Heteroatom-doped Carbon Sheets as Metal-free Electrocatalysts for Promoting Oxygen Reduction Reaction in Zn–air Batteries

Yuanqing Deng, Hongyu Zhang, Yuxuan Lin, Qi Ying, Fengjiao Yu* and Yang Yang*

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 211816, China

* Corresponding Authors; Email: fjyu@njtech.edu.cn, yangy@njtech.edu.cn

1. Experimental

1.1 Materials

Dicyanodiamide (DCDA, $C_2H_4N_4$), hydrochloric acid (HCl) were purchased from national pharmaceutical reagents. Ammonium chloride (NH_4Cl), glucosum anhydricum ($C_6H_{12}O_6$) was purchased from Shanghai Lingfeng Reagent. L-methionine($C_6H_{11}NO_2S$) was obtained from Huixing Biochemical reagent. All the above reagents are AR reagent. Phytic acid solution(70%) was purchased from Aladdin.

1.2 Synthesis of S-N-C, P-N-C and N-C

Synthesis of S-N-C

S, N-doped carbon sheets (S-N-C) were prepared with dcyandiamide (DCDA) and L-methionine (Met) as N and S sources respectively. 2 g of dicyandiamide and 10 g of NH_4Cl were successively added to 50 mL deionized water, followed by addition of 2 mmol L-methionine. The mixture was ultrasonicated for 10 minutes and stirred until complete dissolution. The obtained solution was freeze-dried, and heated to 450 °C at a rate of 2 °C/min in air for 2 h to obtain sulfur-doped graphite-phase carbon nitride (S-C_3N_4). 0.5 g of S-C_3N_4 was added to 35 mL of 0.03 mol/L glucose solution followed by ultrasound for 2 h.

The obtained suspension dried for 12 h in an oven at 90 °C. The powder was annealed to 850 °C in a tubular furnace under nitrogen atmosphere.

In order to study the effect of annealing temperature, samples at different annealing temperatures were prepared at 750 °C, 850 °C and 950 °C respectively. The samples obtained were named as S-N-C-750, S-N-C-850 (SNC) and S-N-C-950. In order to study the influence of S doping content, 1 mmol, 2 mmol and 3 mmol of L-methionine were added in the synthesis process, and corresponding samples were named as S-N-C-1, S-N-C-2 (S-N-C) and S-N-C-3.

Synthesis of P-N-C and N-C

P, N-doped carbon (P-N-C) was prepared with the same procedure but replacing L-methionine with phytic acid. Nitrogen-doped carbon (N-C) material was prepared with the same procedure except for adding L-methionine.

1.2 Characterizations

The structure of the samples was characterized by X-ray diffractometers (XRD, Rigaku D/Max 2400) with a Cu Kα radiation source. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 microscope. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) studies were performed on a JEOL 2100 Plus microscope equipped with an energy dispersive X-ray detector (EDX) at 200 kV. X-ray photoelectron spectroscopy (XPS) was obtained by a Thermo 250XI instrument. Raman spectra were collected on the Labram HR Evolution instrument with a wavelength range from 500 to 2000 cm^{-1}. The thickness of the samples was characterized by atomic force microscopy (AFM, Bruker Dimension Icon).

1.3 Electrochemical Measurements

The electrocatalytic performance of the samples was tested on the Ivium-n-STAT workstation at room temperature. The ink was prepared by dispersing 2 mg of electrocatalyst sample in a mixture of 380 μL anhydrous ethanol, 20 μL Nafion, and 100 μL deionized water. The mixture was ultrasonicated for 2 h until a uniformly dispersed black suspension was formed. A pipette gun was used to drop 16 μL of ink onto the surface of the rotating disc electrode (RDE) with a final load of 0.326 mg/cm^2 to obtain a catalyst-coated working electrode. Electrochemical measurements were carried out in a three-electrode cell system with RDE as the working electrode, graphite rod as the counter electrode, and Ag/AgCl (3.5m KCl) as the reference electrode. The applied potential is converted to reversible hydrogen electrode (RHE) potential according to the following equation:

$$E_{\mathrm{RHE}} = E_{\mathrm{Ag/AgCl}} + 0.059 \cdot \mathrm{pH} + E^{0}_{\mathrm{Ag/AgCl}}$$

