Supporting Information

Toward Enhanced Activity of Graphitic Carbon Nitride Based

Electrocatalyst in Oxygen Reduction and Hydrogen Evolution

Reactions via Atomic Sulfur Doping

Zengxia Pei, Jingxiang Zhao,^b Yan Huang,^a Yang Huang,^a Minshen Zhu,^a Zifeng Wang,^a Zhongfang Chen,^{b,*} and Chunyi Zhi^{a,c,*}

^a Department of Physics and Materials Materials Science, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong 999077, China

^b Department of Chemistry, The Institute for Functional Nanomaterials, University of Puerto Rico, Rio Piedras Campus, San Juan, PR 00931, USA

^c Shenzhen Research Institute, City University of Hong Kong, High-Tech Zone, Nanshan District, Shenzhen 518057, China

* Address correspondence to: zhongfangchen@gmail.com (Z. C), cy.zhi@cityu.edu.hk (C. Z.)

Experimental

Materials Synthesis

Mesoporous carbon (MPC) was synthesized using colloidal silica (Ludox HS 40, particle size 12 nm, Sigma-Aldrich) as a hard template and sucrose as carbon precursor. Typically, 5 mL silica solution was dispersed into 50 mL DI water, followed by addition of 3 g sucrose and 0.3 g sulfuric acid (96-97 wt%). This mixture solution was then sonicated for 10 min before being heated at 100 $^{\circ}$ C to evaporate all the water under stirring. The resulted solid was then heated at 160 $^{\circ}$ C for 3 h for the polymerization of sucrose, and was eventually calcined at 900 $^{\circ}$ C for 3 h under Ar atmosphere with a ramp rate of 3 $^{\circ}$ C/min for carbonization of sucrose on the silica spheres (denoted as C@SiO₂). The silica template was removed by immersing the C@SiO₂ in excessive 20 wt% HF solution for 24 h with magnetic stirring, followed by thorough washing with DI water until pH ~7.

The MPC supported sulfur-doped carbon nitride (SCN-MPC) catalyst was fabricated by *in-situ* polycondensation of thiourea (or trithiocyanuric acid) with the presence of MPC. In a typical procedure, given amount of thiourea was added into 10 mL ethanol with 100 mg MPC. The mixture was sonicated for 1 h, and heated at 70 °C under stirring to volatilize the solvent. The powder was then grinded and calcined at 600 °C for 4 h under Ar protection with a ramp rate of 5 °C/min in a crucible (with cover). The mass of initial thiourea was varied as 200, 400 and 800 mg to review the influence of C₃N₄ loading amount (the final product was marked as 1#, 2# and 3#, accordingly). The sulfur-free CN-MPC catalyst was synthesized with an identical procedure except the thiourea was replaced by dicyandiamide. For comparison, sulfur and nitrogen co-doped graphene (S-N-G) was also prepared and the details can be found elsewhere.¹

Characterization

The crystal structure of the catalyst was identified by a Bruker D2 Phaser X-ray diffractometer (XRD) with Cu K_a radiation ($\lambda = 0.15418$ nm) operating at 30 kV and 10 mA, respectively. Fourier transformed infrared (FTIR) spectra were recorded from Nicolet 6700 FT-IR instrument. The morphology and microstructure of the samples were revealed by a JEOL-2001F field-emission transmission electron microscope (TEM), and the accessory Electron energy loss spectroscopy (EELS) was used to determine to composite elements. X-ray photoelectron spectroscopy (XPS) analyses were conducted on an ESCALAB 250 photoelectron spectroscopy (Thermo Fisher Scienctific) at 1.2×10^{-9} mbar using Al K_a X-ray beam (1486.6 eV). The XPS spectra were charge corrected to the adventitious C 1s peak at 284.5 eV. Thermal gravimetric (TG) analyses were carried out on a TA #SDT Q600 analyser at 30-900 °C with an Ar flow of 100 mL/min. The nitrogen adsorption and desorption isotherms were characterized using a Micrometrics ASAP 2020 analyzer. Pore size distribution and specific surface area were obtained via Barrett-Joyner-Halenda (BJH) and Brunauer-Emmett-Teller (BET) methods from adsorption branch of the isotherm, at a relative pressure range of P/P₀ = 0.06-0.3.

