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Synthesis and oxygen reduction properties of three-

dimensional sulfur-doped graphene networks†

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Experimental

Instrumentation and chemicals. Electrochemical experiments were conducted on a CHI760E electrochemical workstation (CH Instrument Co., USA). A conventional three-electrode system included a glassy carbon rotating disk electrode (RDE) or a rotating ring-disk electrode (RRDE) (Pine Research Instrumentation) coated with catalysts coated with catalysts, a Pt auxiliary electrode and a saturated calomel reference electrode (SCE). All the potentials are reported with respect to the reversible hydrogen electrode (RHE) and all electrochemical data were obtained at room temperature. The potential of SCE was calibrated with RHE, in 0.1 M KOH, E (RHE) = E(SCE) + 0.99 V.^{S1} Scanning electron microscopy (SEM) studies and were performed on a Hitachi S4800 scanning electron microscope. The samples were prepared by dropping ethanol dispersions of the samples onto Pt foils and immediately evaporating the solvent. Transmission electron microscopy (TEM) studies were performed on a TECNAI F-30 highresolution transmission electron microscope. X-ray diffraction (XRD) studies were performed on a PANalytical X'pert Pro X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI QUANTUM 2000 X-ray photoelectron spectroscopic instrument. Surface area and pore size were determined by a surface area and porosity analyzer (Micromeritics Instrument Corp. ASAP2020). The Ni residues were determined by inductively coupled plasma mass spectrometry (ICP-MS, HP4500) analysis (Agilent, USA), and the samples were pretreated with a dry ashing method coupled with acid extraction.^{S2} The commercial Pt/C 20 wt% catalyst was purchased from Johnson-Matthey (JM). All chemicals were of analytical grade and used without further purification. Ultrapure water (Millipore, $\geq 18M\Omega$ cm) was used throughout.

Synthesis of 3D S-GNs. The pretreated sulfonic acid ion exchange resin (732-type) was impregnated with Ni²⁺ in 100 mL nickel acetate solution with concentration of 0.05 M for 8 h. The ion exchange resin was washed with deionized water and dried at 60 °C. The Ni²⁺⁻ impregnated ion exchanged resin (10 g) was added in a 400 mL KOH/ethanol solution containing 40 g KOH and stirred at 80 °C until the mixture solution became an 'ink-paste', followed by another 6 hours of static soaking in ambient conditions. Then the mixture was dried at 70 °C for 60 hours and then smashed by a disintegrator. Finally, the mixture was heated at 850 °C for 2 h in N₂ atmosphere, with a heating ratio of 2 °C min⁻¹. Finally, the resulting sample was etched in excessive 0.1 M HCl aqueous solution. The resulting products were collected by centrifugation, washed with deionized water and finally dried at 60 °C for 12 h.

Synthesis of S-CNCs and sulfur-free 3D GNs. The pretreated sulfonic acid ion exchange resin (732-type) was impregnated with Ni²⁺ in 100 mL nickel acetate solution with concentration of 0.05 M for 8 h. The ion exchange resin was washed with deionized water and dried at 60 °C. Then, the Ni²⁺-impregnated ion exchanged resin was heated at 850 °C for 2 h in N₂ atmosphere, with a heating ratio of 2 °C min⁻¹. Finally, the resulting sample was etched in excessive 0.1 M HCl aqueous solution. The resulting products were collected by centrifugation, washed with deionized water and finally dried at 60 °C for 12 h. Sulfur-free 3D GNs were synthesized following a reported methodology using D113-type ion exchange resin as carbon precursor.^{S3}

Electrochemical studies. The RDE was polished with 1 and 0.05 μ m alumina slurry sequentially and then washed ultrasonically in water and ethanol for 15 min, respectively.

Then the RDE was subjected to potential cycling (0 to 1.1 V vs. RHE, 50 mV s⁻¹) in 0.10 M aqueous HClO₄ until reproducible cyclic voltammograms were obtained. 5 mg catalysts were dispersed in 5 ml ethanol, and then ultrasonicated to form a uniform black ink. The catalysts modified RDE was prepared by cast-coating a designed volume of well-dispersed catalyst ink onto pre-polished RDE. The catalyst loading was 200 µg cm⁻² for each case. After drying at room temperature, 5 µL of 0.1 wt% Nafion solution was further cast-coated to form a protection layer against catalyst detaching from the electrode surface. 0.1 M KOH aqueous solution saturated with oxygen by bubbling O_2 for 30 min served as the supporting electrolyte. A flow of O₂ was maintained over the electrolyte solution for continued O₂ saturation during cyclic voltammetry experiments. In control experiments, cyclic voltammetry measurements were also performed in N2-saturated 0.1 M KOH aqueous solution by switching a N2 flow through the electrochemical cell. For the oxygen reduction reaction at a RDE, the working electrode was scanned cathodically at a rate of 10 mV s⁻¹ with varying rotating speed from 400 to 2500 rpm in O₂-saturated 0.1 M KOH aqueous solution. Koutecky-Levich plots were analyzed at various electrode potentials. The slopes of their linear fit lines are used to calculate the electron transfer number (n) on the basis of the Koutecky-Levich equation:^{S4}

$$\frac{1}{j} = \frac{1}{j_{\rm L}} + \frac{1}{j_{\rm K}} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_{\rm K}}$$

