Supplementary Material

Nitrogen- and Sulfur-doped Carbon Nanoplatelets via Thermal Annealing Alkaline Lignin with Urea as Efficient Electrocatalysts for Oxygen Reduction Reaction

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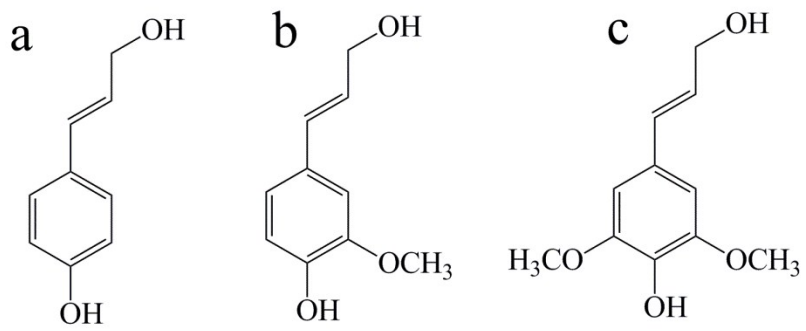


Fig. S1 The three common monolignols: paracoumaryl alcohol (a), coniferyl alcohol (b) and sinapyl alcohol (c).

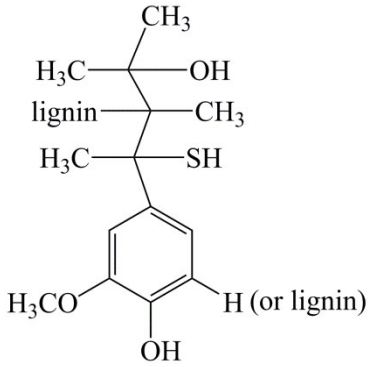


Fig. S2 Molecular structure of alkaline lignin (AL) used in this work.

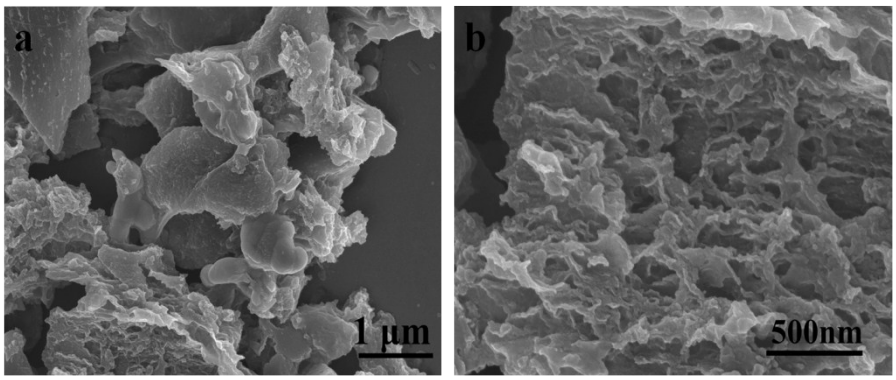


Fig. S3 SEM images of N-S-C 900 with different magnifications.

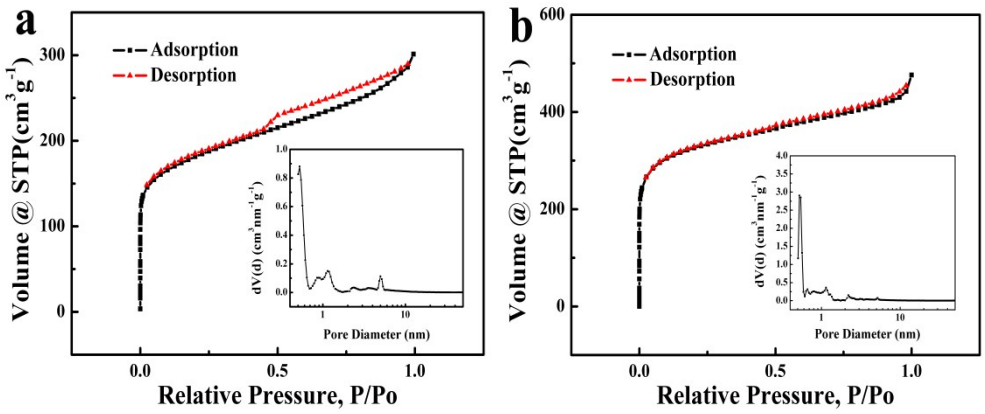


Fig. S4 Nitrogen adsorption/desorption isotherms of S-C 900 (a), N-S-C 900 (b) and its corresponding pore size distribution (inset).

