# Iron Nanoparticles Encapsulated in S,N-Codoped Carbon: Sulfur Doping Leads to Enriched Surface Electron Density and Enhanced Electrocatalytic Activity towards Oxygen Reduction

Shanyong Chen<sup>a</sup>, Yong Yan<sup>a</sup>, Panpan Hao<sup>a</sup>, Muhong Li<sup>a</sup>, Jiyuan Liang<sup>b</sup>, Jia Guo<sup>a</sup>, Yu Zhang<sup>a</sup>, Shaowei Chen<sup>c, \*</sup>, Weiping Ding<sup>a</sup>, Xuefeng Guo<sup>a, \*</sup>

<sup>a</sup> Key Laboratory of Mesoscopic Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Nanjing University, 163 Xianlin Road, Nanjing 210023, China <sup>b</sup> Key Laboratory of Optoelectronic Chemical Materials and Devices, Ministry of Education, School of Chemical and Environmental Engineering, Jianghan University, Wuhan 430056, China

<sup>c</sup> Department of Chemistry and Biochemistry, University of California, 1156 High Street, Santa Cruz, California 95064, United States

### List of contents

- Experimental Section
- 5 tables
- 28 figures

<sup>\*</sup>Corresponding authors. E-mail addresses: guoxf@nju.edu.cn (X. Guo), shaowei@ucsc.edu (S. Chen).

#### **Experimental Section**

#### Chemicals

Basic ferric acetate (Fe(OAc)<sub>2</sub>OH.) was purchased from MAYA Reagents Co. Ltd. Hexamethylenetetramine (C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>), thiourea and urea were purchased from Sinopharm Chemical Reagents Co. Ltd. Activated carbon (AC) was purchased from XFNANO Materials Tech Co. Ltd. Pt/C 20 wt.% catalyst and Nafion solution (5 wt. %) were purchased from Alfa Aesar China. All reagents were directly used without further purification.

#### Characterization

Powder X-ray diffraction (XRD) patterns were acquired on a Shimadzu XRD-6000 diffractometer with Cu Ka radiation ( $\lambda$  = 1.54 Å) or Co Ka radiation ( $\lambda$  = 1.7902Å). Transmission electron microscopy (TEM) measurements were carried out with a JEOL JEM-2100 instrument at the accelerating voltage of 200 kV. Nitrogen adsorption-desorption isotherm measurements were conducted on an ASAP 2020 apparatus. The specific surface area was evaluated by the Brunauer-Emmett-Teller (BET) method and the pore distribution was acquired from the Barrett-Joyner-Halenda (BJH) model. Raman spectra were recorded on a Renishaw inVia spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI 5000 Versa Probe with AI K<sub> $\alpha$ </sub> radiation, where the binding energies were calibrated against the C 1s peak at 284.6 eV. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris 1 instrument from room temperature to 900 °C under an air atmosphere. XANES spectra were collected in the beamline BL12B-a in National Synchrotron Radiation Laboratory (NSRL). Ultroviolet photoelectron spectroscopy (UPS) experiments were conducted at ESCALAB250 (Thermo VG Co., Ltd) using He I (hv = 21.22 eV), where a negative bias voltage of 15 V was applied to the sample to accelerate electrons of low kinetic energy and determine the secondary electron cutoff. Oxygen temperature programmed desorption (O<sub>2</sub>-TPD) was performed on a TP-5080 automatic multi-purpose adsorption apparatus using a TCD detector. The samples underwent a pretreatment at 300 °C for 1 h in an Ar atmosphere, O<sub>2</sub> adsorption was conducted at room temperature, and the subsequent desorption curves were collected from 100 °C to 600 °C with a flow of Ar. The Fe loading of the catalyst also has been determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) with an Optima 5300 DV instrument.