The cyclic voltammetry (CV) measurements were tested in N_2 or O_2 saturated 0.1 M KOH electrolyte at a scanning rate of 50 mV/s with a scanning range of 0.2-1.2 V *vs.* RHE. The electrochemical surface area (ECSA) of the samples was characterized by testing the double layer capacitance (C_{dl}) by varying the scanning rate (20, 40, 60, 80, 100 mV/s) in potential range of 1.0-1.1 V *vs.* RHE where no faradic current was observed. The linear sweep voltammetry (LSV) was tested at a scan rate 5 mV/s with electrode rotating rate of 1600 rpm.

The electron transfer number (n) was calculated based on the LSV curves at different speeds (900, 1225, 1600, 2025, 2500 rpm) by the Koutecky-Levich (K-L) equation below:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$

$$B = 0.62nFC_{O_2}(D_{O_2})^{2/3}V^{-1/6}$$

where J, J_{K} and J_{L} stand for measured current density, kinetic current density, and diffusion limiting current density. F is the Faraday constant (96485 C/mol). C_{O2} is the saturation concentration in 0.1 M KOH solution (1.2×10^{-3} mol/L). D_{O2} is the oxygen diffusion coefficient (1.9×10^{-5} cm^2/s) and v is the kinetic viscosity (0.01 cm^2 s^{-1}).

Zn–air battery tests

Zn–air battery was assembled with as-prepared S-N-C catalyst or Pt/C on the carbon paper with a loading of 1 mg/cm^2 as the air cathode, and metal zinc plate as the anode. 6 M KOH containing 0.2 M $ZnCl_2$ solution was used as the electrolyte. Galvanostatic discharge plots of the Zn–air batteries were recorded from 5 mA/cm^2 to a high current density of 40 mA/cm^2, following by recovery to initial 5 mA/cm^2. The discharge test was carried out at room temperature with different current densities. The discharge profiles were collected by the Ivium-n-Stat (1xpMod 30 mA/10 V/250 kHz).

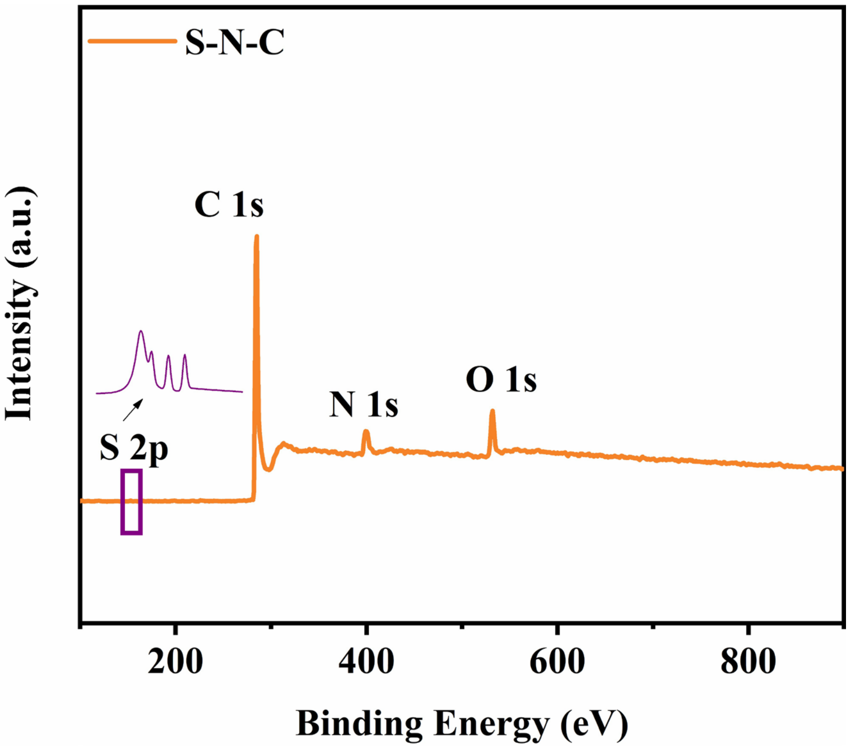

Figure S1 XPS survey spectrum of S-N-C.

