Supporting Information for Materials Horizons

Origin of High Oxygen Reduction Reaction of Nitrogen and Sulfur co-doped MOF-derived Nanocarbon Electrocatalyst

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Experimental section

Synthesis of N, S-co-doped nanocarbon

Synthesis of ZIF-8 crystals was conducted following the procedure outlined by J. Cravillon [1]. In a typical experiment, two solutions are initially prepared by dissolving a known quantity of 2-methylimidazole (6.78 g, 82.0 mmol) in 250 ml of methanol and $Zn(NO_3)_2 \cdot 6\,H_2O$ (6.15 g, 20.5 mmol) in 250 ml of methanol. The solution of $Zn(NO_3)_2 \cdot 6\,H_2O$ was then added to 2-methylimidazole in a dropwise manner. The resulting mixture was stirred for 1h and aged for 24h at room temperature. Subsequently, white powder (ZIF-8 crystals) were collected by centrifugation and washed several times with methanol to remove the excess reactants. After dried in a vacuum at 60°C, the as-prepared ZIF-8 powder was carbonized at 1000°C for 8 h in Ar to produce N-doped nanocarbon (ZIF-C). Then, the as-prepared ZIF-C was treated with ammonia for different time at 1000°C to control pore size, such as 3 min, 5 min, 7 min. The corresponding products were denoted as NH_3-C-3, NH_3-C-5, NH_3-C-7. To synthesis N, S co-doped nanocarbon, 20 mg of NH_3-C-7 was mixed with 300 mg of thiourea (w/w=1:15) in 5 ml of ethanol/water (v/v=4:1) to generate a suspension under sonication. The mixture was continuously stirred for 3h to facilitate a thiourea/NH_3-C-7 solid composite after drying. Finally, the thiourea/NH_3-C-7 mixture was heated at 900°C for 1 h under an Ar atmosphere to generate the N, S-co-doped nanocarbon denoted as N, S-NH_3-C-7. For comparison, the N, S-ZIF-C of N, S-co-doped ZIF-C but no NH_3 treatment was prepared using a same procedure.

Physical characterization

The morphology and microstructure of as-prepared samples were obtained from a scanning electron microscope (SEM, Hitachi S-4800) and high resolution transmission electron microscope (HRTEM, JEOL2010FEG) equipped with an electron energy loss spectrometer (EELS). X-ray diffraction (XRD) patterns were recorded using a Bruker D8-Advance diffractometer equipped with a Cu $K_{ά}$ radiation source. The background was subtracted from the patterns to remove the impact of detector. Raman spectra were performed on a HORIBA Scientific LabRAM HR Raman spectrometer using a laser excitation wavelength of 532.0 nm. Chemical compositions of as-synthesized samples were investigated by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra-spectrometer). The nitrogen absorption-desorption isotherms were measured using the equipment of Micromeritics Tristar II. The total specific surface area is calculated from the Brunauer-Emmett-Teller (BET) equation. The mesopore size distribution is determined by the Barrett–Joyner–Halenda (BJH) method from the adsorption isotherms. The micropore area and volume are obtained from a t-plot method.

Electrochemical measurements

Electrochemical measurements were performed on an Autolab electrochemical workstation in a conventional three-electrode cell, with Ag/AgCl electrode and Pt wire as the reference and counter electrodes. A catalyst-modified glassy carbon electrode was used as the working electrode. Catalyst ink was prepared by ultrasonically dispersing 3.0 mg of each catalyst powder in 3.0 ml ethanol containing 30 uL of Nafion (5wt%) for 0.5 h. Subsequently, 20 uL of prepared catalyst ink was pipetted onto a polished glassy carbon electrode surface (0.196 cm^2), and dried at room temperature. The loading amount of catalyst was determined to be 0.1 $mg \cdot cm^{-2}$. For comparison, commercial 20% Pt/C was prepared on the electrode using a similar procedure as described above with a Pt loading of 10 $ug \cdot cm^{-2}$. Cyclic voltammetry (CV) experiments were conducted in N_2-saturated 0.1 M KOH solution with a scan rate of 50 $mV \cdot s^{-1}$ within a potential range of -0.9 V to 0.3 V (vs. Ag/AgCl). ORR linear sweep voltammetry (LSV) measurements were performed on a rotating disc electrode (RDE) in O_2-satureated 0.1 M KOH solution with background subtraction, at a scan rate of 10 $mV \cdot s^{-1}$ and rotating speed of 1600 rpm. Then, based on Koutecky-Levich equations, exact kinetic parameters, including electron transfer number (n) and kinetic current density (i_k) were analyzed [2]:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} = \frac{1}{i_k} + \frac{1}{B\omega^{\frac{1}{2}}}$$

