Supplementary Information

Molecular Doping of Graphene as Metal-free Electrocatalyst for Oxygen Reduction Reaction

S. Dou, A. Shen, L. Tao, S. Wang*

Experimental Section

Synthesis of NB-Graphene

Graphene oxide was synthesized according to the modified Hummers method.\textsuperscript{S1} To prepare reduced graphene, graphene oxide was thermally reduced at 800°C for 1 h under Ar atmosphere. The as-prepared graphene was immersed in aqueous solution of 2.5 M sodium dodecyl sulfate (SDS) under a constant stirring at 35°C, and 4-NBD (Alfa, Aesar, USA) with different mass ratio to graphene (1:10, 1:20 and 1:30) were dissolved in water followed by slowly dropping into the graphene dispersion, respectively. After reaction for 16 h, the NB-Graphene samples were washed with ultrapure water, acetonitrile, ethanol and dried in a vacuum oven at 65°C overnight.

Physical characterizations

The Raman spectra were collected on a Raman spectrometer (Labram-010) using 632nm laser. The thermogravimetric analysis was carried out by a STA449C instrument with a heating rate of 10 °C in Ar. The morphology of NB-Graphene was analyzed by Transmission electron microscopy (TEM). X-ray photoelectron spectroscopic (XPS) measurements were performed on an ESCALAB 250Xi using a monochromic Al X-ray source (200 W, 20 eV).

Electrochemical measurements

The electrocatalytic performance of NB-Graphene was measured on an electrochemical workstation (CHI 760E, CH Instrument, USA) and a rotating ring disk electrode apparatus (RRDE-3A, ALS, Japan) in a three-electrode cell by using a platinum wire was used as counter electrode and saturated calomel electrode (SCE) as reference electrode. The working electrode was a rotating ring/disk electrode with glass carbon disk (4 mm in diameter). 5.0 mg electrocatalyst was immersed in 5 mL ethanol and 0.25 mL Nafion solution (5 wt%, Sigma Aldrich, USA) and ultrasonicated for 45 min to give a homodispersed ink. To prepare the electrode, 20 μL of the ink was dropped onto the glassy carbon electrode and dried in air.

Figure S1. TEM images of NB-Graphene
Figure S2. Raman spectra of NB-Graphene with different amounts of nitrobenzene group.
Figure S3. RDE voltammograms of NB-Graphene and commercial 20% Pt/C electrocatalyst in an O$_2$-saturated 0.1 M aqueous KOH solution with a scan rate of 10 mV s$^{-1}$ at a constant rotation rate of 1600 rpm.