#### Electrochemistry

Voltammetric measurements were conducted with a CHI760D Electrochemical Workstation in a three-electrode configuration. In acid electrolytes, Ag/AgCl was used as the reference electrode and a graphite rod was used as the counter electrode, whereas in alkaline media, a Hg/HgO reference electrode was used instead. Both reference electrodes were calibrated against a reversible hydrogen electrode (RHE) and all potentials in the present study were referred to the RHE. A rotating ring-disk electrode (RRDE) with a glassy carbon disk (5.61 mm in diameter) was employed as the working electrode. To prepare the working electrode for ORR tests in 0.1 M HClO<sub>4</sub>, 10 mg of the catalysts prepared above and 20  $\mu$ L of 5 wt.% Nafion were added into 1 mL of isopropanol. Then the suspensions were dispersed by ultrasonic treatment for 60 min to obtain a homogeneous ink. 16  $\mu$ L of the ink was then deposited on the polished glassy carbon electrode (catalyst loading 0.65 mg cm<sup>-2</sup>) and dried at room temperature (the loading of commercial Pt/C was 0.12 mg cm<sup>-2</sup>). The preparation of the working electrode for ORR tests in 0.1 M KOH was the same except that the catalyst loading was 0.32 mg cm<sup>-2</sup>. Prior to voltammetric measurement, the electrolyte was purged with O<sub>2</sub> or N<sub>2</sub> by bubbling high-purity O<sub>2</sub> or N<sub>2</sub> for 30 min. Linear sweep voltammograms (LSV) were collected at the scan rate of 10 mV s<sup>-1</sup> and 1600 RPM. The polarization curves were obtained by subtracting the background current from the

LSV curves with iR compensation. The stability of select samples was tested by chronoamperometric measurements at the applied potential of +0.45 V in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> for 100,000 s. Stability tests were also run by 10,000 CV cycles within the potential range of +1.05 V to +0.60 V in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> at the sweep rate of 50 mV s<sup>-1</sup>.

The percentage of hydrogen peroxides  $(H_2O_2)$  produced during ORR and the electron reduction number (n) involved were calculated from the equations below,

$$H_2 O_2(\%) = 200 \frac{I_r/N}{I_d + I_r/N}$$
(1)

$$n = 4 \frac{I_r/N}{I_d + I_r/N}$$
<sup>(2)</sup>

where  $I_d$  represents the disk current,  $I_r$  the ring current, and N the collection efficiency (0.37) of the RRDE. The kinetic current density (J<sub>k</sub>) is calculated as follows

$$J_k = \frac{J \times J_L}{J_L - J} \tag{3}$$

where J is the measured current density,  $J_L$  is the diffusion-limiting current density.

Samples	Fe loading <sup>a</sup> (wt. %)	BET surface area (m <sup>2</sup> /g)	ECSAs (mF/cm <sup>2</sup> )
Fe@S,N-DC	5.9	734	84.8
Fe@S,N-DC <sub>3</sub>	8.5	688	74.2
Fe@S,N-DC <sub>5</sub>	11.5	572	39.5

 $\label{eq:stable} \textbf{Table S1.} Characterization results of Fe@S,N-DC, Fe@S,N-DC_3 and Fe@S,N-DC_5.$ 

a: Fe loading is determined by TGA.

**Table S2.** Elemental content of AC and S,N-DC from XPS analysis.

Samples	C content [at%]	N content [at%]	O content [at%]	S content [at%]
AC	84.69	1.98	13.33	-
S,N-DC	88.05	5.25	5.35	1.35

**Table S3.** Comparison of the ORR performance of commercial Pt/C catalyst in this work and in the reported literatures.

