

Supporting Information

Synergistic Enhancement of Nitrogen and Sulfur Co-doped Graphene with Carbon Nanospheres Insertion for Electrocatalytic Oxygen Reduction Reaction

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Experimental

Synthesis of GO

GO was prepared by chemical oxidation and exfoliation of natural graphite under acidic conditions according to the Hummer's method.

Synthesis of ACB

Typically, 2 g carbon black (Vulcan XC-72) was acid-treated with concentrated HNO₃ (120 ml) at 110 °C for 3 hours. Then the solid products were purified by centrifugation, washed with distilled water and obtained by freeze drying.

Synthesis of NSGCB

12.5 mL ACB solution (2 mg/ mL) was gradually added to the 75 mL GO solution (1 mg/ mL). The mixture solution was ultra-sonication for 1 h to obtain homogenous solution. Then, the resulting aqueous mixture was rotary evaporated at 70 °C to remove water, and a black solid was obtained. Subsequently, the solid was crashed in a mortar with 1 g thiourea into fine power. The mixture was then heated at 900 °C for 2 h under the protection of N₂ to obtain NSGCB. For the purpose of comparison, NSGs, NSCB, Gs, and CB were also prepared similarly by using single carbon source or in the absence of thiourea, respectively.

Material Characterization

Scanning transmission electron microscopy (S-TEM) and TEM images were obtained on STEM (Tecnai G2 F30). Elemental mapping were conducted using EDAX detector attached on Tecnai G2 F30. Thermal gravimetric analysis (TGA) was conducted on Pyris1 TGA Instrument at 40-800 °C in a 20 mL min⁻¹ N₂ flow with a heating rate of 5 °C min⁻¹. X-ray photoelectron spectroscopic (XPS) measurements were performed on an AXIS-ULTRA DLD-600W Instrument. Raman spectra were taken by a LabRam HR800 spectrometer with a 532 nm laser excitation.

Electrochemical Measurements

All the electrochemical measurements were performed using a three-electrode system at room temperature (298 K) with electrochemical workstation CHI 760e and high speed rotators from Pine Instruments. A carbon paper and a reverse hydrogen electrode were used as the counter electrode and reference electrode, respectively. 0.1 M KOH solution was employed as electrolyte. To prepare the working electrode, 4 mg of samples was dispersed in 1 mL 0.1 wt. % Nafion solution (diluted with isopropyl alcohol) and sonicated to form a homogeneous ink. 15 μ L of the ink was dipped onto a polished 5 mm (0.196 cm²) glassy carbon electrode uniformly, and dried naturally. The loading quantity of commercial Pt/C is about 25 μ g cm⁻². Cyclic voltammograms (CV) were measured in N₂- or O₂-saturated 0.1 M KOH aqueous solution. The linear sweep voltammetry (LSV) measurements of the samples are operated on a rotating disk electrode (RDE) in O₂-saturated 0.1 M KOH solution at a sweep rate of 5 mV s⁻¹ and different rotation rates. The rotating ring-disk electrodes (RRDE) were conducted in O₂-saturated 0.1 M KOH solution at the rotation rate of 1600 rpm. The Koutecky-Levich plots were obtained by linear fitting of the $\omega^{-1/2}$ versus reciprocal current density j^{-1} collected at different potentials.

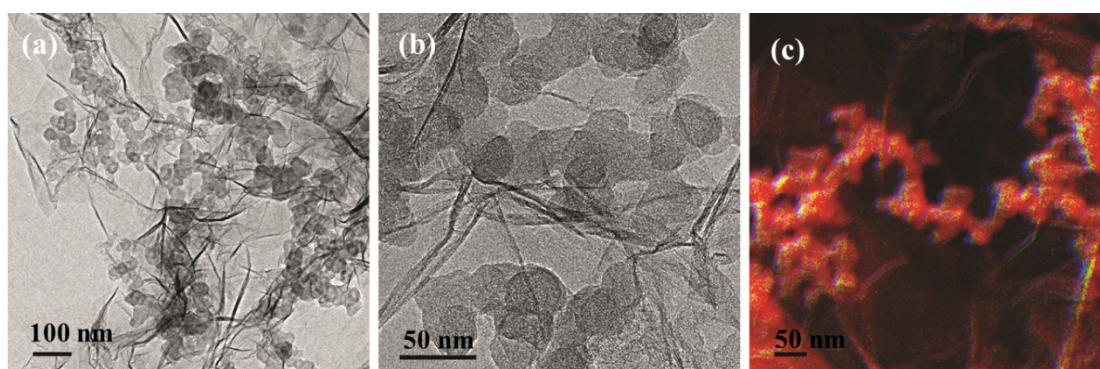


Figure S1.(a, b) TEM images of NSGCB nanocomposite; (c) overlap elemental mapping of C (red), N (blue), and S (green) of NSGCB.

