Supplementary Information

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

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Experimental Section

Synthesis of NB-Graphene

Graphene oxide was synthesized according to the modified Hummers method.[S1] To prepare reduced graphene, graphene oxide was thermally reduced at 800℃ 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℃, 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℃ 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.

Reference S1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339-1339.

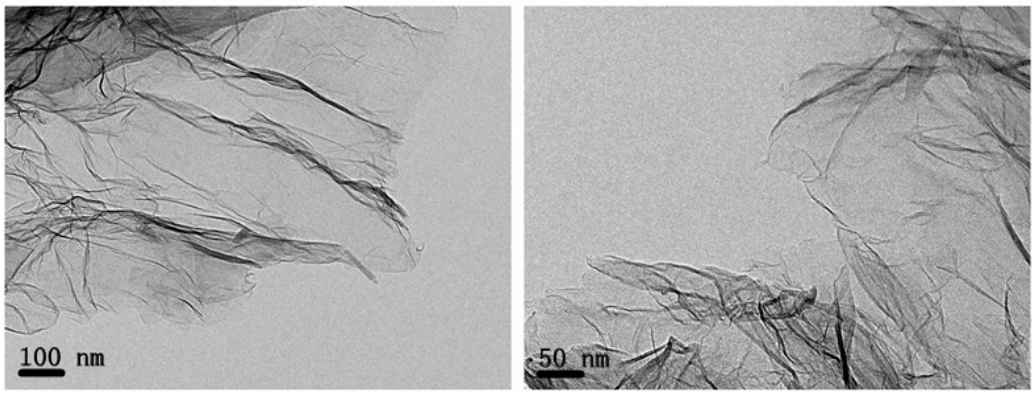

Figure S1. TEM images of NB-Graphene

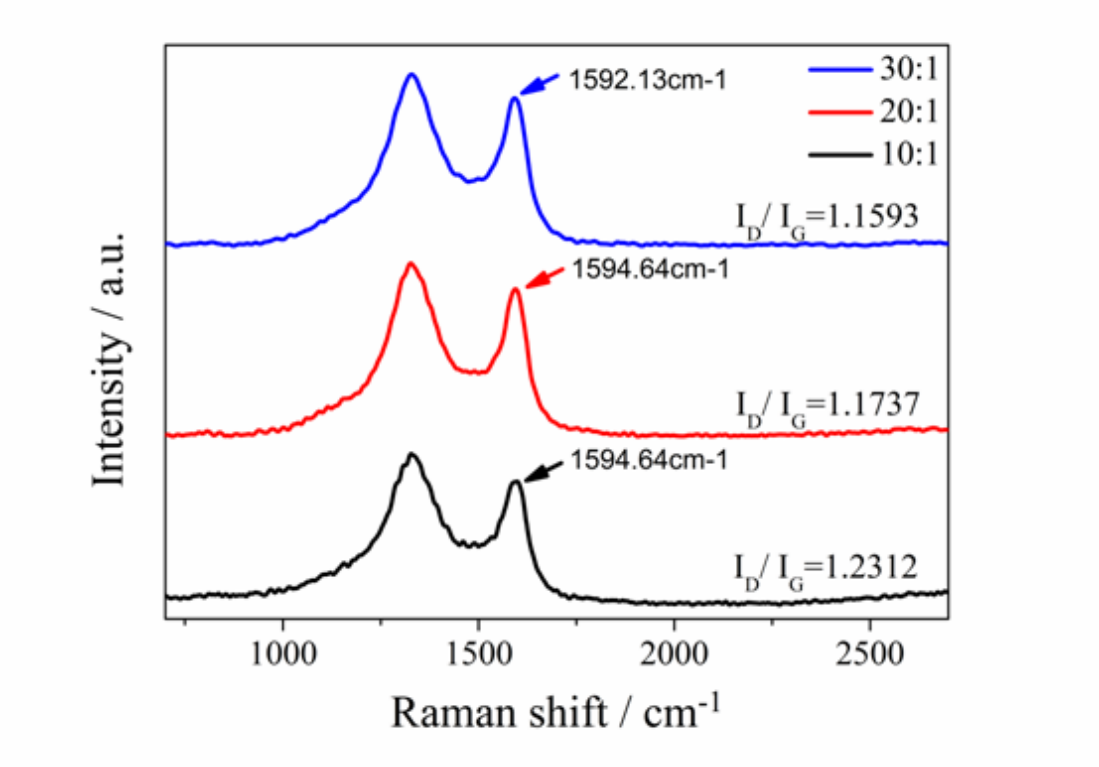

Figure S2. Raman spectra of NB-Graphene with different amounts of nitrobenzene group.

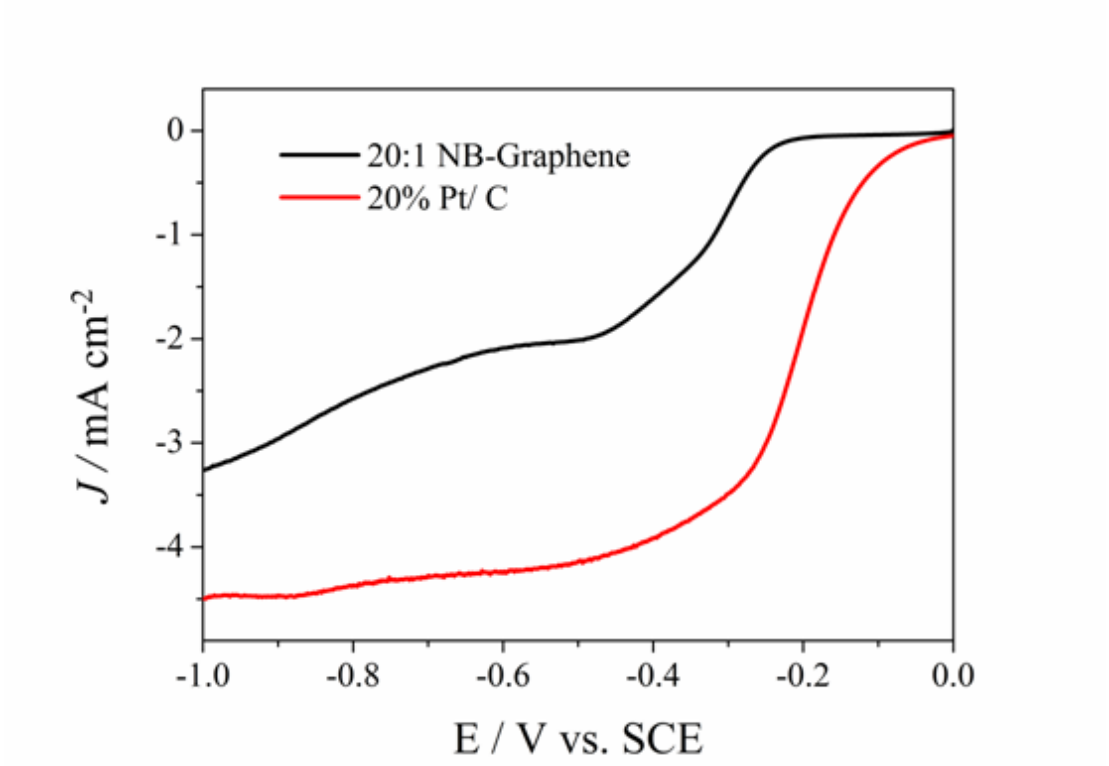

Figure S3. RDE voltammograms of NB-Graphene and commercial 20% Pt/C electrocatalyst in an O_2-saturated 0.1 M aqueous KOH solution with a scan rate of 10 mV s^{-1} at a constant rotation rate of 1600 rpm.