Samples	Catalyst loading	Pt loading	half-wave potential	Reference
			(vs RHE)	
Pt/C-20%	0.12 mg cm <sup>-2</sup>	0.024 mg cm <sup>-2</sup>	0.833 V (0.1 M KOH)	This work
10/C-2070	0.12 mg cm	0.024 mg cm	0.827 V (0.1 M HClO <sub>4</sub> )	1ms work
Pt/C	0.239 mg cm <sup>-2</sup>	-	0.826 V (0.1 M KOH)	J. Am. Chem. Soc.2018,140,5,1737- 1742
Pt/C-20%	0.285 mg cm <sup>-2</sup>	0.057 mg cm <sup>-2</sup>	0.841 V (0.1 M KOH) 0.820 V (0.1 M HClO <sub>4</sub> )	ACS Appl. Mater. Interfaces 2018, 10, 39735–39744
Pt/C-20%	0.102 mg cm <sup>-2</sup>	0.02 mg cm <sup>-2</sup>	$0.800 \text{ V} (0.5 \text{ M} \text{ H}_2\text{SO}_4)$	Chem. DOI.10.1016/j.chempr.2019.07.020
Pt/C-20%	0.102 mg cm <sup>-2</sup>	0.02 mg cm <sup>-2</sup>	0.83 (0.1 M KOH) <0.700 V (0.5 M H <sub>2</sub> SO <sub>4</sub> )	ACS Appl. Mater. Interfaces 2017, 9, 10610–10617
Pt/C-20%	0.4 mg cm <sup>-2</sup>	0.08 mg cm <sup>-2</sup>	0.827 V (0.1 M HClO <sub>4</sub> )	Angew.Chem.Int.ed. DOI.10.1002/anie.201808383
Pt/C-20%	0.102 mg cm <sup>-2</sup>	0.02 mg cm <sup>-2</sup>	0.830 V (0.1 M KOH)	ACS Appl. Mater. Interfaces 2017, 9, 20963–20973
Pt/C-20%	0.24 mg cm <sup>-2</sup>	0.048 mg cm <sup>-2</sup>	0.830 V (0.1 M HClO <sub>4</sub> )	Proc. Natl. Acad. Sci. USA. DOI.10.1073/pnas.1800771115
Pt/C-30%	0.05 mg cm <sup>-2</sup>	0.015 mg cm <sup>-2</sup>	<0.800 V (0.1 M KOH)	ACS Appl. Mater. Interfaces 2015, 7, 18170–18178
Pt/C-20%	0.127 mg cm <sup>-2</sup>	0.0254 mg cm <sup>-2</sup>	0.826 V(0.1 M KOH) ~0.830 V (0.1 M HClO <sub>4</sub> )	Angew. Chem. Int. Ed. 2019, 58, 2622–2626
			0.850 V (0.1 M KOH)	ACS Appl. Mater. Interfaces 2019,
Pt/C-20%	0.2 mg cm <sup>-2</sup>	0.04 mg cm <sup>-2</sup>	0.800 V (0.1 M HClO <sub>4</sub> )	11, 25976-25985
Pt/C-20%	-	0.02 mg cm <sup>-2</sup>	~0.830 V (0.1 M KOH) <0.750 V (0.1 M HClO <sub>4</sub> )	Nat Commun. DOI: 10.1038/s41467-018-05878-y
Pt/C-20%	0.08 mg cm <sup>-2</sup>	0.016 mg cm <sup>-2</sup>	0.810 V (0.1 M KOH)	ACS Appl. Mater. Interfaces 2016, 8, 20635–20641
Pt/C-20%	0.12 mg cm <sup>-2</sup>	0.024 mg cm <sup>-2</sup>	0.831 V (0.1 M KOH)	J. Mater. Chem. A, 2018,6, 21313- 21319
Pt/C-20%	0.5 mg cm <sup>-2</sup>	0.1 mg cm <sup>-2</sup>	~0.830 V (0.1 M KOH) 0.850 V (0.1 M HClO <sub>4</sub> )	ACS Appl. Mater. Interfaces 2017, 9, 9699–9709
Pt/C-20%	0.21 mg cm <sup>-2</sup>	0.042 mg cm <sup>-2</sup>	~0.820–0.830 (0.1 M KOH) ~0.790 V (0.1 M HClO <sub>4</sub> )	Applied Catalysis B: Environmental DOI. 10.1016/j.apcatb.2019.01.050
Pt/C-20%		0.04 mg cm <sup>-2</sup>	~0.835 V (0.1 M HClO <sub>4</sub> )	ACS Appl. Mater. Interfaces 2019, 11, 6111–6117
			~0.825 (0.1 M KOH)	
Pt/C-20%	-	0.02 mg cm <sup>-2</sup>	<0.800 V (0.1 M HClO <sub>4</sub> )	ACS Catal. 2015, 5, 3887–3893
Pt/C-20%	-		0.811 V (0.5 M H <sub>2</sub> SO <sub>4</sub> )	Journal of Catalysis 370 (2019) 130–137
Pt/C-20%	0.102 mg cm <sup>-2</sup>	0.02 mg cm <sup>-2</sup>	-0.144 V vs Ag/AgCl (0.1 M KOH) 0.368 V vs Ag/AgCl (0.5 M H <sub>2</sub> SO <sub>4</sub> )	ACS Nano 2018, 12, 208–216
Pt/C-20%	0.102 mg cm <sup>-2</sup>	0.02 mg cm <sup>-2</sup>	0.840 V (0.1 M HClO <sub>4</sub> )	Energy Environ. Sci., 2018, 11, 2208-2215
Polycrystalli ne Pt	-	-	~0.850 V(0.1 M HClO <sub>4</sub> , 333 K)	Science 2007, 315 (5811), 493-497
Pt/C-46%	0.657 mg cm <sup>-2</sup>	0.302 mg cm <sup>-2</sup>	~0.940 V (pH=1)	ACS Appl. Mater. Interfaces 2009, 1, 8, 1623-1639
Pt/C-20%	$0.05 \text{ mg cm}^{-2}$	0.01 mg cm <sup>-2</sup>	0.860 V (0.1 M HClO <sub>4</sub> ) 0.840 V (0.1 M KOH)	Nat Commun. DOI:10.1038/ncomms9618
c-Pt/CB	-	0.0102 mg cm <sup>-2</sup>	~0.845 V (0.1 M HClO <sub>4</sub> )	ACS Appl. Mater. Interfaces 2012, 4, 6982–6991
Pt/C-47 %	-	0.0158 mg cm <sup>-2</sup>	0.865 V (0.1 M HClO <sub>4</sub> )	Science 362, 1276–1281 (2018). DOI: 10.1126/science.aau0630.
Pt/C	-	0.00765 mg cm <sup>-2</sup>	0.860 V (0.1 M HClO <sub>4</sub> )	Science 2016, 354 (6318), 1414- 1419, DOI:10.1126/science.aaf9050.

