Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information

N- and S- doped mesoporous carbon as metal-free cathode catalysts for direct biorenewable alcohol fuel cells

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1. Experimental Section:

Reagents: the precursors of glucose (⩾99.5%), Pluronic P123, thiophene (⩾99%), iron chloride (⩾ 99.99%) and potassium hydroxide (⩾85%) were purchased from were Sigma-Aldrich; hydrochloric acid (37.5%), hydrofluoric acid (51.0%) and sulfuric acid (98.0%) were brought from Fisher Scientific; commercial 20wt% and 40wt% Pt/C was gained from FuelCell Store. Anhydrous ammonia gas (NH3) (99.999%)was obtained from Airgas. All reagents were directly used without any further purification.

2. Supplementary Figures:

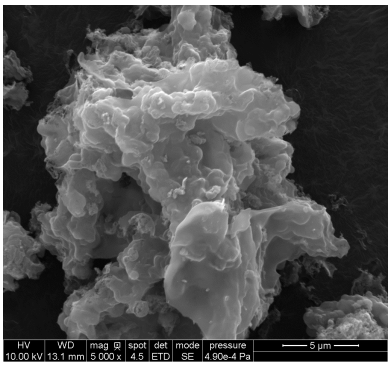


Fig. S1 SEM image of CMK-3.

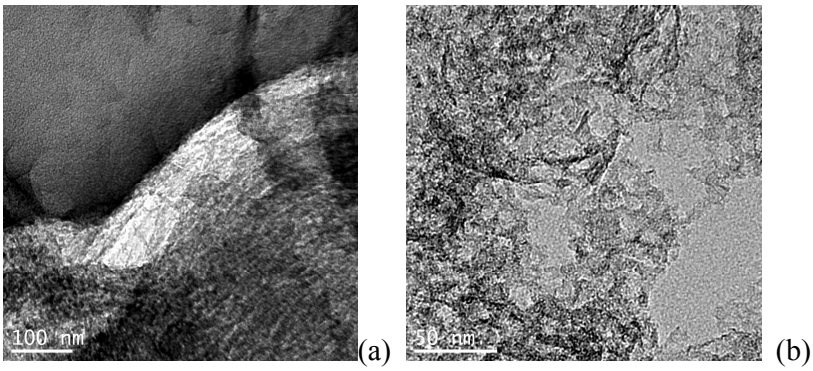


Fig. S2 TEM images of (a) N-S-CMK-3 700 °C and (b)N-S-CMK-3 900 °C.

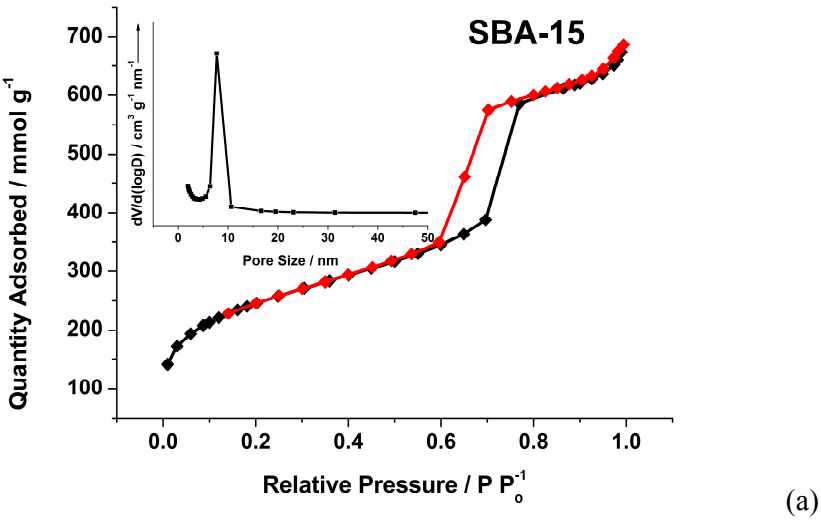


Fig. S3. Nitrogen adsorption-desorption isotherms and pore size distribution (Inset) of (a) SBA-15 and (b) CMK-3.