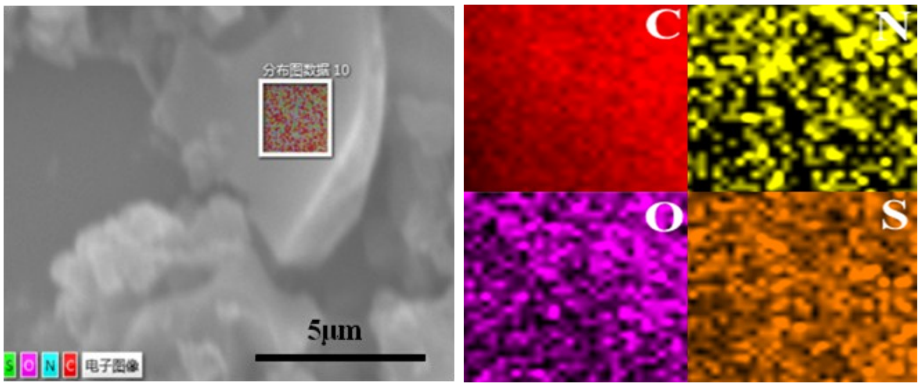
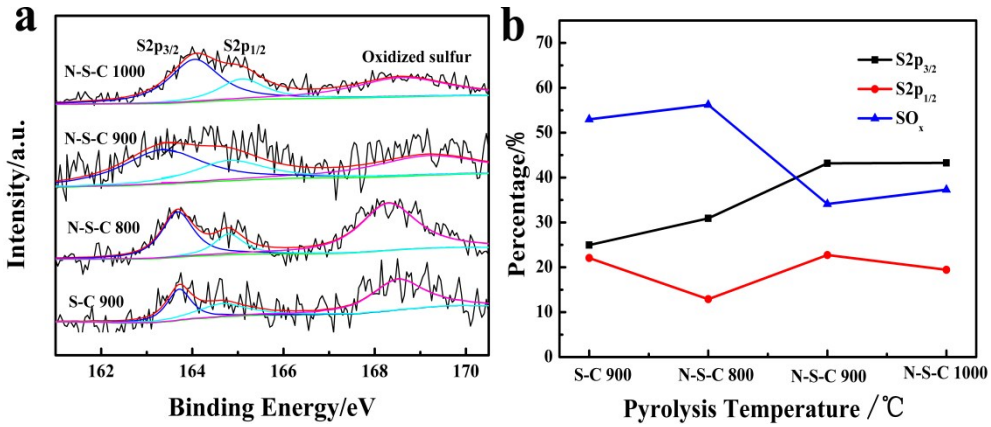


Fig. S5 SEM image of N-S-C 900 and the corresponding EDS mapping of the C, N, O and S elements.



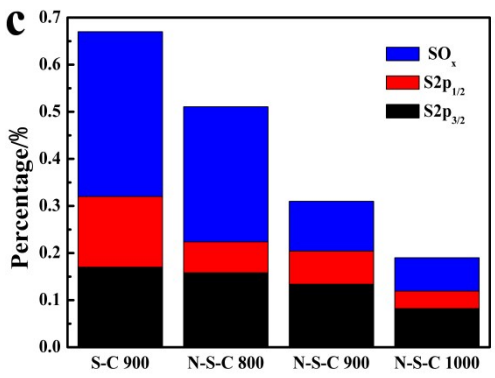


Fig. S6 (a) High-resolution S2p XPS spectra of as-prepared catalysts. (b) The percentage of three sulfur species in sulfur. (c) The atomic percentage of three sulfur species.

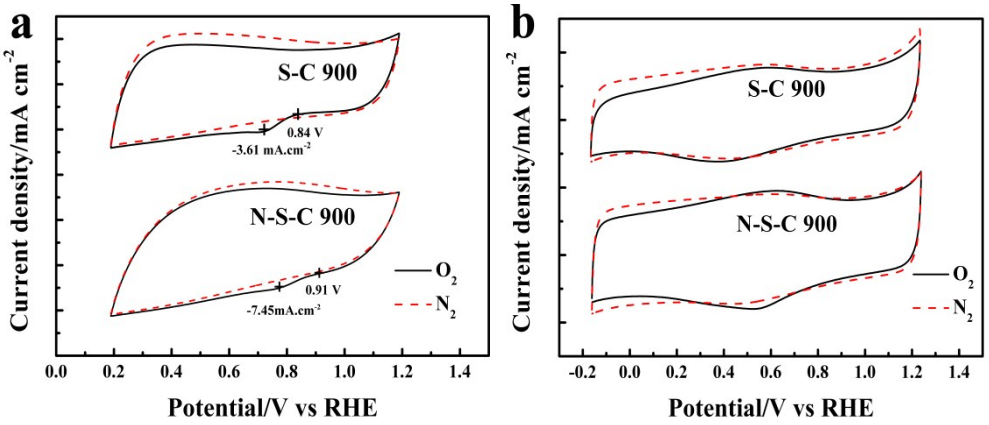


Fig. S7 Cyclic voltammograms of as-prepared N-S-C 900 compared to S-C 900 in (a) 0.1 M KOH and (b) 0.5 M H_2SO_4.

Table S1 Nitrogen sorption data of S-C 900, N-S-C 900.