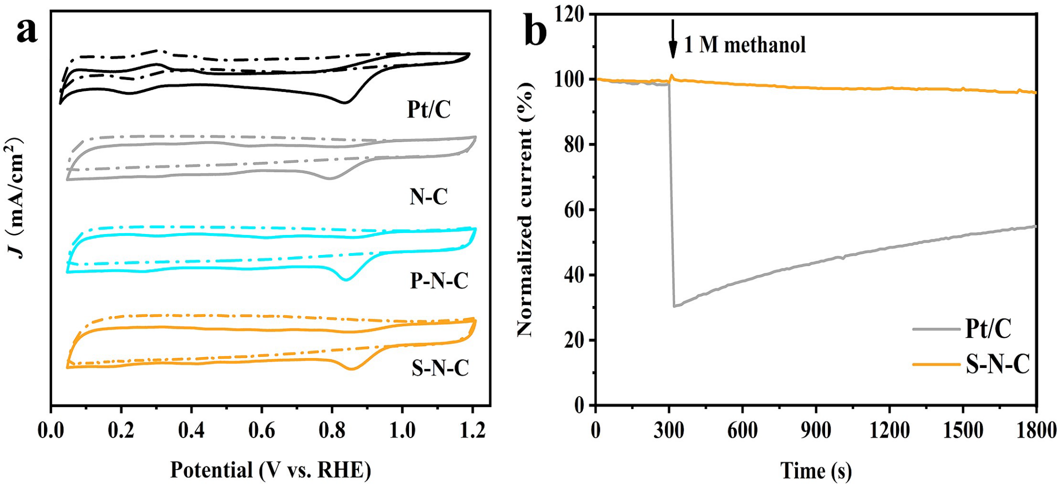

Figure S2 (a) CV curves of the catalysts in N_2 or O_2-saturated 0.1 M KOH solution. (b) Methanol tolerance test of Pt/C and S-N-C.