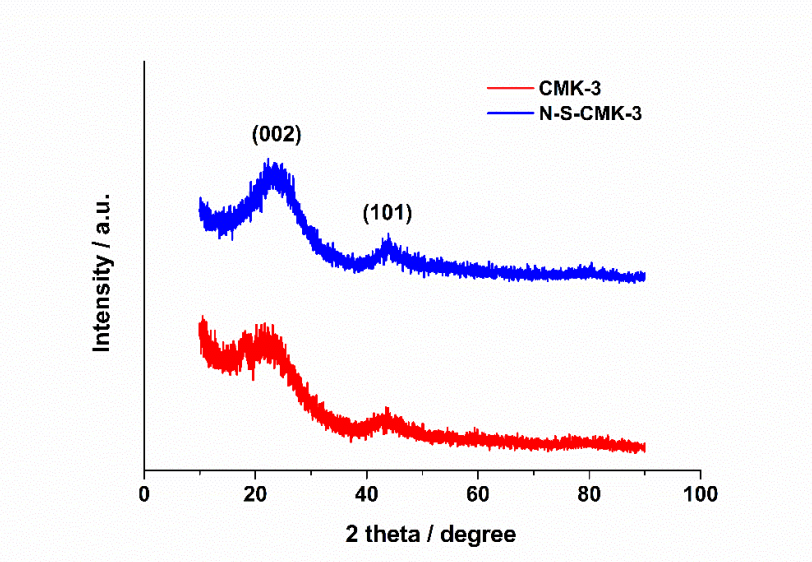


Fig. S4 Wide-angle XRD patterns of N-S-CMK-3 800 °C and CMK-3 catalysts

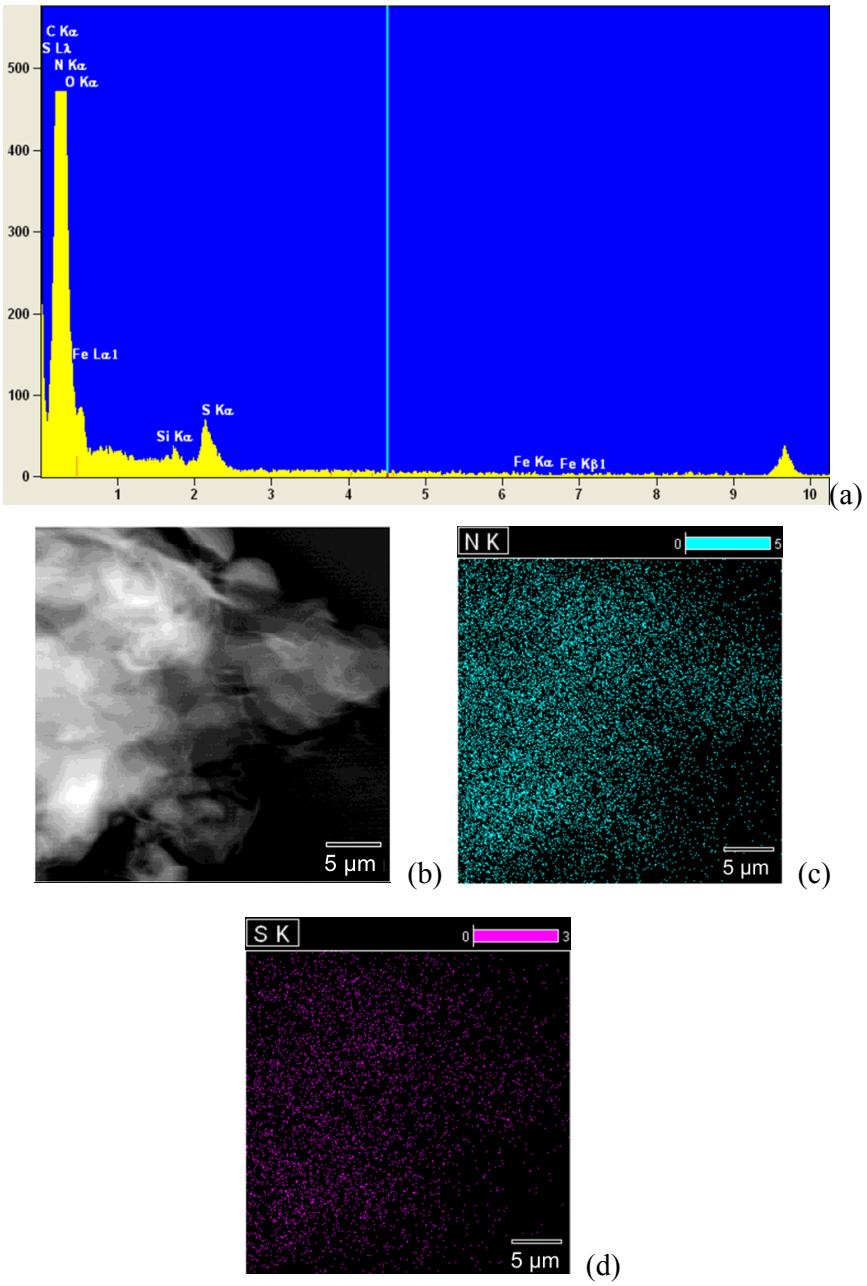
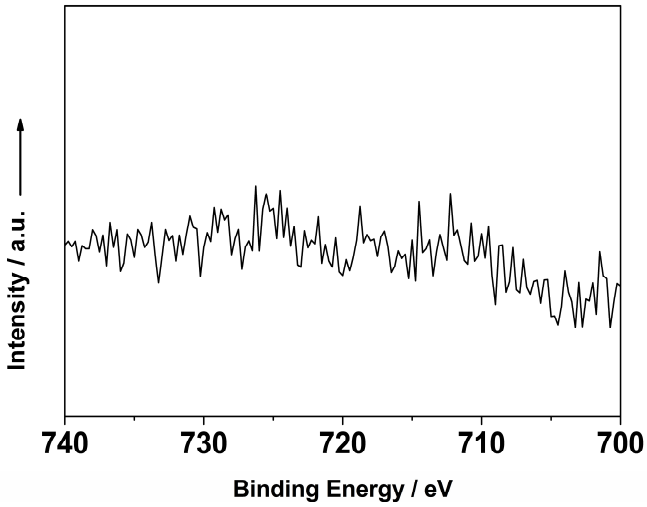
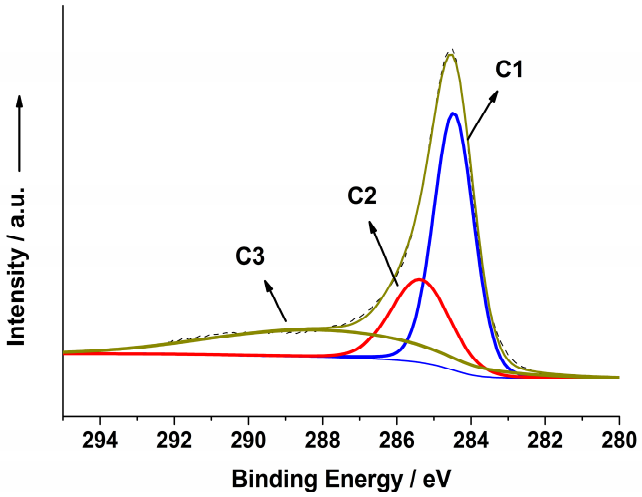


Fig. S5 (a) EDS spectrum of N-S-CMK-3 800 °C; (b-d) EDS elemental mapping in conjunction with the TEM images of N and S in N-S-CMK-3 800 °C.



(a)



(b)

Fig S6 XPS high-resolution spectrum of (a) Fe_{2p} and (b) C_{1s} (b) of N-S-CMK-3 800 °C.

