Electronic Supporting Information

**One-step Synthesis of Sulfur doped Graphene Foam for Oxygen Reduction Reactions**

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**Experimental Section**

**Chemicals**

Graphite flakes, was purchased from Alfa Aesar. Sulfuric acid (H\(_2\)SO\(_4\), 95-98 %), potassium permanganate (KMnO\(_4\), 99 %), H\(_2\)O\(_2\), NaNO\(_3\), hydrochloric acid (HCl), Na\(_2\)S·9H\(_2\)O were purchased from Shanghai Chemical Reagents Company and directly used without further treatment or purification.

**Materials Synthesis**

Graphene oxide (GO) was synthesized by modified Hummer’s method\(^1, 2\). Briefly, graphite (3.0 g) was added to concentrated sulfuric acid (70 mL) under stirring at room temperature, then sodium nitrate (1.5 g) was added, and the mixture was cooled to 0 °C. Under vigorous stirring, potassium permanganate (9.0 g) was added slowly to keep the temperature of the suspension lower than 20 °C. Subsequently, the reaction system was transferred to a 35-40 °C water bath for 0.5 h, forming a thick paste. Then, 140 mL of water was added, and the solution was stirred for another 15 min. An additional 500 mL of water was added followed by a slow addition of 20 mL of H\(_2\)O\(_2\) (30%), turning the color of the solution from brown to yellow. The mixture was filtered and washed with 1:10 HCl aqueous solution (250 mL) to remove metal ions followed by repeated
washing with water and centrifugation to remove the acid. The resultant solid was dispersed in water by ultrasonication for 1h to make a GO aqueous dispersion (0.5 wt %). The obtained brown dispersion was then subjected to 30 min of centrifugation at 4000 rpm to remove any aggregates, and then, it was purified by dialysis for 1 week to remove the remaining salt impurities for the following experiments.

Aqueous suspensions of GO at concentrations of 0.1–2.0 mg ml\(^{-1}\) were prepared, and reducing agent Na\(_2\)S (54 mmol L\(^{-1}\)) were added. The mixed suspension was heated at 90°C for 3 h without stirring. Then, the as-prepared graphene hydrogel was washed by deionized water and ethanol to remove residual inorganic compounds. For graphene foam preparation, the as-prepared graphene hydrogel was freeze-dried to remove absorbed water. For comparison, sulfur doped reduced graphene oxide sheet (S-rGO-sheet) was also obtained through a similar procedure with vigorously stirring. NaBH\(_4\) reduced graphene foam was also synthesized by a similar method for comparison.

**Characterization**

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Nicolet 7000-C spectrometer in the range of \(\nu = 400-4000\) cm\(^{-1}\) by using pressed KBr tablets. The field emission scanning electron microscopy (FE-SEM) was performed on a hitachi-S4800 while the transmission electron microscopy (TEM) images in this work and energy-dispersive X-ray (EDX) spectra were collected from a JEOL-2010F electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) signals were collected on a VG Micro MK II instrument using monochromatic Mg Ka X-rays at
1253.6 eV operated at 150 W, and spectrum calibration was performed by taking the C 1s electron peak (BE = 285 eV) as internal reference. Raman spectra were recorded on a DXR Raman Microscope with a 532 nm excitation length, Thermal Scientific Co., USA.

**Electrochemical measurement**

Electrochemical experiments were performed on CHI 660A electrochemical workstation (CH Instrument, Inc.) with a standard three-electrode cell. Glassy carbon disks of 6 mm diameter (0.283 cm$^2$) served as substrate for the catalyst materials. Catalyst ink with 5 mg mL$^{-1}$ (ethanol : water = 1 : 1, volume scale) and 25 μL Nafion solution (5%) was dispersed ultrasonically, and 20 μL catalyst ink was transferred onto the glassy carbon substrate, yielding a catalyst loading level of 0.35 mg cm$^{-2}$. A platinum wire and Ag/AgCl (3 M KCl) were used as counter and reference electrodes, respectively. 0.1 M KOH solution was used as electrolyte for electrochemical measurements and methanol electro-oxidation studies, respectively. High purity O$_2$ was used prior to the measurements to deaerate the electrolyte. The catalysts were characterized by cyclic voltammetry (CV) test at room temperature.
Figure S1. TEM images of S-rGO-sheet
Figure S2. EDS of S-rGO-sheet
Figure S3. High resolution XPS C1s spectra of S-rGO-foam (A) and GO (B), and high resolution S2p peak (C) of S-rGO-foam (the peaks are fitted to two energy components centered at around 163.5 eV and 164.9 eV, corresponding to C-S-C 2P 3/2, and C-S-C 2P 1/2, respectively).
Figure S4. Cyclic voltammograms curves of synthesized samples in 0.1 M KOH electrolyte saturated with O$_2$ at a scan rate of 0.05 V s$^{-1}$ at 25$^{\circ}$C
Figure S5. Nitrogen adsorption/desorption isotherms of samples.

Reference