Electrochemical Measurements

For ORR tests: all electrochemical measurements were conducted on a CHI 760D electrochemical workstation integrated with a RRDE-3A rotating ring disk electrode apparatus in a typical 3-eletrode system, in which a glassy carbon electrode (GCE, 3mm in diameter) loaded with different catalysts was used as working electrode, with Ag/AgCl (in 3 M KCl) electrode and Pt mesh as reference and counter electrode, respectively. 0.1 M KOH solution served as the electrolyte for all measurements. For the fabrication of working electrode, 6 mg catalyst was dispersed in a 1.5 mL H₂O-isoproponal (v: v=4:1) mixture together with 15 μ L Nafion solution (5 wt%). The mixture was sonicated for 1 h to get a homogeneous slurry, and 2.5 μ L of the solution was then pipetted onto the pre-mirror-polished GCE, which was dried under a N₂ flow. The loading mass was used for reference. The cyclic voltammetric (CV) curves were obtained at a scan rate of 20 mV s⁻¹ in N₂ or O₂ saturated electrolyte in the potential window of -1.0 V to 0.2 V (vs. Ag/AgCl). Polarization curves within the same potential range were recorded in the O₂ saturated electrolyte solution with a scan rate of 5 mV s⁻¹ at various rotating speeds from 400 to 3600 rpm. Each catalyst was repeated at least 3 times of the above measurements to exclude possible incidental errors.

The transferred electron numbers (n) per O_2 molecule and the kinetic current densities (J_K) were determined from the Koutecky–Levich (K–L) equation expressed as follows:

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

where J is the measured current density, J_K and J_L are the kinetic-limiting current density and the diffusion-limiting current density, respectively. ω is the rotation rate of the RDE, and B is the Levich slope given by

$$B = 0.2nFC_0 D_0^{2/3} v^{-1/6}$$

in which n is the number of electrons transferred in the reduction of one O_2 molecule, F is the Faraday constant (F = 96 485 C mol⁻¹), C_0 is the concentration of O_2 in the solution ($C_0 = 1.2 \times 10^{-1}$)

⁶ mol cm⁻³), *v* is the kinematics viscosity of the electrolyte ($v = 0.01 \text{ cm}^2 \text{ s}^{-1}$) and D₀ is the diffusion coefficient of O₂ in 0.1 M KOH (D₀ = 1.9 x10⁻⁵ cm² s⁻¹). Constant 0.2 is adopted when rotating speed is in rpm.

The RRDE tests were conducted with a Pt-ring surrounded 4mm diameter GCE (with loading mass about 120 μ g cm⁻²). The value of n was also calculated through RRDE tests:

$$n = \frac{4I_d}{I_d + \frac{I_r}{N}}$$

the HO₂⁻ yield was calculated from equation:

$$HO_{2}^{-}\% = \frac{200I_{r}}{N(I_{d} + \frac{I_{r}}{N})}$$

here I_d and I_r are the disk current and ring current, respectively, and N is the current collection efficiency of the Pt ring and was determined to be 0.37.

Long term stability tests were conducted by measuring the current changes of the GCE loaded catalysts at a fixed potential of -0.3 V (vs. Ag/AgCl) and rotation speed of 1600 rpm in O₂ saturated electrolyte. The cross-over tolerance tests were performed under same conditions with the addition of 10 vol% methanol during the amperometric process.