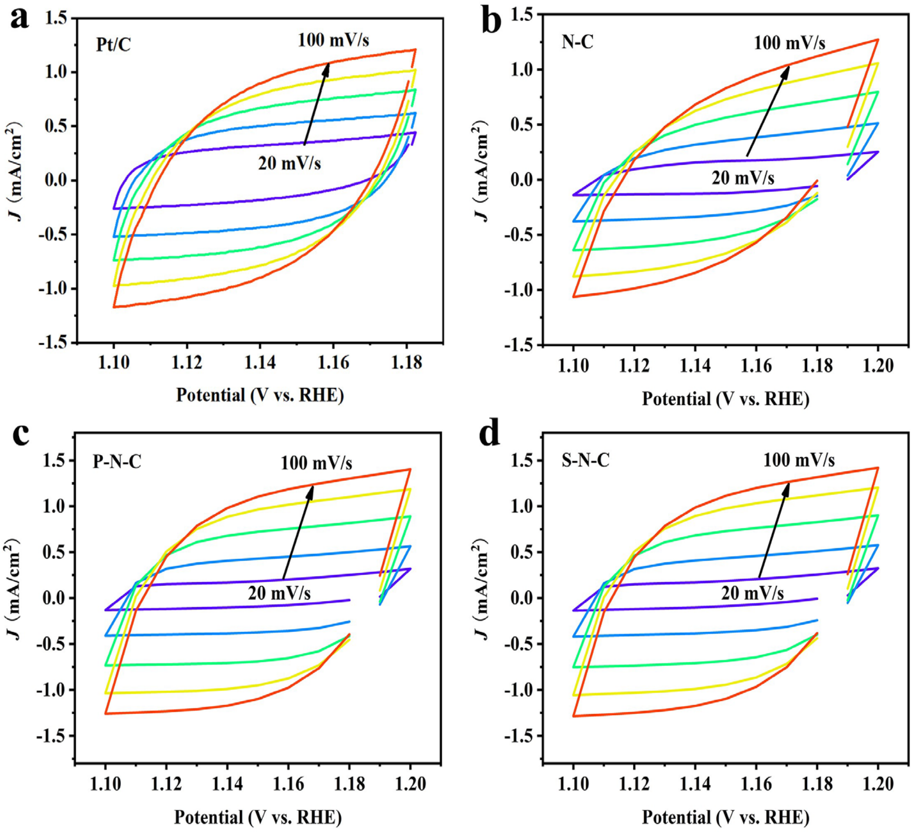

Figure S3 CV curves of the catalysts with different scan rates in 0.1 M KOH.

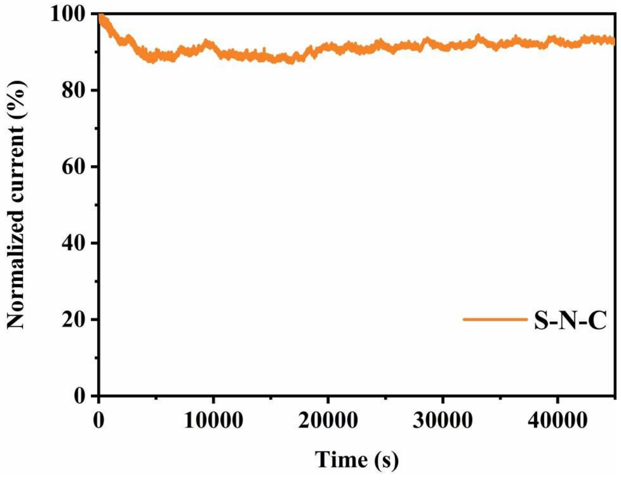

Figure S4 Chronoamperometric response of S-N-C catalyst in O_2-saturated 0.1 M KOH.