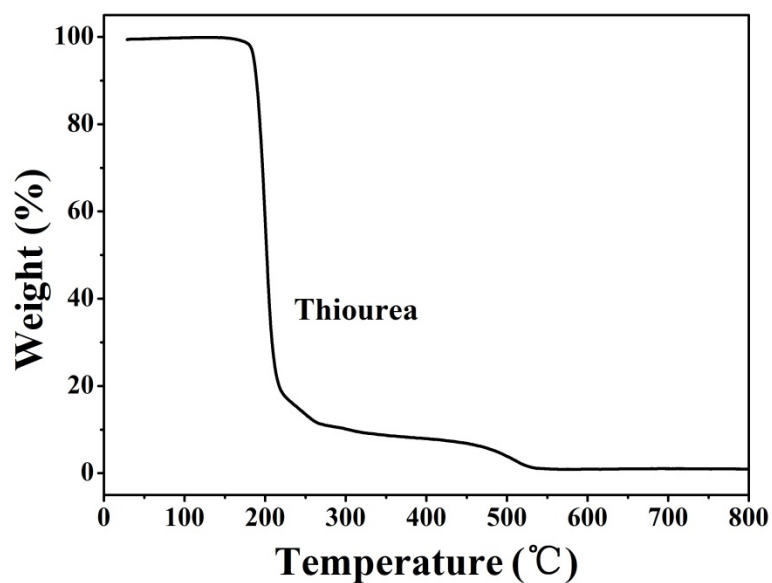


Figure S2. Thermo gravimetric analysis (TGA) of thiourea tested in N₂ atmosphere with a temperature rising of 5 °C/min.

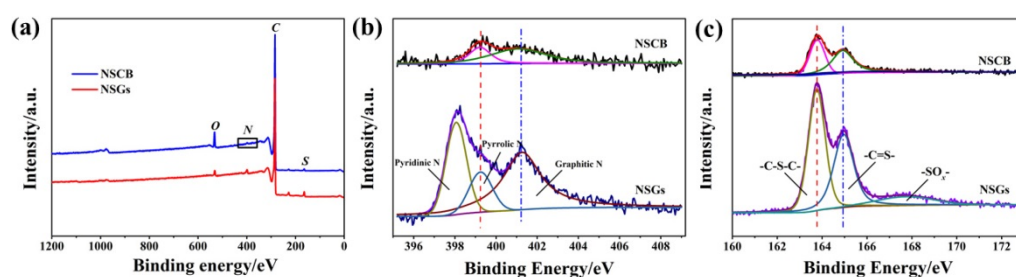


Figure S3. (a) XPS spectra of NSGs and NSCB, (b) high resolution N 1s spectra of NSGs and NSCB, (c) high resolution S 2p spectra of NSGs and NSCB.

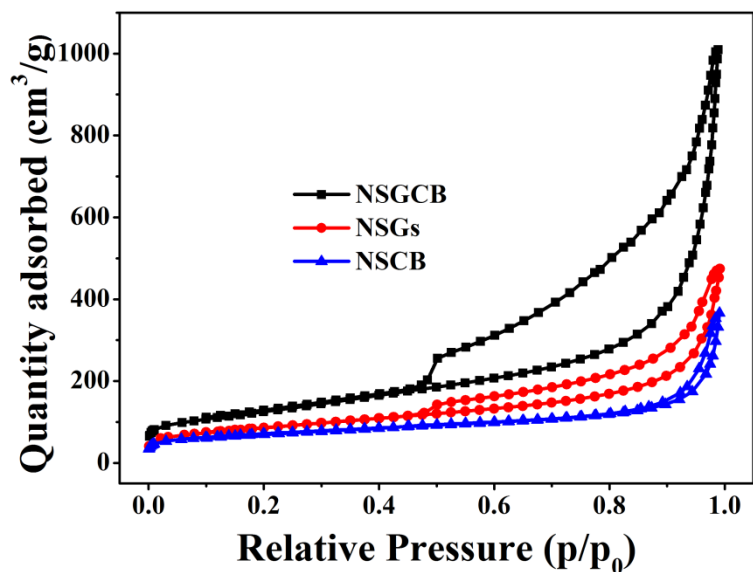


Figure S4. Nitrogen adsorption/desorption isotherms of NSGCB, NSGs, and NSCB.