For HER tests: all measurements were conducted in the same system as that in the ORR tests except that 0.5 M H₂SO₄ (purged with N₂) served as the electrolyte solution. The potential was converted to a reversible hydrogen electrode (RHE). The working electrode was prepared by pipetting 5 μ L of the catalyst ink solution onto the 3 mm GCE and dried under N₂ stream, which gave a loading mass of 280 μ g cm⁻². Linear sweep voltammetry was carried out at 5 mV s⁻¹ from - 0.6 to 0.2 V (vs. RHE) and CV curves were recorded at a non-faradaic overpotential between 0.15 and 0.25 V (vs. RHE) at scan rates from 20 to 200 mV s⁻¹ to investigate the effective surface area of the catalyst. All polarization curves were corrected for the iR contribution from the cell. The working electrode was rotated at speed of 1600 rpm to alleviate the accumulation of evolved hydrogen bubbles on the catalyst surface. The durability of the catalyst was conducted by potential cycling between -0.6 to 0.2 V (vs. RHE) at 100 mV s⁻¹ for 5000 cycles, during which a graphite rod was used as the counter electrode to avoid the possible contamination of Pt species.

Computation Details

The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof exchange correlation functional² (including a Grimme van der Waals (vdW) correction³ to account for the dispersion interactions) and the double numerical plus polarization (DNP) basis set were employed to perform all the density functional theory (DFT) computations within the frame of the DMol³ code.^{4, 5} Self–consistent field (SCF) calculations were performed with a convergence criterion of 10^{-6} a.u. on the total energy and electronic computations. The real–space global orbital cutoff radius was chosen as high as 4.7 Å in all the computations to ensure high quality results. The Brillouin zone was sampled with a $5 \times 5 \times 1 k$ points setting in geometry optimizations, and a $12 \times 12 \times 1$ grid was used for electronic structure computations. For all the calculations, the symmetrization was switched off. The Hirshfeld charge population analysis⁶ was adopted to compute the charge transfer and magnetic moment.

The hydrogen absorption energy (ΔE_{H^*}) was calculated as: $\Delta E_{H^*} = E_{H\text{-catalyst}} - E_{\text{catalyst}} - E_{\text{H2}/2}$,

where $E_{\text{H-catalyst}}$ is the total energy of the doped C_3N_4 sheet with hydrogen atom absorbed on the surface, E_{catalyst} is the total energy of the doped C_3N_4 sheet, E_{H2} and is the energy of a hydrogen molecule in the gas phase. The Gibbs free energy for the hydrogen absorption was corrected for change in entropy and zero point energy as: $\Delta G = \Delta E_{\text{H*}} + \Delta ZPE - T\Delta S_{\text{H*}}$, where $\Delta E_{\text{H*}}$ is the hydrogen absorption energy, ΔZPE is the difference in zero point energy between the adsorbed hydrogen and hydrogen in the gas phase, $\Delta S_{\text{H*}}$ is the entropy difference between the adsorbed state and the gas phase, and *T* is set to 298.15 K. As the contribution from the vibrational entropy of H in the adsorbed state is negligibly small, the entropy of hydrogen adsorption is $\Delta S_{\text{H}} \approx -\frac{1}{2}S_{\text{H2}}$, where S_{H2} is the entropy of H₂ in the gas phase at the standard conditions. Then the Gibbs free energy with the overall corrections is taken as $\Delta G = \Delta E_{\text{H*}} + 0.24 \text{ eV}.^7$

The O₂ absorption energy (ΔE_{O2^*}) was calculated as: $\Delta E_{O2^*} = E_{O2\text{-catalyst}} - E_{catalyst} - E_{O2}$, where $E_{O2\text{-catalyst}}$ is the total energy of the doped C₃N₄ sheet with O₂ absorbed on the surface, $E_{catalyst}$ is the total energy of the doped C₃N₄ sheet, E_{O2} and is the energy of the oxygen molecule in the gas phase.



Figure S1. High resolution S 2p XPS spectrum of the SCN sample.

High resolution S 2p spectrum could be deconvoluted into two peaks centered at 163.8 eV and 165.0 eV, which can be attributed to the binding energies of the doublet $2p_{3/2}$ and $2p_{1/2}$ peaks of sulfur originated from the C-S bonds, respectively. This result indicated that the incorporated sulfur substituted some lattice nitrogen atoms within the C_3N_4 matrix in the form of $C_3N_{4-x}S_x$, similar to previous work.⁸ The S/N ratio was determined to be 0.8 %.