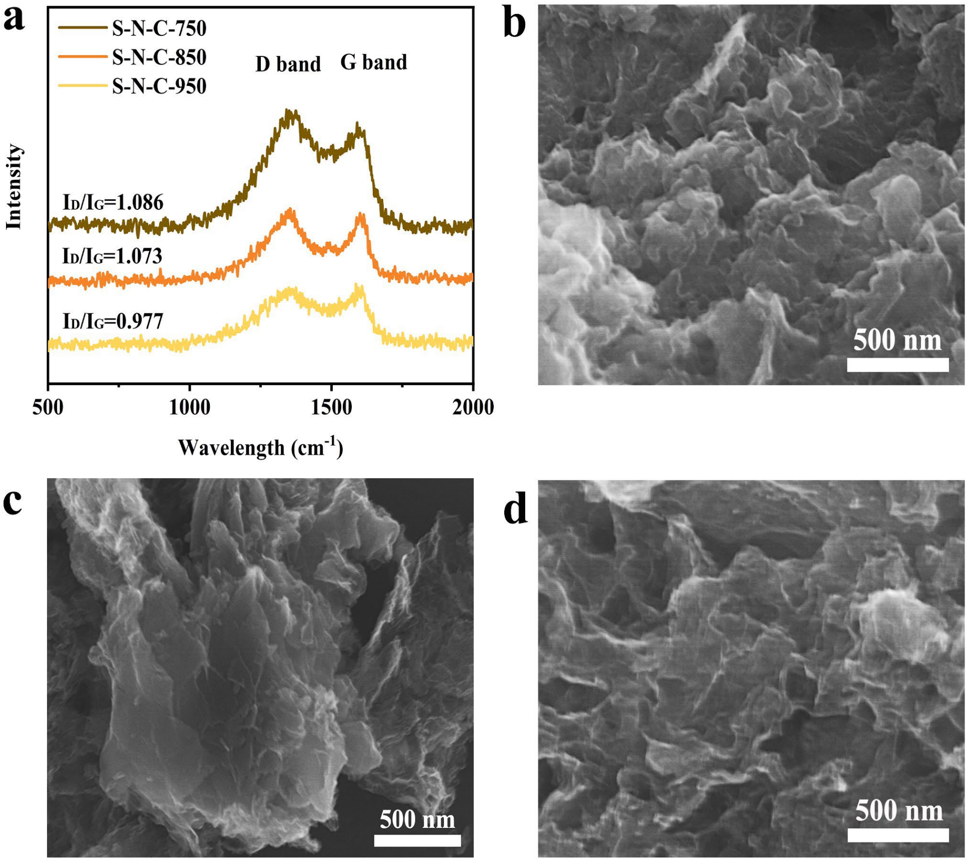

Figure S5 (a) Raman spectra of the S-N-C-T (T=750, 850 and 950) catalysts. (b-d) SEM images of S-N-C-750, 850 and 950 respectively.

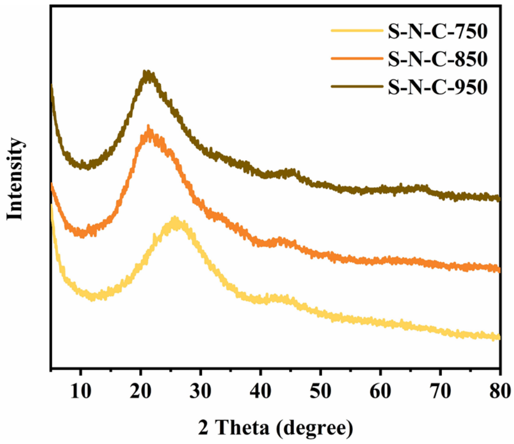

Figure S6 XRD patterns of the S-N-C-T (T=750, 850 and 950) catalysts.

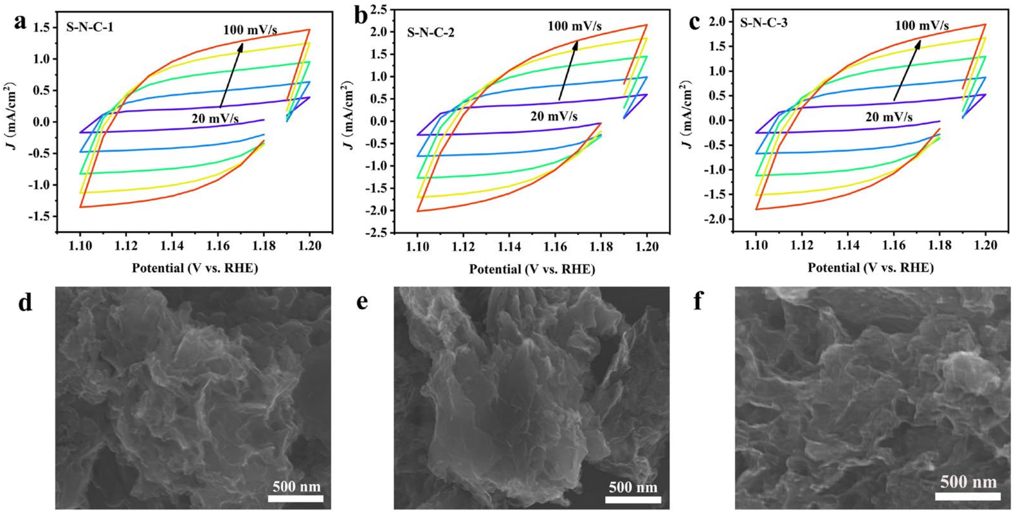

Figure S7 (a-c) CV curves with different scan rates in 0.1 M KOH, (d-e) SEM images of the S-N-C-x (x=1, 2 and 3) catalysts.

