Plasma-induced High-efficient Synthesis of Boron Doped Reduced Graphene Oxide for Supercapacitors

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Experimental Section.

Materials. Natural graphite powder ($\leq 30\mu$ m) was purchased from Huayi Chemical Co. Ltd. (Shanghai, China). H₂SO₄ (ACS grade, 95-98%), H₃PO₄ (ACS grade, $\geq 85\%$), KMnO₄ (ACS grade, $\geq 99\%$), H₃BO₃ (ACS grade, $\geq 99\%$), HCl (ACS grade, 36-38%), H₂O₂ (ACS grade, 30% aqueous solution), and ethanol (ACS grade, $\geq 99.8\%$) were purchased from Chuandong Chemical Co. Ltd. (Chongqing, China). All chemicals were used as received without further purification.

Preparation. Graphite oxide (GO) was synthesized by the modified Hummer's method [1]. In brief, a sample of graphite powders (ca. 3.0 g) was added to 400 mL mixed acid (360 mL H_2SO_4 and 40 mL H_3PO_4) in an ice bath under vigorous stirring. Then, 18.0 g of KMnO₄ was slowly added to the mixture. After that, the mixture was heated up to 323 K and maintained at the temperature for 48 h under continuous stirring. After the mixture was cooled to room temperature, 300 mL of deionized water was added into the system. In addition, 10 mL of H_2O_2 and 50 mL of HCl were added to remove the impurities. The obtained bright yellow dispersion was then centrifuged and the solid material was washed multiple times by a large amount of deionized water. Finally, the brown precipitate was dried at 333 K in a vacuum oven for 24 h.

The plasma reduced graphene oxide (rGO) was prepared by direct exfoliation and reduction of GO in a DBD plasma reactor (Fig. S1) [2]. In brief, 200 mg of GO powders were placed in the middle of a quartz tube and held by quartz wool. Before discharge, the working gas (H₂, 99.99%) at a flow rate of 120 mL·L⁻¹ was introduced for 20 min to purge the quartz tube. The rGO was obtained under 80 V and 1.6 A AC input power at room temperature and ambient pressure. The plasma treatment last for ca. 3 min.

To prepare plasma reduced boron doped reduced graphene oxide (B-rGO), 200 mg of GO and 100 mg of boric acid were added in 50 mL of deionized water and the mixture was stirred for 30 min. Then, the homogeneous brown dispersion was dried in a vacuum oven for 6 h. Subsequently, the obtained paper like precursor was placed in the DBD reactor for plasma treatment. The operation condition was the same as the preparation of rGO. After plasma treatment, the obtained sample was washed by hot deionized water and ethanol to remove the unreacted boric acid. B-rGO was finally obtained after being dried in a vacuum oven for 4 h.

Dielectric barrier discharge (DBD) plasma reactor. The plasma treatment was performed in a coaxial DBD reactor (Fig. S1) [3, 4]. The reduction gas (H₂) was injected into the annular gap between the inner ceramic-tube (φ 16×2) and outer quartz-tube (φ 25×2.5) to reduce and exfoliate the sample. The quartz-tube was covered with wire entanglement and connected to a high voltage supply while the ceramic-tube was filled with Mg and Al powders and served as the ground electrode. The discharge gap and discharge length are 2 and 150 mm, respectively.



Figure S1. Schematic diagram of the DBD plasma reactor.

Characterizations. The samples were characterized by X-ray diffraction (XRD, Rigaku-D/max-3B) with Cu K α radiation ($\lambda = 0.154056$ nm), using a voltage of 40 kV, a current of 30 mA, and a scanning rate of 2°/min. FTIR spectra were recorded on a PerkinElmer Spectrum 400 spectrophotometer using KBr pellet samples. Raman spectra were taken with He-Ne laser (532 nm) as the excitation source by using confocal Raman microscopy (LabRAM HR Evolution, Jobin Yvon S.A.S, France). N₂ adsorption-desorption measurements were conducted on a Quadrasorb 2MP analyzer at 77 K. Brunauer-Emmett-Teller (BET) surface areas were determined by using the desorption data. Pore size distribution was obtained using the Barrett-Joyner-Halenda (BJH) method. X-ray photoelectron spectra (XPS) were recorded on a Thermal ESCALAB 250 XI. Field emission scanning electron microscopy (FESEM, Hitachi S-4800) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai F20) instruments were utilized to study the morphology of the synthesized samples.

Electrochemical measurement. Electrochemical characterizations were performed on an electrochemical work station (PARSTAT 4000, USA) using a three-electrode system. A Pt mesh and an Ag/AgCl electrode (3.0 M KCl, 0.227 V vs. SHE at 298 K) were used as the counter electrode and reference electrode, respectively. To prepare working electrode, the asprepared samples were dispersed in an ethanol solution with Nafion[®] (5%) as the binder via ultrasonication for 1 h to form inks, and then the dispersed samples were dropped onto a 2.5 mm diameter glassy carbon electrode. All the experiments were performed in 6.0 M KOH electrolyte. The specific capacitance was obtained from the constant-current charge/discharge curves.



Figure S2. (a) SEM image of rGO; (b) SEM, (c) TEM, and (d) HR-TEM image of B-rGO. The inset in (d) shows an SAED pattern of B-rGO.



Figure S3. Cyclic voltammograms of rGO (a) and B-rGO (b) at scan rates from 20 to 200 mV S⁻¹ in 6.0 M KOH solution; Cyclic voltammograms of rGO (c) and B-rGO (d) at scan rates 5 and 10 mV S⁻¹ in 6.0 M KOH solution; galvanostatic charge/discharge curves of rGO (e) and B-rGO (f) at current densities from 0.5 to 20 A g⁻¹.

Sample	Specific Surface Area (m ² g ⁻¹)	Pore Volume (mL g ⁻¹)	Pore Size (nm)	
rGO	312.5	0.218	2.4	
B-rGO	276.7	0.749	2.0	

Table S1. BET surface areas of samples.

Electrode materials	Preparation methods	Capacitance	Rate	Electrolyte	Reference
B-doped rGO	H_2 DBD plasma reduction of GO with boric acid	446.24 F g ⁻¹	0.5 A g ⁻¹	6 M KOH	Present work
Graphene	Template growth on MgO layers	245 F g ⁻¹	1.0 A g ⁻¹	6 M KOH	[5]
rGO	Reduction of GO by H ₂ DBD plasma	210 F g ⁻¹	1.0 A g ⁻¹	6 M KOH	[2]
B-doped rGO	Reduction of GO with BH ₃ -THF	177 F g ⁻¹	0.5 A g ⁻¹	6 М КОН	[6]
B-doped graphene	Pyrolysis of GO with boric acid	172 F g ⁻¹	0.5 A g ⁻¹	6 М КОН	[7]
N-doped graphene	Ammonia flame treatment of GO	246 F g ⁻¹	1.0 A g ⁻¹	6 M KOH	[8]
N-doped graphene	Reduction of GO with cyanamide	302 F g ⁻¹	5 mv s ⁻¹	6 M KOH	[9]
B/N-doped carbon	Arc synthesis method	277 F g ⁻¹	0.2 A g ⁻¹	6 M KOH	[10]
B/N-doped porous carbon	Carbonization of the B and N contained gel	216 F g ⁻¹	0.5 A g ⁻¹	6 M KOH	[11]

Table S2. Comparison of preparation methods and capacitances for the reported doped graphene supercapacitor electrodes.

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