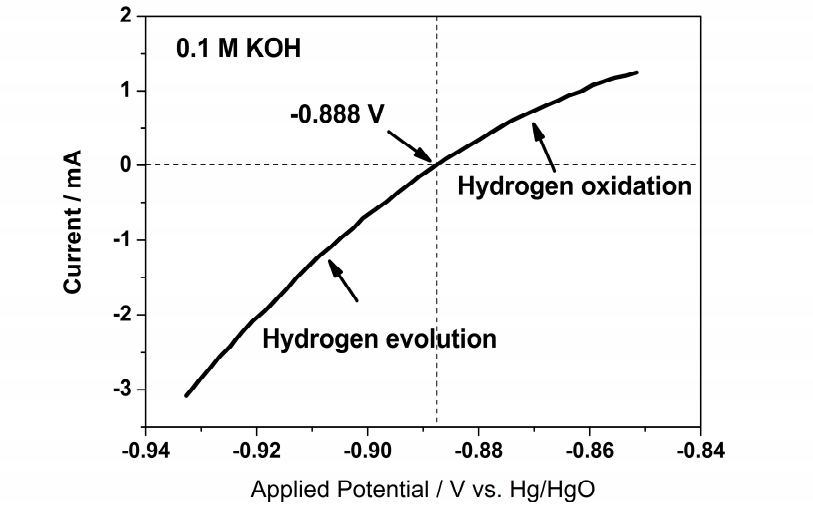


Fig. S7 Potential calibration of the Hg/HgO reference electrode in 0.1 M H_2-saturated KOH solution.

In this case, the potentials showed were calculated by the following equation:

E(RHE) = E(Hg/HgO) + 0.888 V

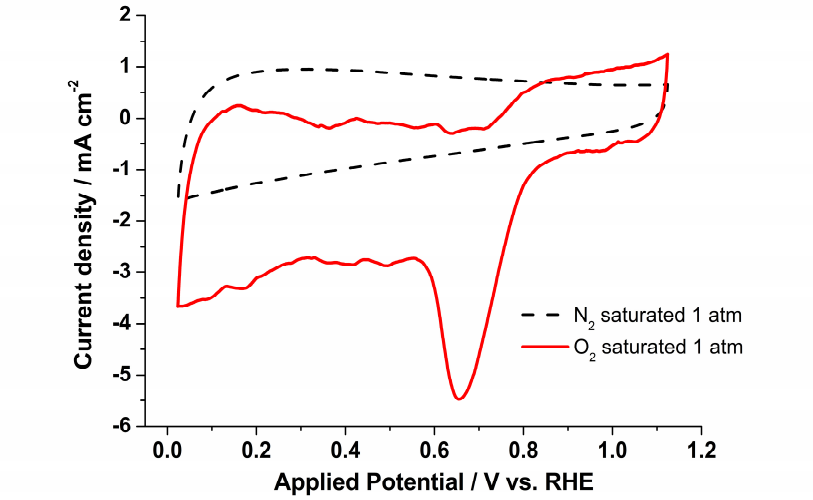


Fig. S8 Polarization curves of cyclic voltammetry (CV) tests for N-S-CMK-3 800 °C in 0.1M KOH solution saturated with N_2 (dash line) and O_2 (solid line) at a scan rate of 50 mV s^{-1}.