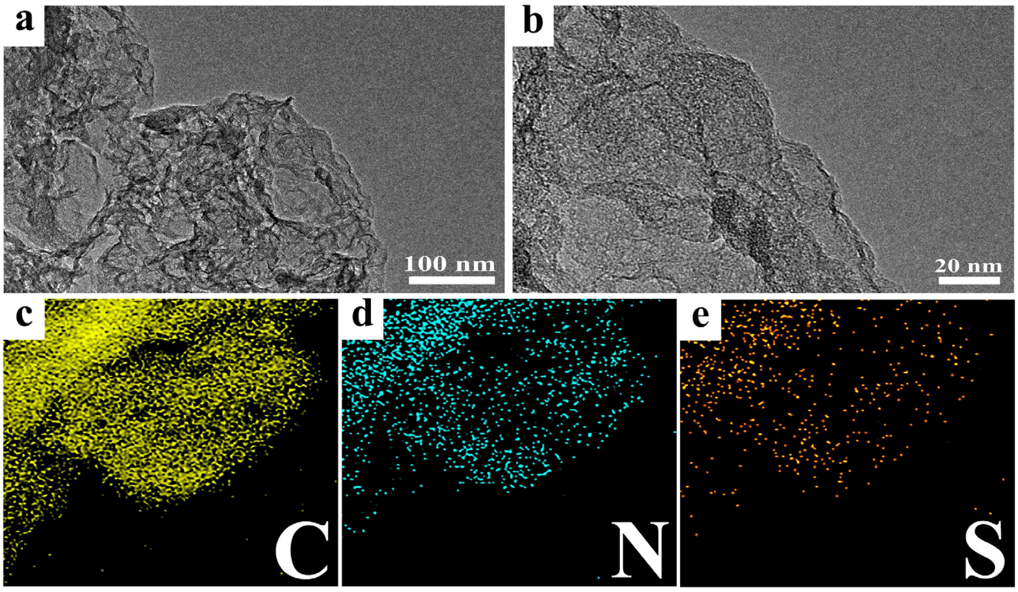

Figure S8 TEM images and elemental mappings of S-N-C catalyst after 48 h discharging test in a Zn–air battery.

Table S1 Summary of ORR performances of reported electrocatalysts.

Electrocatalysts	$E_{1/2}$(V vs. RHE)	E_{onset}(V vs. RHE)	References
ZnNC	0.857	0.92	*Nat. Comm.* **10**, 2623 (2019)
Fe/SNC	0.77	0.89	*Angew. Chem. Int. Ed.* **56**, 13800-13804 (2017)
Fe-CNT/PC	0.79	0.95	*J. Am. Chem. Soc.* **138**, 15046-15056 (2016)
Fe-ISAs/CN	0.79	0.9	*Angew. Chem. Int. Ed.* **56**, 6937-6941 (2017)
SA-Fe/NG	0.8	0.9	*PNAS.* **115**, 6626-6631 (2018)
Mn/C-NO	0.86	0.94	*Adv. Mater.* **30**, 1801732 (2018)
NCo@CNT-NF700	0.861	0.927	*J. Am. Chem. Soc.* **140**, 15393-15401, (2018)
Fe@Aza-PON	0.839	0.9	*J. Am. Chem. Soc.* **140**, 1737-1742(2018)
Co_3O_4/N-rmGO	0.83	0.91	*Nat. Mater.* **10**, 780 (2011)
Cu-CPG-900	0.87	0.978	*Nat. Comm.* **5**, 5285 (2014)
NPMC-1000	0.85	0.94	*Nat. Nanotechnol.* **10,** 444 (2015)
CoN_4/NG	0.87	0.98	*Nano Energy.* **50**, 691 (2018)
2D-PPCN-2/6	0.85	0.92	*ACS Catal.* **8**, 2464 (2018)
NPCS	0.82	0.92	*ChemCatChem.* **10**, 5297 (2018)
NCHCs	0.8	0.92	*Nanoscale.* **9**, 1059 (2017)
P, S-CNS	0.87	0.97	*ACS Nano.* **11**, 347 (2017)
UNT Co SAs/N-C	0.89	0.97	*Nano Energy.* **61**, 245 (2019)
FePc@N,P-DC	0.903	0.979	*Appl. Catal. B Environ.* **260**, 118198 (2020)