Figure S2. (a) Nitrogen adsorption/desorption isotherms of the MPC and carbon nitride incorporated mesoporous composite materials, the specific surface areas of each sample are also listed; (b) Pore diameter distribution of all the samples.



Figure S3. Thermal gravimetric analyses of the weight change of different samples with a ramp rate of 5 °C/min under Ar flow (100 mL/min).



Fig. S4 Raman spectra of different samples.



Fig. S5 TEM images showing the mesoporous structure of the bare MPC sample.



Figure S6. High resolution XPS spectra of (a) C 1s of the MPC sample; (b) C 1s and (c) N 1s of the pure SCN sample; (d) C 1s and (e) N 1s of the SCN-MPC composite material.

Note the characteristic C 1s peak at 288.0 eV from carbon atoms within the N-C=N bonds in the carbon nitride basal motifs was observed in the SCN-MPC sample, indicating the incorporation of the SCN material in the MPC.



Fig. S7 Electrochemical catalytic performance toward ORR in 0.1 M KOH solution of the control samples: CV scans of the bare MPC (a) and commercial 20 wt% Pt/C (c) samples; LSV curves of the bare MPC (b) and Pt/C (d) samples at different rotating speeds.

Note: An obvious platform can be observed in the bare MPC sample in its reduction current,

indicating a significant and unfavorable $2e^{-}$ reduction pathway at moderate potential, which can result in the formation of HO₂⁻ species and the subsequent corrosion of the carbon block.



Figure S8. Linear sweep voltammetric curves at different rotation speeds from 400 to 3600 rpm of different samples and the Koutecky–Levich plots of the samples at different potentials. The corresponding electron transfer numbers are also given.



Fig. S9 (a) LSV curves reviewing the influence of SCN concentration, with the CN-MPC sample as a reference recorded from RDE tests at 1600 rpm in O₂ saturated 0.1 M KOH; (b) comparison of kinetic current density obtained within the mixed kinetic-diffusion region (-0.15 V vs Ag/AgCl) upon normalization of the electrode area and the BET surface area.

Note that the ORR activity will be influenced by both the surface area and the active species $(C_3N_4 \text{ motifs here})$.⁹ With larger (doped) C_3N_4 loading amount, the surface area of the composite will decrease (as evidenced by the Fig. S2 and S3). However, it was found that the kinetic-limiting current densities of the SCN-MPC(2#) and SCN-MPC(3#) samples within the mixed kinetic-diffusion region in ORR were still much larger than the dopant-free CN-MPC sample, indicating the intrinsic higher activity of the sulfur-doped C_3N_4 species. The lower activity of the SCN-MPC(1#) sample is probably caused by the less loading amount of the C_3N_4 species since the activities should be compared between comparable amount of active species. These results reveal that the increased surface area can contribute, but only partly, to the enhanced ORR activity. The sulfur-doping protocol is thus evidently validated to act as another key factor. Also note that the SCN-MPC(3#) one shows the highest kinetic-limiting current density by unit surface area, but under operational condition, the SCN-MPC(2#) sample serves as better candidate for practical ORR performance. The prominent ORR activity of the SCN-MPC(2#) sample over the dopant-free one is additionally proven by the EIS analysis as shown below.



Fig. S10 Electrochemical impedance spectroscopy data for the representative SCN-MPC (2#) and control CN-MPC sample in KOH; data were collected for the electrodes at -0.3 V (vs. Ag/AgCl), frequency range: 1 Hz to 1 MHz; inset is the equivalent circuit.



Fig. S11 TEM images showing the morphology and the mesoporous structure of the SCN-MPC(2#) sample after 50 hours of chronoamperometric durability tests at 1600 rpm and -0.3 V (vs Ag/AgCl).

