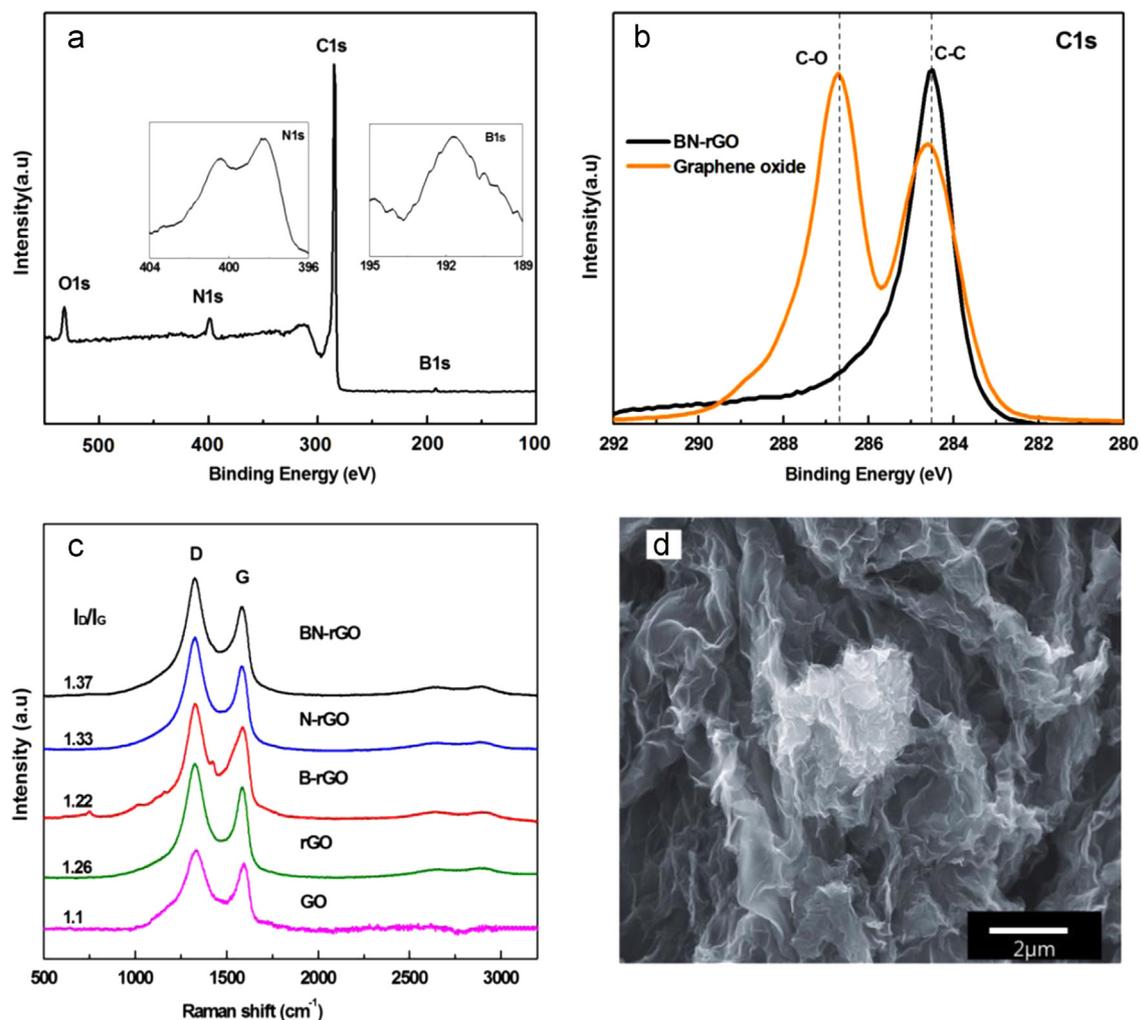*E-mail address:* shhur@ulsan.ac.kr (S.H. Hur).

Fig. 1. (a) The XPS survey spectrum of the BN-rGO. Inset: XPS spectra of B1s (right) and N1s (left). (b) C1s XPS spectra of the pristine GO and BN-rGO. (c) Raman spectra of GO, rGO, B-rGO, N-rGO, and BN-rGO. (d) The SEM image of the BN-rGO.

atoms to GO [12]. Fig. 1(b) shows that the main peak position of C1s (284.4 eV) was unchanged after the doping, but the shoulder peaks significantly decreased at a high binding energy, indicating the reduction of the oxygen-related functional groups of GO during the acid treatment and thermal annealing [10]. The elemental analysis shows that the B and N contents of BN-rGO were highest among all samples and some amount of nitrogen atoms in B-rGO can be incorporated by the NMP (Table 1).

The Raman spectra of the GO and doped graphene shown in Fig. 1(c) exhibit two intense peaks at 1328 and 1595 cm^{-1}, corresponding to diamondoid (D) and graphitic (G) peaks, respectively [13]. The higher I_D/I_G value of the BN-rGO than those of B-rGO and N-rGO (Fig. 1c) can be attributed to the formation of B–N bonds on the graphene sheets [12]. The morphology of the BN-rGO nanosheet is wrinkled and folded as shown in Fig. 1(d), which enhances the electrochemical reactions due to the formation of mid-gap states [14]. The increased van der Waals force between the rGO sheets after the reduction of the functional groups and the incorporation of heteroatoms such as B and N caused the wrinkled and disordered structures in the BN-rGO, facilitating the adsorption of oxygen and improving the ORR activity [15].

The cycle voltammogram (CV) of the BN-rGO was studied in the air, O$_2$, and N$_2$ saturated 0.1 M KOH using a haft-cell system with an Ag/AgCl as the reference electrode at a scan rate of 50 mV s^{-1}. As shown Fig. 2(a), an oxygen reduction peak at −0.37 V was clearly observed in an O$_2$ saturated environment and decreased in

Table 1
Atomic contents of samples.

	Atomic content (%)				
	C	N	B	O	H
B-rGO	75.9	4.7	2.2	4.2	13.0
N-rGO	85.2	6.0	0.0	2.5	6.3
BN-rGO	80.4	6.0	3.2	2.1	8.3

an air-saturated condition and completely disappeared in a N$_2$ saturated condition. The highest peak intensity of the BN-rGO in the O$_2$-saturated environment indicates its electrocatalytic oxygen reduction capability in the alkaline media, and thus potential candidates for metal-free electrocatalysts of AAEMFCs.

Linear sweep voltammetry (LSV) of the BN-rGO was performed using the Rotating disk electrode (RDE) in an O$_2$ saturated 0.1 M KOH solution at a scan rate of 10 mV s^{-1}. Fig. 2(b) shows that the current density of the BN-rGO was the highest among those of the B-rGO, N-rGO, rGO, and GO, indicating the synergetic effects of B and N atoms on the ORR activity. To investigate the kinetics during the ORR for each sample, the electron transfer number was obtained and compared by changing rotating speed of the RDE. The electron transfer number for ORR was obtained from the