Samples	E <sub>Onset</sub> (vs RHE)	E <sub>1/2</sub> (vs RHE)	Limit current	Electrolyte	Shifts of $E_{1/2}$	Reference
			(mA cm <sup>-2</sup> )		after durability	
Fe@S,N-DC	0.940 V	0.785 V	5.91	0.1 M HClO <sub>4</sub>	13 mV (10,000CV)	This work
p-Fe–N-CNF	0.85 V	0.74 V	5.5	0.1 M HClO <sub>4</sub>	-	Energy Environ. Sci., 2018, 11, 22082215
Fe-ISAs/CN	0.9 V	0.79 V	5.8	$0.1 \mathrm{~M~HClO}_4$	-	Angew. Chem. Int. Ed. 2017, 56, 6937 –6941
Fe-N-DSC	-	0.456 V	~4.7	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	-	ACS Nano 2018, 12, 208–216
Fe,N-nanoshells	0.85 V	0.76 V	5.5	0.1 M HClO <sub>4</sub>	-	ACS Catal. 2015, 5, 3887-3893
Fe <sub>3</sub> C@NP-PCFs	0.863 V	, 0.736 V	5.59	0.5 M H <sub>2</sub> SO <sub>4</sub>	7.4 mV (5,000CV)	J. Mater. Chem. A, 2019,7, 17923-17936
Fe/SNC	-	0.77 V	-	$0.5 \mathrm{~M~H_2SO_4}$	-	Angew. Chem. Int. Ed. 2017, 56, 13800-13804
Fe-N-C-950	0.92 V	0.78 V	5.9	0.1 M HClO <sub>4</sub>	12 mV (10,000CV)	ACS Catal. 2018, 8, 2824-2832
Co@SNHC	0.852 V	0.682 V	5.53	0.1 M HClO <sub>4</sub>	~40 mV (10,000CV)	J. Mater. Chem. A, 2019,7, 14291-14301
FeNC–S–Fe <sub>x</sub> C/Fe	0.92 V	0.821 V	5.75	0.1 M HClO <sub>4</sub>	21 mV (10,000CV)	Adv. Mater. 2018, 30, 1804504
FeNC-S-MSUFC2	-	0.730 V	~4.9	$0.5~\mathrm{M}~\mathrm{H_2SO_4}$	-	J. Am. Chem. Soc. 2019, 141, 6254–6262
Fe@NSC20-700 <sub>1</sub> - 900 <sub>1</sub>	-	0.794 V	5.5	$0.5 \mathrm{~M~H_2SO_4}$	~41 mV (10,000CV)	Journal of Catalysis 370 (2019) 130–137
Fe–N–C/VA-CNT	0.97 V	0.79 V	6	$0.5 \mathrm{~M~H_2SO_4}$	16 mV (10,000CV)	Adv. Funct. Mater. 2016, 26, 738–744
Fe-NMCSs	-	~0.73 V	5.6	0.1 M HClO <sub>4</sub>	29 mV (10,000CV)	Adv. Mater. 2016, DOI: 10.1002/adma.201602490
Fe(1.5)/N/S-PAD	-	0.68 V	7.4	0.1 M HClO <sub>4</sub>	19 mV (10,000CV)	Journal of Catalysis 352 (2017) 208–217
Fe-N-S CNN	-	78 V	-	$0.5~\mathrm{MH_2SO_4}$	-	Applied Catalysis B: Environmental 250 (2019) 143– 149
NSPC-0.2-900	~0.81	~0.71 V	~5.60	0.1 M HClO <sub>4</sub>	-	Applied Catalysis B: Environmental 246 (2019) 89–
SA-Fe/NG	0.9 V	0.8 V	5	0.5 M H <sub>2</sub> SO <sub>4</sub>	8 mV (5,000CV)	PNAS,2018,DOI:10.1073/pnas. 1800771115
NSCA-700-1000	0.885 V	0.76 V	6.5	0.1 M HClO <sub>4</sub>	-	Chem, 2018, 10.1016/j.chempr.2018.07.005
Fe <sub>3</sub> C/NG-800	0.92 V	0.77 V	5.7	0.1 M HClO <sub>4</sub>	11 mV (10,000CV)	Adv. Mater. 2015, 27, 2521– 2527