Figure S12. HER polarization curves (a) and corresponding Tafel plots (b) reviewing the influence of SCN concentration, with the CN-MPC sample as a reference; (c) comparison of exchange current density of different samples upon normalization of the electrode area and the BET surface area.

Note that in the HER tests, the SCN-MPC (3#) sample (with SCN loading mass of *ca.* 33%) presented the best performance, which is different from the ORR results in Fig. S9, suggesting a distinct kinetics of the two different reactions. However, the variation trend of the activity parameters (including onset potential, current density at given potential as well as Tafel plots) shows the merit of sulfur-doped samples. More specifically, the exchange current density, J_0 (one significant parameter that the reveals the intrinsic activity for HER materials) of the SCN-MPC(3#) sample is obviously larger than the counter sample after normalization given their similar carbon nitride loading mass. It is therefore reasonable to conclude that sulfur doping could significantly boost the performance of the carbon nitride material in both HER and ORR.

Fig. S13 HER polarization curve of the bare MPC sample.

Fig. S14 Electrochemical impedance spectroscopy data for the representative SCN-MPC (3#) and control CN-MPC sample in H₂SO₄; data were collected for the electrodes under HER overpotential of 200mV, frequency range: 1 Hz to 1 MHz; inset is the equivalent circuit.

Figure S15. Cyclic voltammetric curves of the SCN-MPC(3#) sample recorded at a overpotential window between 0.15 and 0.25 V (vs. RHE) at scan rates from 20 to 200 mV s⁻¹.

Catalyst	Onset Potential	Electron	HO ₂ - yield	Reference
	(V)	transfer		
		number (n)		
SCN-MPC	-0.11	3.8-4.0	< 12%	This work
	(vs. Ag/AgCl)			
C ₃ N ₄ @CMK-3	~ 0.1	~4.0	-	J. Am. Chem. Soc. 2011,
	(vs. Ag/AgCl)			133, 20116
Macroporous	-0.14	~3.0	< 50%	Angew. Chem. Int. Ed.
C ₃ N ₄ @C	(vs. Ag/AgCl)			2012 , 51, 3892
s-g-C ₃ N ₄ @GQD	-0.07	~3.5	< 30%	J. Mater. Chem. A, 2015,
	(vs. Ag/AgCl)			3, 1841
N-doped Graphene	-0.18	3.7	< 20%	Angew. Chem. Int. Ed.
Framework	(vs. Ag/AgCl)			2012 , 51, 11371
S,N co-doped	-0.06	3.3-3.6	-	Angew. Chem. Int. Ed.
Mesoporous	(vs. Ag/AgCl)			2012 , 51, 11496
Graphene				
P-doped Graphene	0.92	3.0-3.8	-	Adv. Mater. 2013, 25,
	(vs. RHE)			4932.
3D N-doped	-0.05	3.71-3.96	< 14.7%	Small 2015 , 11, 1423
Garphene	(vs. Ag/AgCl)			
Nanoribbons				
N-doped Porous	-	~3.20-3.94	< 20%	Adv. Mater. 2016, 28,
Carbon				1981
Superstructures				

Table S1. Comparison study of ORR performance of different metal-free catalysts in 0.1 M KOH