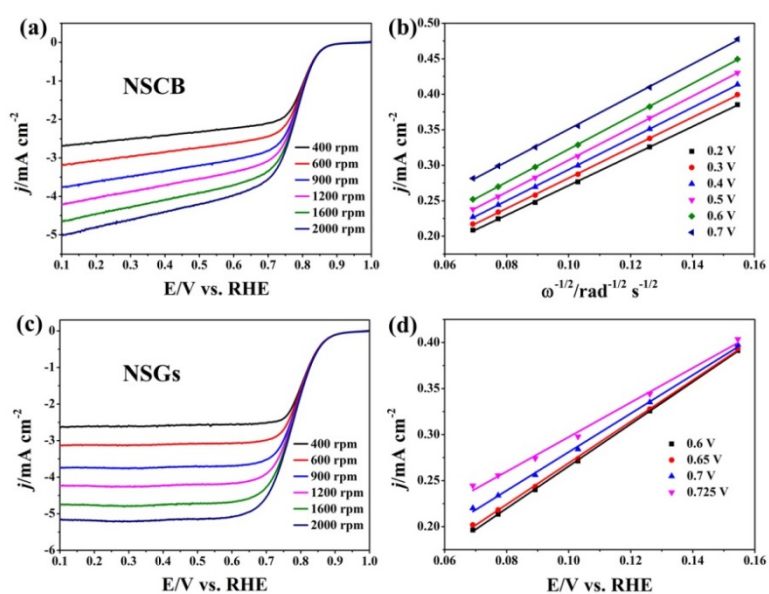


Figure S5. (a,c) Oxidation reduction Reaction (ORR) curves of NSCB and NSGs at various rotating speed (sweep rate 5 mV s^{-1}) in O_2 -saturated 0.1 M KOH solution. (b,d) Koutecky-Levich plots (i^{-1} versus $\omega^{-1/2}$) of NSCB and NSGs at different electrode potential.

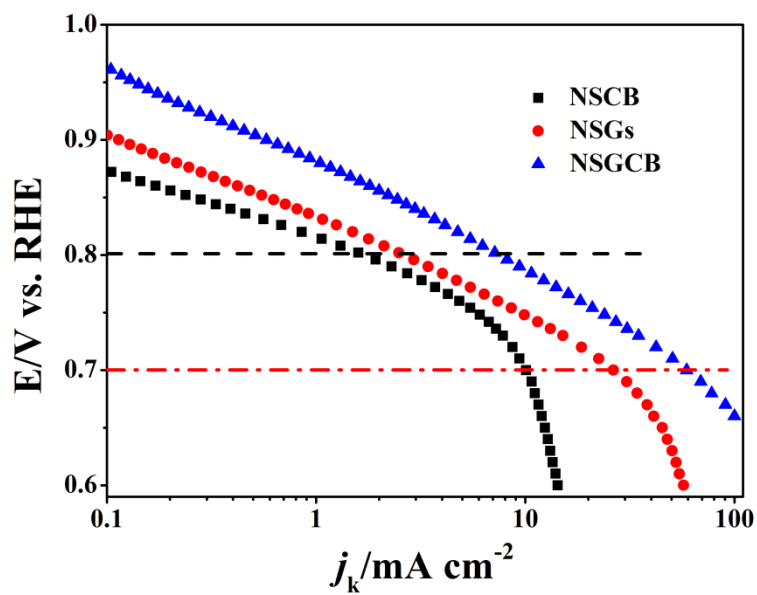


Figure S6. Tafel-plots of NSGCB, NSCB, and NSGs derived from ORR curves and Koutecky-Levich equation.