$$B = 0.2nFC_0\,(D_0)^{\frac{2}{3}}v^{-\frac{1}{6}}$$

$$i_k = nFkC_{\mathbf{0}}$$

Where i is the measured current density, i_k and i_d are the kinetic and limiting diffusion current densities, ω is the angular velocity of the disk ($\omega = 2\pi N$, N is the linear rotating speed), n is the overall number of electrons transferred in oxygen reduction, F is the Faraday constant ($F = 96{,}485\ C \cdot mol^{-1}$), C_0 is the bulk concentration of O_2 ($C_0 = 1.2 \times 10^{-3}\ mol \cdot L^{-1}$), D_0 is the diffusion coefficient of O_2 in 0.1 M KOH ($D_0 = 1.9 \times 10^{-5}\ cm \cdot s^{-1}$), υ is the kinetic viscosity of the electrolyte ($\upsilon = 0.1\ m^2 \cdot s^{-1}$ in 0.1 M KOH), and κ is the electron transfer rate constant and the constant of 0.2 is adapted when the rotating speed is expressed in rpm.

Simulation method and computation modeling

Spin polarized density functional theory (DFT) [3] computations were performed at the generalized gradient approximation (GGA) level within the projector augmented-wave-Perdew-Burke-Ernzerhof (PAW-PBE) [4] formalism using the plane wave basis set Vienna a b initio simulation package (VASP) code [5-7]. The models were built in a 6×6 orthorhombic graphene supercell with lattice parameters of a = 14.81 Å, b=14.81 Å, which contains a defect of 6-carbon atoms missing and with periodic boundary conditions in 3-dimensions. A large vacuum layer of 15 Å is maintained along the z-axis to avoid artificial interactions between graphene layers. A Monkhorst-Pack grid [8] of 3×3×1 was used for geometric optimization. The simulation was run with a setup using 520 eV cutoff energy. All atoms are allowed completely relax during optimization to gain an optimized cell shape with minimum energy while convergence criterion was set to 1×10^{-5} eV. The structural optimization process for all atoms were finished until the final force on each atom was less than 0.01 eV/Å.

In alkaline media, ORR could occur over N, S-co-doped nanocarbon in the following four-electron reaction pathways [9]:

$$O_2 + * \rightarrow O_2* \tag{1}$$

$$O_2* + H_2O + e- \rightarrow OOH* + OH^- \tag{2}$$

$$OOH* + e^- \rightarrow O* + OH^- \tag{3}$$

$$O* + H_2O + e^- \rightarrow OH* + OH^- \tag{4}$$

$$OH* + e^- \rightarrow OH^- + * \tag{5}$$

Where * stands for an active site on carbon surface, and OOH*, O*, OH* are adsorbed intermediates. Then the free energy of each reaction ($\triangle G$) above has been calculated using eq [10]:

$$\triangle G = \triangle E + \triangle ZPE - T\triangle S,$$

Where $\triangle E$, $\triangle ZPE$, $\triangle S$ are the differences in the DFT calculated ground state energy, zero-point energy and entropy, respectively. The $\triangle ZPE$ correction for each intermediate has been taken from the CRC book [11], using the entropy change ($\triangle S$) at the temperature (T) of 298 K.