Catalyst	Loading	Onset	η @	Tafel slope	J ₀ ,	Cdl	Reference
	Mass	potential	10 mA cm ⁻²	(mV dec ⁻¹)	geometric	(mF cm ⁻²)	
	(µg cm ⁻²)	(mV vs. RHE)	(mV vs. RHE)		(µA cm ⁻²)		
SCN-MPC	280	-60 *	-145	51	33.3	28.4	This work
MoO ₃ -MoS ₂	60	-(150-200)	~ -250	50-60	0.082	2.2	Nano Lett.
Nanowires							2011 , 11, 4168.
MoS ₂	285	-120	~ -180	50	8.9	-	Adv. Mater.
Nanosheets							2013 , 25, 5807.
CoS ₂ NW		-75	-145	52	15.1	21.5	J. Am. Chem.Soc.
CoS ₂ MW		-75	-158	58	18.8	14.2	2014 , 136,10053
N,P-doped	200	-290 *	-420	91	0.24	-	ACS Nano,
Graphene							2014 , 8, 5290.
C ₃ N ₄ @NG	~100	-	-240	51	0.35	5.0	Nature Comm.
							2014 , 5, 3783.
g-C ₃ N ₄	143	-80	-207	54	39.8	13.0	Angew. Chem. Int. Ed.
Nanoribbon-							2014 , 126, 14154.
G							
N/Co-doped	357	-58	-229	126	-	-	Adv. Funct.Mater.
PCP//NRG							2015 , 25, 872.
0							
Porous	2000	-20	-133	57	70	-	Nature Comm. 2015,
CoN _x /C							DOI:10.1038/ncomms8
							992
N,S-doped	-	-130	-276	81	8.4	-	Angew. Chem. Int. Ed.
Graphene							2015 , 54, 2131.
500C							
N,S-doped	285	-27	~-130	68	-	27.4	Nano Energy, 2015,
carbon							16, 357.
nanosheets							
g-C ₃ N ₄ @P-	280	-76*	-340	90	3.33	4.18	ChemCatChem 2015,
pGr							7, 3873.
g-C ₃ N ₄ @S-	280	-92*	-300	86	6.27	4.35	J. Mater. Chem. A,
Se-pGr							2015 , 3, 12810.
Au@Fe-Zn-	285	-80	-123	130	-	-	ACS Catal. 2016, 6,
C							1045.

Table S2. Comparison study of HER performance of different catalysts in 0.5 M H₂SO₄

*In these works, the onset potential is defined as the critical potential where the current density reaches

0.5 mA cm⁻².

Table S3: The charge and magnetic moment of S-doped C_3N_4 sheet, adsorption energies of O_2 molecule (E_{ads}) on the most favorable site, and the Gibbs free energies of H atom ($\Delta G(H^*)$) on possible sites around S-dopant. The data for pure C_3N_4 is given in the last row for comparison.

Site	charge (e)	μ (μ _B)	$E_{\rm ads}$ (eV)	$\Delta G(\mathrm{H}^*)$ (eV)
S	0.11	0.10	/	+1.04
N_1	-0.18	0.02	/	-0.03
N_2	-0.01	0.01	/	-0.89
N_3	-0.17	0.09	/	+0.81
C_1	0.07	0.18	-0.57	-0.83
C_2	0.09	0.05	/	-0.74
C ₃	0.13	0.16	/	-0.35
pure C ₃ N ₄	_	_	-0.08	-0.58

References

- 1. X. Wang, J. Wang, D. Wang, S. Dou, Z. Ma, J. Wu, L. Tao, A. Shen, C. Ouyang and Q. Liu, *Chem. Commun.*, 2014, **50**, 4839-4842.
- 2. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 3. S. Grimme, J. Comput. Chem., 2006, 27, 1787-1799.
- 4. B. Delley, J. Chem. Phys., 1990, 92, 508-517.
- 5. B. Delley, J. Chem. Phys., 2000, **113**, 7756-7764.
- 6. F. L. Hirshfeld, *Theor. Chim. Acta*, 1977, **44**, 129-138.
- 7. D. Voiry, H. Yamaguchi, J. Li, R. Silva, D. C. Alves, T. Fujita, M. Chen, T. Asefa, V. B. Shenoy and G. Eda, *Nat. Mater.*, 2013, **12**, 850-855.
- G. Liu, P. Niu, C. Sun, S. C. Smith, Z. Chen, G. Q. Lu and H.-M. Cheng, J. Am. Chem. Soc., 2010, 132, 11642-11648.
- 9. H.-W. Liang, X. Zhuang, S. Brüller, X. Feng and K. Müllen, *Nat. Commun.*, 2014, DOI: 10.1038/ncomms5973