## Table S4. Comparison of the ORR performance of Fe@S,N-DC and relevant samples in the literature.

Table S5. Fe contents in Fe@S,N-DC, Fe/S,N-DC, and Fe@N-DC.

Samples	Fe Loading <sup>a</sup>	Fe Loading <sup>b</sup>
Fe@S,N-DC	5.9 wt. %	6.6 wt. %
Fe/S,N-DC	-	8.5 wt. %
Fe@N-DC	6.9 wt. %	7.3 wt. %

a: determined by TGA. b: determined by ICP-AES.



Figure S1. (a) TEM and (b) HRTEM images of Fe@S,N-DC



Figure S2. EDS elemental maps of Fe@S,N-DC: (a) Fe, (b) S, (c) N, and (d) combined.



Figure S3. XRD patterns of Fe@S,N-DC and Fe/S,N-DC<sub>MW</sub>.



**Figure S4**. (a) TGA curves, (b) nitrogen adsorption-desorption isotherms (inset is the pore distribution) of the Fe@S,N-DC, Fe@S,N-DC<sub>3</sub>, and Fe@S,N-DC<sub>5</sub>.



Figure S5. (a,b) TEM and HRTEM images of (a,b) Fe@S,N-DC<sub>3</sub>, and (c,d) Fe@S,N-DC<sub>5</sub>.