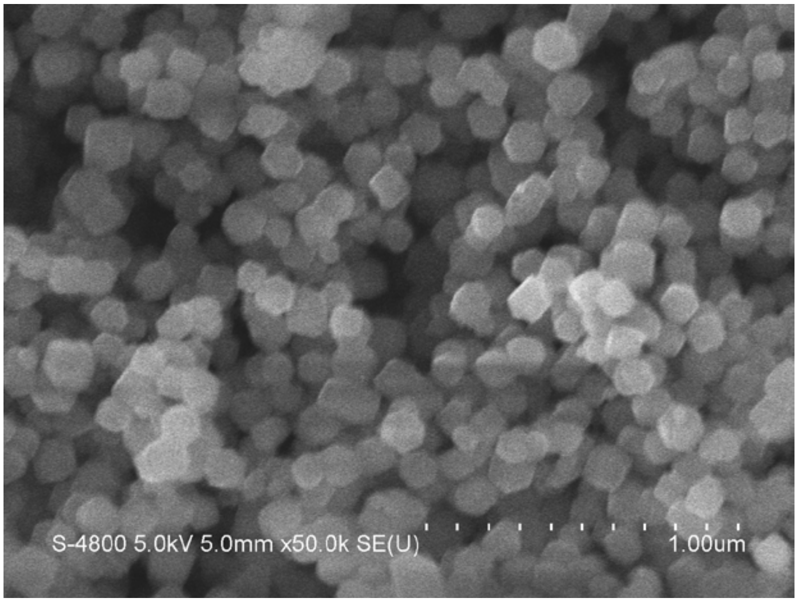


Figure S1. SEM image of ZIF-8

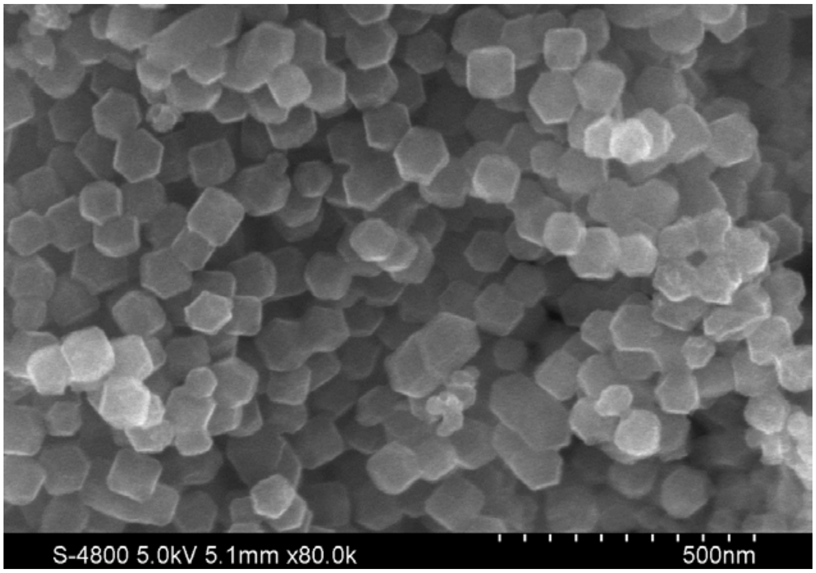


Figure S2. SEM image of ZIF-C nanocarbon

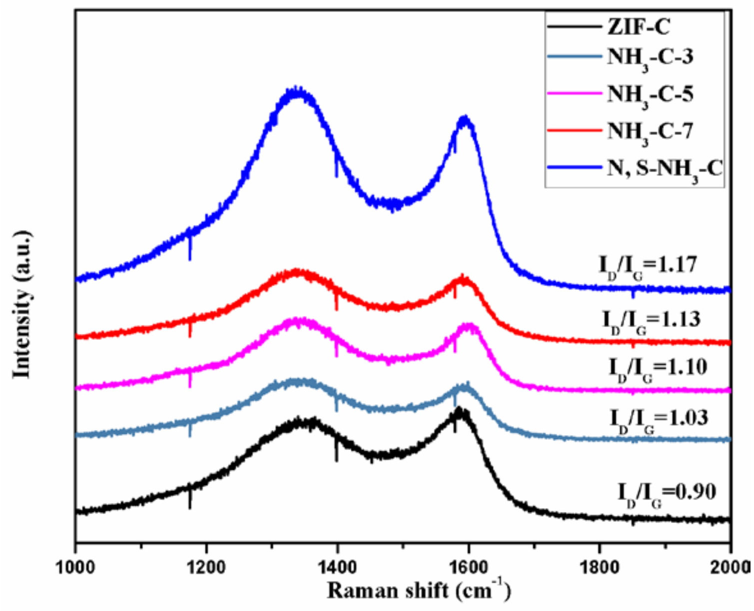


Figure S3. Raman spectra of the as-synthesized samples of ZIF-C, NH_3-C-x and N, S-NH_3-C-7.