$$B = 0.62 n F C_{\rm o} D_{\rm o}^{2/3} v^{-1/6}$$

where *j* is the experimentally measured current, j_L is the diffusion-limiting current, and j_K is the kinetic current, ω is the angular velocity, *F* is the Faraday constant, C_0 is the bulk concentration of O₂, and *v* is the kinematic viscosity of the electrolyte. For the RRDE measurements, the disk electrode was scanned cathodically at a rate of 10 mV s⁻¹ and the ring potential was kept at 1.5 V vs. SCE. The percentage of HO_2^- and the electron transfer number (*n*) were determined by the followed equations:

$$\text{HO}_{2}^{-}\% = 200 \times \frac{i_{\rm r}/N}{i_{\rm d} + i_{\rm r}/N}$$

$$n = 4 \times \frac{I_{\rm d}}{i_{\rm d} + i_{\rm r} / N}$$

where I_d is the disk current, I_r is the ring current and N is the current collection efficiency of the Pt ring. N was determined to be 0.38 from the reduction of K₃Fe[CN]₆, well consistent with the manufacturer's value (0.37).

	BET surface area (m ² g ⁻	Micropore area (m ² g ⁻	External surface area (m ² g ⁻	Total pore volume (cm ³ g ⁻¹)	Micropore volume (cm ³ g ⁻¹)	Average pore diameter (nm)
3D S-GNs	2129	606	1523	1.30	0.35	2.5
3D S-GNs	1768	498	1270	1.05	0.28	2.4
S-CNCs	96.6	14.0	82.6	0.22	6.7×10 ⁻³	13.3

Table S1. Textural properties of 3D S-GNs, 3D S-GNs and S-CNCs.

Electrocatalysts	Cathodic peak	Oneset	Reference
	potential	potential	
3D S-GNs	0.85 V vs RHE	1.01 V vs RHE	This
			work
3D S-GNs ^a	-0.12 V vs	0.04 V vs	This
	Ag/AgCl	Ag/AgCl	work
Sulfur-containing carbon	-0.27 vs	-0.16 V vs	S5
	Ag/AgCl	Ag/AgCl	
Sulfur doped graphite oxide	-0.22 V vs	-0.165 V vs	S6
	Ag/AgCl	Ag/AgCl	
Nitrogen/sulfur co-doped graphene	-0.36 V vs		S7
	Ag/AgCl		
Sulfur and nitrogen doped carbon		-0.13 V vs	S 8
aerogels		Ag/AgCl	
Nitrogen and sulfur dual-doped non-noble	0.812 V vs RHE	0.92 V	S9
catalyst			
Nitrogen and sulfur Co-doped graphene	~-0.3 V vs SCE		S10
sulfur and nitrogen dual-doped, ordered	-0.16 V vs	-0.05 V vs	S11
mesoporous carbon	Ag/AgCl	Ag/AgCl	
Sulfur-doped graphene	-0.32 V vs		S12
	Ag/AgCl		
Sulfur-doped ordered mesoporous carbon	\sim -0.2 V vs		S13
	Ag/AgCl		
Sulfur-nitrogen co-doped three-	-0.20 V vs		S14
dimensional carbon foams	Ag/AgCl		
Sulfur and Nitrogen Dual-Doped	-0.24 V vs	-0.06 V vs	S15
Mesoporous Graphene	Ag/AgCl	Ag/AgCl	
Nitrogen and sulfur dual doped	-0.11 V vs	-0.02 V vs	S16
hierarchically porous carbons	Ag/AgCl	Ag/AgCl	

Table S2. F	Performance	comparison	among the	e reported	sulfur	doped	carbon	catalysts

^a $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E_{\text{Ag/AgCl} vs \text{ RHE}}^{0} + 0.0592 \text{ pH}$, where $E_{\text{Ag/AgCl} vs \text{ RHE}}^{0}$ is 0.199 V at 25 °C.^{S17}

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Fig. S1 SEM (a, b) and TEM (c, d) images of S-CNCs.



Fig. S2 XRD patterns (a) and Raman spectra (b) of 3D S-GNs, 3D GNs, and S-CNCs.

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Fig. S3 SEM images of sulfur doped carbons which were obtained at carbonization temperature of 750 (a), 800 (b), 850 (c), and 900 °C (d). (e) Sulfur content of sulfur doped carbons as a function of carbonization temperatures.

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Fig. S4 SEM (a, b) and TEM (c, d) images of 3D GNs.



Fig. S5 Nitrogen adsorption/desorption isotherms (a) and pore distribution (b) of 3D S-GNs,3D GNs, and S-CNCs. Inset shows pore distribution of S-CNCs.



Fig. S6 (a) Ring current and disk current of 3D S-GNs catalyst obtained from the rotating ring-disk electrode measurements in O_2 -saturated 0.1 M KOH at a sweep rate of 10 mV s⁻¹ and a rotation rate of 1,600 rpm. (b) Percentage of peroxide and the electron transfer number (d) of 3D S-GNs catalyst at various potentials.



Fig. S7 (a) Chronoamperometric responses of 3D S-GNs and Pt/C catalysts at 0.75 V in O_2 -saturated 0.1 M KOH, which are normalized to the initial current responses. (b) Chronoamperometric responses at 0.75 V to injection of 1 M methanol into O_2 -saturated 0.1 M KOH solution at 3D S-GNs and Pt/C catalysts modified electrodes.

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