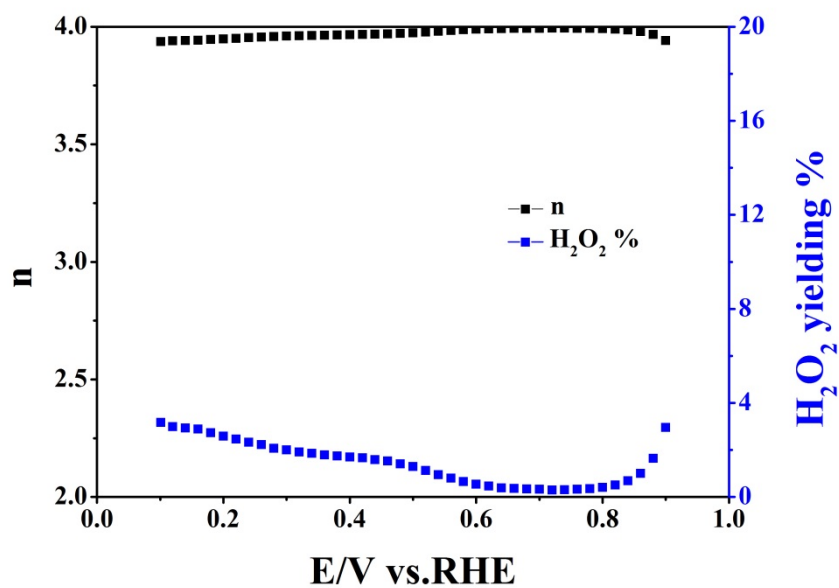


Figure S7. The electron-transfer number and H_2O_2 yield for commercially Pt/C catalyst.

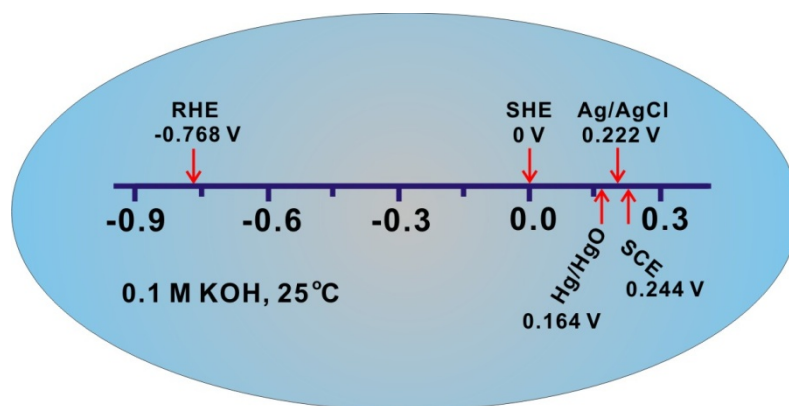


Figure S8. Calibration of Hg/HgO, Ag/AgCl, SCE and RHE reference electrodes.

Table S1. Comparison of the ORR performance of some metal-free carbons reported in literature.

Catalysts	ORR activity (V vs. RHE) ^a			Loading (mg/cm ²)	Ref.
	ORR	Onset	Half-wave		
	peak ^b	potential ^c	potential ^c		
NSGCB	0.78	0.96	0.81	0.3	this study
N-carbon	0.66	0.89	0.72	0.238	[1]
N-porous carbon	0.67	0.8	0.73	0.354	[2]
N-porous carbon	0.73	0.86	0.7	0.1	[3]
P-carbon	0.7	0.81	0.72	0.79	[4]
B,N-porous carbon	0.66	0.68	0.64	unknown	[5]
porous polymer	0.64	0.87	0.69	0.6	[6]
N,O-OMC	0.65	0.87	0.68	unknown	[7]
N-GNR	0.7	0.77	0.69	0.14	[8]
N-graphene	0.54 mv s ⁻¹	0.81	0.67	0.4	[9]
N-graphene	0.66	0.79	0.68	0.14	[10]
N-graphene	0.63mv s ⁻¹	0.91	0.78	0.6	[11]
P-graphene	0.57 mv s ⁻¹	0.9	0.54	unknown	[12]
B,N-graphene	0.69	0.93	0.76	0.28	[13]
B,N-graphene	0.69	0.89	0.72	unknown	[14]
B,N-graphene	0.65	0.81	0.65	0.283	[15]
N,S-graphene	0.62	0.86	0.68	unknown	[16]
N,S-graphene	0.73	0.85	0.75	0.306	[17]

N,S-graphene	0.68	0.87	0.69	0.208	[18]
edge sulfurized graphene	0.52	0.69	0.55	0.075	[19]
N-graphene/CNT	0.67	0.83	0.68	0.051	[20]
N-graphene/C	0.65	0.87	0.73	0.416	[21]

^a Conversions of Hg/HgO electrode, Ag/AgCl electrode, and SCE into RHE scale were achieved by adopting the calibration results, as shown in Figure S8.

^b ORR peak was obtained from cyclic voltammetry measured in O₂-saturated 0.1 M KOH aqueous solution with a sweep rate of 50 mV s⁻¹ unless otherwise noted.

^c Onset potential and Half-wave potential were obtained from linear sweep voltammetry performed on RDE in O₂-saturated 0.1 M KOH solution with a rotation rate of 1600 rpm.

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