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Supplementary Information

Electrochemical and electrocatalytic reaction characteristics of boron-incorporated graphene via a simple spin-on dopant process

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Experimental method

Fabrication of boron-doped graphene

An SOD procedure was used to incorporate elemental boron into graphene. SOD film was prepared on Si substrate by spin-coating a boron-containing dopant solution (Filmtronic B155 compounds). The SOD films were placed at a distance of 10 mm above the graphene flakes (Graphene nanopowder with 3 nm of thickness and ~8 μm of lateral dimensions, Grade AO-1, Graphene supermarket) or CVD-G to avoid direct contact between the graphene and SOD film. The samples were loaded into a tube furnace, and the temperature was increased at 15°C/min to 500 and 600 °C with 2000 sccm of Ar gas for 5 min.[R1]

Characterization of boron-doped graphene

The surface morphology of pristine graphene flakes, SOD500-GFs, and SOD600-GFs were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi). The elemental distribution was examined using an energy-dispersive X-ray spectrometer (EDS). The Raman spectra were measured using a micro Raman spectrometer (HORIBA) with a 532-nm laser. The chemical bonding states of the SOD-treated graphene flakes were investigated by FT-IR spectroscopy and X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific). Furthermore, to compare the specific surface area for three as-prepared samples, we performed the nitrogen adsorption and desorption isotherms using a Micromeritics ASAP 2020 at 77K. Also, the specific surface area for each sample was calculated using the BET adsorption isotherm theory based on following equations:

$$\left[\frac{1}{V_a\left(\frac{P_0}{P}-1\right)}=\frac{C-1}{V_m C}\times\frac{P}{P_0}+\frac{1}{V_m C}\right]$$

where, P is partial vapor pressure of adsorbate nitrogen gas in equilibrium with the surface at 77.4 K, P_0 is saturated pressure of adsorbate nitrogen gas, V_a is volume of gas adsorbed at STP, V_m is volume of gas adsorbed at STP to produce an apparent monolayer on the sample surface, and C is dimensionless constant that is related to the enthalpy of adsorption of the adsorbate nitrogen gas on sample.

$$S = \frac{V_m \times N \times a}{m \times 22400}$$

where A is specific surface area, N is Avogadro constant, a is effective cross-sectional area of one adsorbate molecule (0.162 nm^2 for nitrogen), and m is mass of sample.

Electrochemical property analysis of boron-doped graphene

The electrochemical properties of the boron-doped graphene flakes were measured in a three-electrode system using a potentiostat (Autolab PGSTAT302N). The pseudo-capacitive and electrochemical oxygen reduction of the treated flakes were estimated using cyclic voltammograms (CVs) in 1.0 M KOH electrolyte.

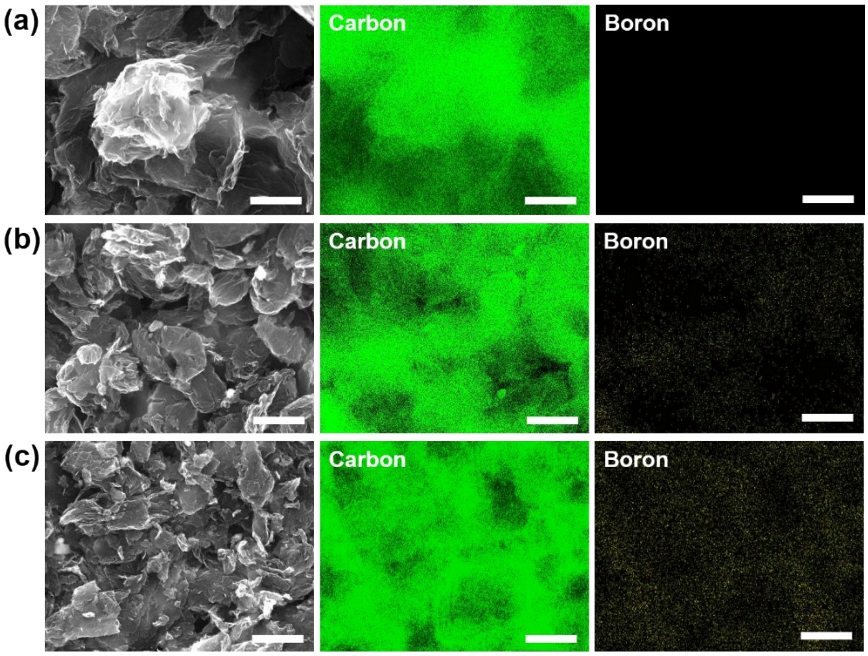

Figure S1. FE-SEM images and elemental mapping of the carbon (green), and boron (yellow) for (a) pristine GFs, (b) SOD500-GFs and (c) SOD600-GFs. Scale bar is 10 um.

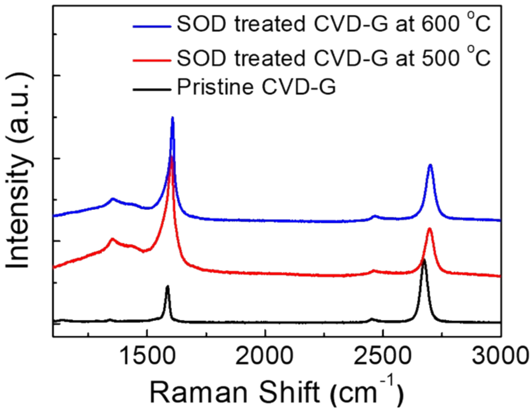

Figure S2. Raman spectra of pristine CVD-G, and SOD-treated CVD-G at 500 °C and 600 °C.