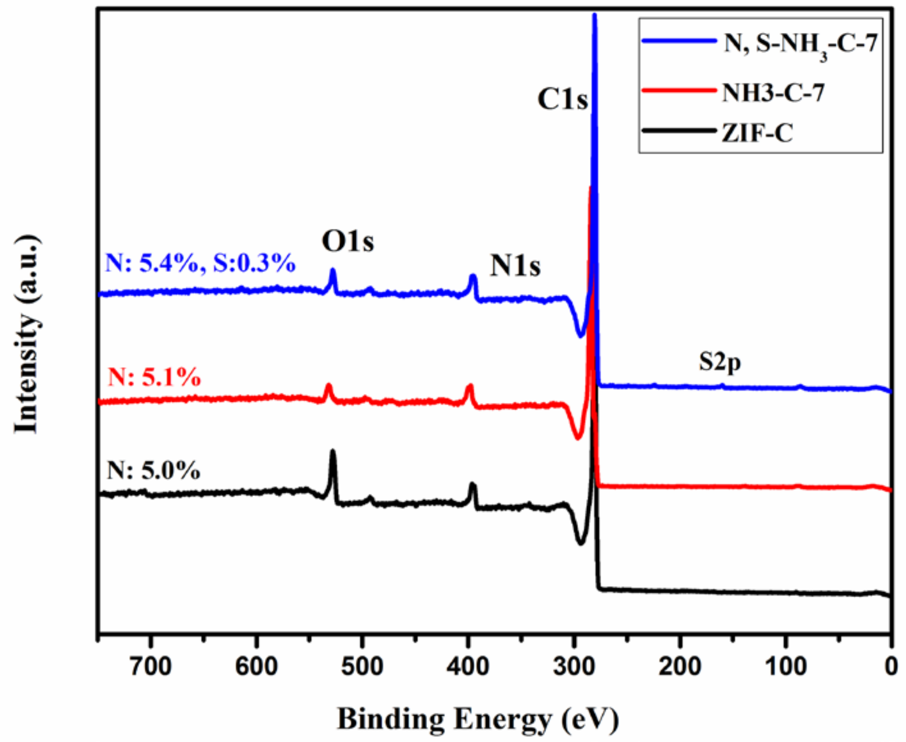


Figure S4. XPS spectra of samples of ZIF-C, NH_3-C-7 and N, S-NH3-C-7

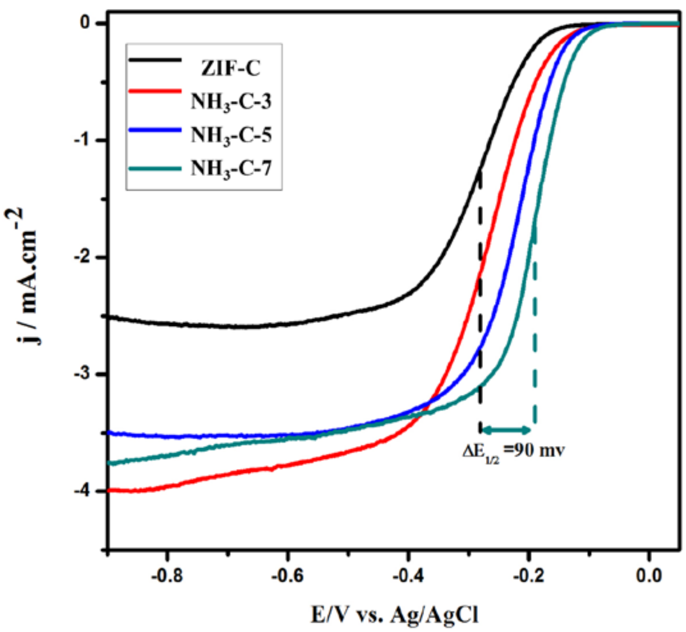


Figure S5. Linear sweep voltammograms (LSVs) of ZIF-C (black), NH_3-C-3 (red), NH_3-C-5 (blue) and NH_3-C-7 (cyan) in O_2-saturated 0.1 M KOH solution at 1600 rpm with a scan rate of 10 mV·s^{-1}.

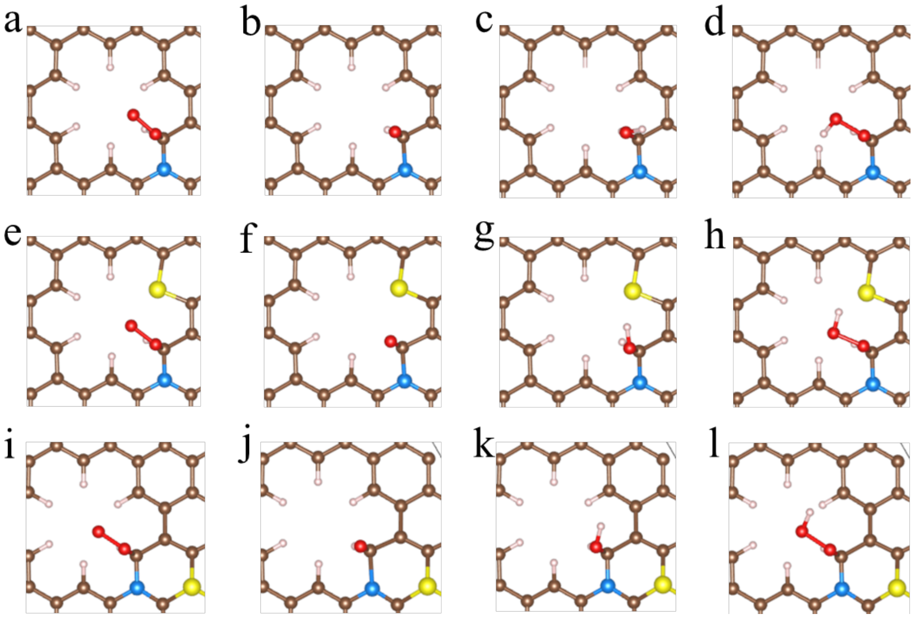
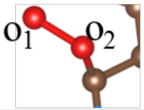


Figure S6. Optimized structures for the stable adsorbed O_2, O, OH, OOH on N-doped nanocarbon (a-d), N, S-isolated nanocarbon, (e-h), and N, S-coupled nanocarbon, (i-l), respectively.

Table S1. Bader charge of the stable adsorbed O_2 on the structures of N-doped nanocarbon, N, S-isolated nanocarbon and N, S-coupled nanocarbon.

structure 	N-doped	N, S-isolated	N, S-coupled
Bader charge	6.2539 (o_1) 6.3281 (o_2)	6.4038 (o_1) 6.7855 (o_2)	6.3985 (o_1) 6.9002 (o_2)

References:

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