**Figure S6.** Electron-transfer numbers (n) and hydrogen peroxide yields (H<sub>2</sub>O<sub>2</sub>) of AC, S,N-DC and Pt/C in (a) 0.1 M KOH and (b) 0.1 M HClO<sub>4</sub>.



**Figure S7.** (a) Nitrogen adsorption-desorption isotherm of AC and S,N-DC (inset is the pore size distribution). XPS N 1s spectra of (b) AC and (c) S,N-DC. (d) XPS S 2p spectrum of S,N-DC. (e) Nyquist plots of AC and S,N-DC.



**Figure S8**. (a) Tafel plots of the series of catalysts at different potentials. b) Kinetic current densities of the series of catalysts at +0.85 V. Data are derived from Figure 4a.



Figure S9. Double-layer capacitances of Fe@S,N-DC, Fe@S,N-DC3 and Fe@S,N-DC5.



Figure S10. ORR polarization curves of Fe@S,N-DC and Pt/C in 0.1 M KOH.



**Figure S11**. (a) Tafel plots of the series of samples. (b) Kinetic current densities of the series of samples at +0.85 V.



Figure S12. (a-c) TEM images of Fe@N-DC. Inset to panel (d) is the corresponding SAED patterns.



**Figure S13.** (a) Nitrogen adsorption-desorption isotherm. Inset is the pore distribution. (b) TGA curve of Fe@N-DC.



Figure S14. (a) Fe 2p and (b) N 1s spectra of Fe@N-DC.



Figure S15. Raman spectra of Fe@S,N-DC and Fe@N-DC.



**Figure S16.** (a) UPS spectra of Fe@S,N-DC, Fe@N-DC, and Au. UPS spectra in the energy regions of (b) cutoff ( $E_{cutoff}$ ) and (c) onset ( $E_{f}$ ) for Fe@S,N-DC. (d) UPS spectra in the energy regions of cutoff ( $E_{cutoff}$ ) and (e) onset ( $E_{f}$ ) for Fe@N-DC. The work function is determined by the equation of  $\phi$  =21.2 eV-( $E_{cutoff}$  -  $E_{f}$ ).



Figure S17. Nyquist plots of Fe@S,N-DC and Fe@N-DC. Inset is the zoom in of the semicircle regions.



**Figure S18.** (a) Possible ORR pathway for Fe@S,N-DC. (b) Schematic illustration of the electron transfer and ORR for Fe@S,N-DC.



Figure S19 (a-b) TEM images of Fe@S,N-DC after 10,000 CV cycles in 0.1 M HCIO<sub>4</sub>.



**Figure S20.** (a) CV and (b) current-time curves of Fe@S,N-DC and Pt/C before and after the addition of 2.5 M methanol. ORR polarization curves of (c) Fe@S,N-DC and (d) Fe/S,N-DC before and after the addition of NaSCN.



Figure S21. Oxygen TPD curves of Fe@S,N-DC and S,N-DC.



Figure S22. (a) TEM and (b) HRTEM images of Co@S,N-DC2.



Figure S23. (a) XRD pattern (Co K $\alpha$  radiation,  $\lambda$  = 1.7902Å) and (b) TGA curve of Co@S,N-DC<sub>2</sub>.



Figure S24. Nitrogen adsorption-desorption isotherms of Co@S,N-DC2



Figure S25. (a) TEM and (b) HRTEM images of Ni@S,N-DC2.



Figure S26. (a) XRD patterns of Ni@S,N-DC2 and Ni@S,N-DC5. (b) TGA curve of Ni@S,N-DC2.



Figure S27. Nitrogen adsorption-desorption isotherms of Ni@S,N-DC2 and Ni@S,N-DC5.



**Figure S28.** Hydrogen evolution reaction (HER) performances of Co@S,N-DC<sub>5</sub>, Co@S,N-DC<sub>3</sub>, and Co@S,N-DC<sub>2</sub>.