We confirmed that the SOD method can apply to a monolayer graphene grown by chemical vapor deposition method (CVD-G). Raman spectroscopy is a powerful nondestructive tool for identifying the doping of graphene. Fig. S2 shows the Raman spectra of pristine CVD-G and SOD-treated CVD-G at 500 °C and 600 °C. The Raman spectra of all the samples show the G and 2D peaks at 1586 cm^{-1}, and 2674 cm^{-1} for the pristine CVD-G, 1600 cm^{-1} and 2698 cm^{-1} for SOD treated CVD-G at 500 °C, and 1608 cm^{-1} and 2700 cm^{-1} for SOD treated CVD-G at 600 °C, respectively, confirming the structural properties of graphene. However, interestingly, both the G and 2D peak positions of SOD-treated CVD-G are shifted to higher wave numbers compared to the pristine CVD-G. Moreover, SOD-treated CVD-G samples show an increase in peak intensities of D peaks. These Raman results clearly indicate that the SOD-treated CVD-G is successfully p-type doped by boron dopants.[R2,R3]

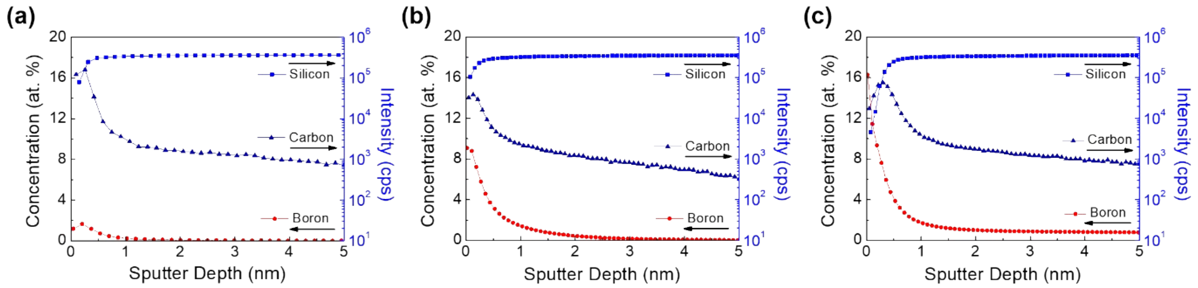

Figure S3. Secondary ion mass spectroscopy (SIMS) depth profiles results of (a) pristine CVD-G, and SOD-treated CVD-G (b) at 500 °C and (c) 600 °C.

Material	Conductivity (S/m)
Pristine CVD-G	0.19 X 10^4
SOD treated CVD-G at 500 °C	1.86 X 10^4
SOD treated CVD-G at 600 °C	2.01 X 10^4

Table S1. The electrical conductivity of pristine CVD-G, and SOD-treated CVD-G at 500 °C and 600 °C.

In order to further confirm the incorporation of boron dopants into CVD-G crystal, we performed secondary ion mass spectroscopy (SIMS) depth profiles. **Fig. S3** shows secondary ion mass spectroscopy (SIMS) depth profiles results of (a) pristine CVD-G, and SOD-treated CVD-G (b) at 500 °C and (c) 600 °C. We clearly observed the boron signal from the both of SOD treated CVD-G at 500 °C and 600 °C, whereas no boron signal was detected from pristine CVD-G before SOD treatment. These results further confirm that CVD-G is successfully doped with boron through relatively low-temperature processing of SODs. The electrical properties of pristine CVD-G and SOD-treated CVD-G are measured using a Hall measurement system

(ECOPIA HMS-5000). The electrical conductivity of SOD-treated CVD-G is enhanced about 10 times higher than that of pristine CVD-G, because of the p-type doping effect of graphene by boron dopants (**Table S1**). By combining the structural and chemical analyses, it can be expected that the SOD-treated graphene can be acted as the active site for pseudo-capacitive behavior in the supercapacitor and ORR in alkaline fuel cell because the boron doped graphene with p-type conductivity can not only improve electrical conductivity compared to pure graphene but also can be acted as an electron acceptor for reaction with the OH^- ions.

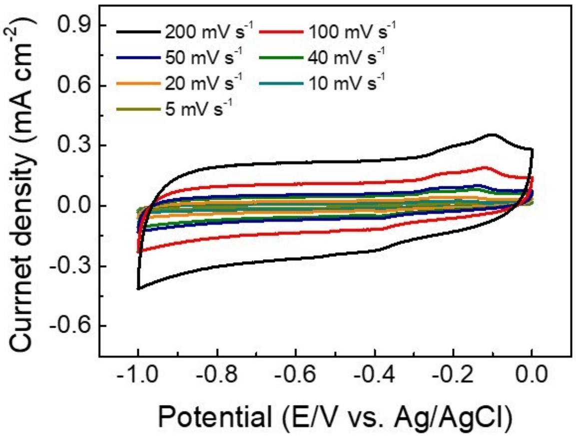

Figure S4. CV curves for the pristine GFs at different scan rates from 5 to 200 mV s^{-1}.

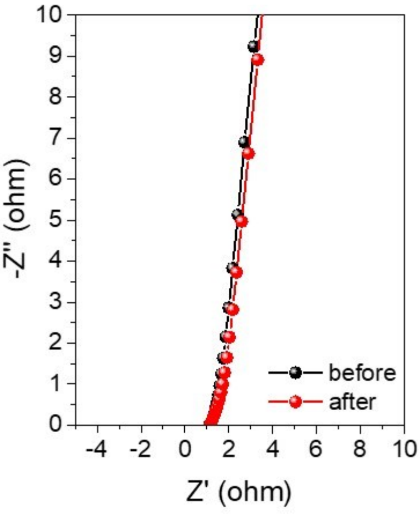

Figure S5. Nyquist plots of the SOD600-GFs before and after stability tests.

References

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