Sample	Physical Characteristics			
	S_{BET}[a] ($m^2\ g^{-1}$)	S_{mic}[b] ($m^2\ g^{-1}$)	S_{mes}[c] ($m^2\ g^{-1}$)	Pore volume[d] ($cm^3\ g^{-1}$)
S-C 900	656	602	54	0.47
N-S-C 900	1209	1035	173	0.74

[a]Specific surface area from multiple BET method; [b]Micropore surface area from t-plot method; [c]t-method external surface area ($S_{mes} = S_{BET}-S_{mic}$); [d]Total pore volume at $P/P_0 = 0.99$.

Table S2 Summary of the porous features of carbon materials reported in literature.

Catalyst	S_{BET}[a] ($m^2\ g^{-1}$)	S_{mic}[b] ($m^2\ g^{-1}$)	Pore volume[d] ($cm^3\ g^{-1}$)	References
N-S-C 900	1209	1035	0.74	In this work
BP-800	1578	1133	1.09	S1

AC900NH3	1694	1236	0.61	S2
NGPC-1000-10	932	-	0.99	S3
TTF-F	2570	-	2.14	S4
N-MCNs-7-1000 3:1	1171	-	1.46	S5

Table S3 The physical properties of N-S-C (800, 900, 1000) and S-C 900.

Catalyst	Nitrogen distribution (%)				Total N Content (%)	Total S Content (%)	N/C ratio
	N1	N2	N3	N4			
N-S-C 800	1.25	1.11	1.41	0.20	3.97	0.51	0.046
N-S-C 900	0.37	0.74	1.56	0.31	2.98	0.31	0.031
N-S-C 1000	0.06	0.11	0.39	0.05	0.61	0.19	0.0063
S-C 900	-	-	-	-	-	0.67	-

Table S4 The CHNS elemental analysis of as-prepared samples.

Catalyst	C	H	N	S	N/C ratio
N-S-C 800	70.74	2.51	6.24	0.74	0.088
N-S-C 900	62.72	3.13	3.10	0.85	0.049
N-S-C 1000	77.81	2.06	1.47	0.68	0.019
S-C 900	78.63	2.08	-	1.50	-

Table S5 Electrochemical parameters for ORR estimated from RDE polarization curves in 0.1 M KOH solution.

Electrocatalysts	E_{onset} V *vs.* RHE	$E_{1/2}$ V *vs*. RHE	j_L (mA cm^{-2}) at 0.2 V *vs*. RHE	J_k (mA cm^{-2}) at 0.5 V *vs*. RHE
S-C 900	0.86	0.24	4.28	9.6
N-S-C 800	0.92	0.78	5.40	11.5
N-S-C 900	0.97	0.83	7.06	49.4
N-S-C 1000	0.95	0.82	6.97	38.4
Pt/C	0.97	0.81	6.09	55.9

Table S6 Electrochemical parameters for ORR estimated from RDE polarization curves in 0.5 M H_2SO_4 solution.

Electrocatalysts	E_{onset} V *vs.* RHE	$E_{1/2}$ V *vs*. RHE	j_L (mA cm^{-2}) at 0.04 V *vs*. RHE	J_k (mA cm^{-2}) at 0.34 V *vs*. RHE
S-C 900	0.57	0.34	3.43	1.4
N-S-C 800	0.69	0.44	4.14	4.8
N-S-C 900	0.78	0.57	5.82	36.6
N-S-C 1000	0.75	0.55	5.63	33.2
Pt/C	0.81	0.71	5.73	49.4

ORR Activity Calculations

The kinetic parameters (n and J_k) were analyzed by Koutecky-Levich (K-L) eq 1 and 2 as follows:

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{NFKC_0} + \frac{1}{B\omega^{1/2}} \quad (1)$$

$$B = 0.62nFC_0(D_0)^{2/3}\upsilon^{-1/6} \quad (2)$$

Where J is the measured current density, J_K and J_L are the kinetic and diffusion limiting current densities, respectively, n is the overall number of electrons transferred, F is the Faraday constant, C_0 is the bulk concentration of O_2 dissolved in the electrolyte, D_0 is the O_2 diffusion coefficient, υ is the kinematic viscosity of the electrolyte, K is the electron transfer rate constant, and ω is the angular velocity of the disk ($\omega = 2\pi N$, N is the linear rotation speed). The constant 0.2 is adopted when the rotating speed is expressed in rpm.

An additional rotating ring disk electrode (RRDE) experiment can be used to estimate n and further verify the ORR pathways, in which peroxide species produced during the ORR process at the disk electrode can be detected by the ring electrode. The electron transfer number and the percentage of hydrogen peroxide species can be determined by the following equations:

$$n = \frac{4I_D}{I_D + I_R / N} \quad (3)$$

$$\%HO_2^- = \frac{200 \times I_R / N}{I_D + I_R / N} \quad (4)$$

Where I_d is the disk current, I_r is the ring current, and N is the current collection efficiency of the Pt ring.

Supporting references

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