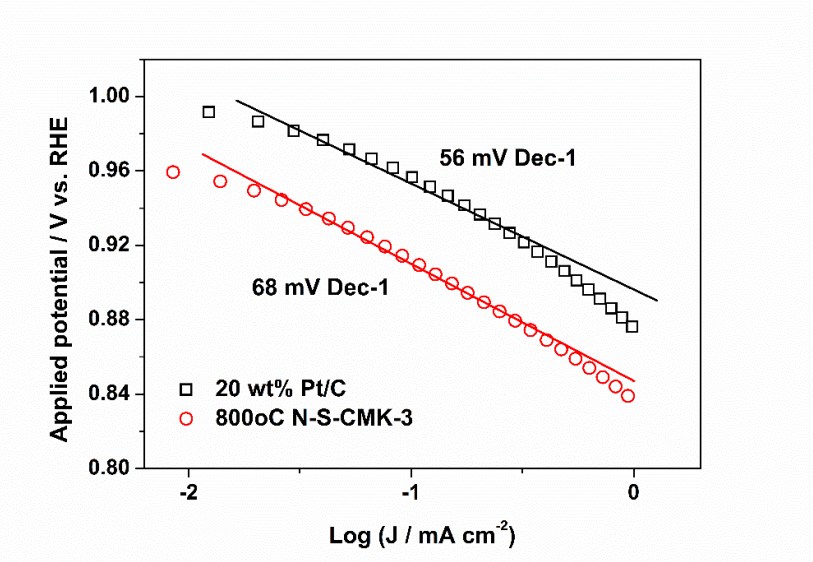


Fig. S9 Tafel plots of ORR currents for N-S-CMK-3 800 °C and commercial Pt/C catalysts

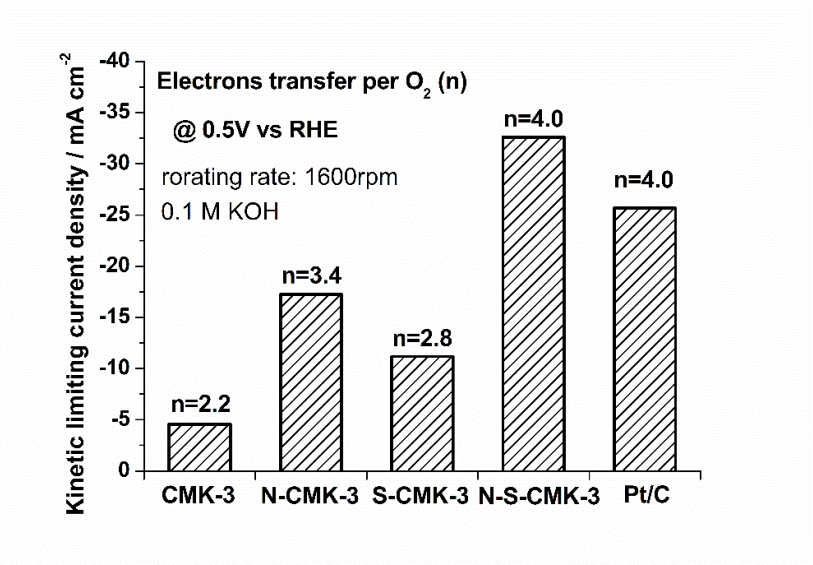


Fig. S10 Kinetic limiting current density (j_k) and the calculation of electron transfer number for CMK-3 based and commercial Pt/C catalysts at 0.5V.

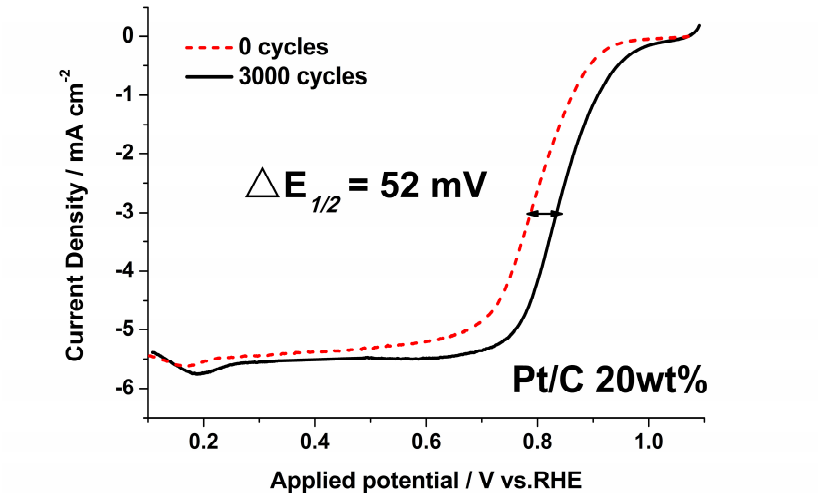


Fig. S11 Polarization curves of commercial Pt/C before and after 3000 potential cycles in O_2-saturated 0.1M KOH solution.

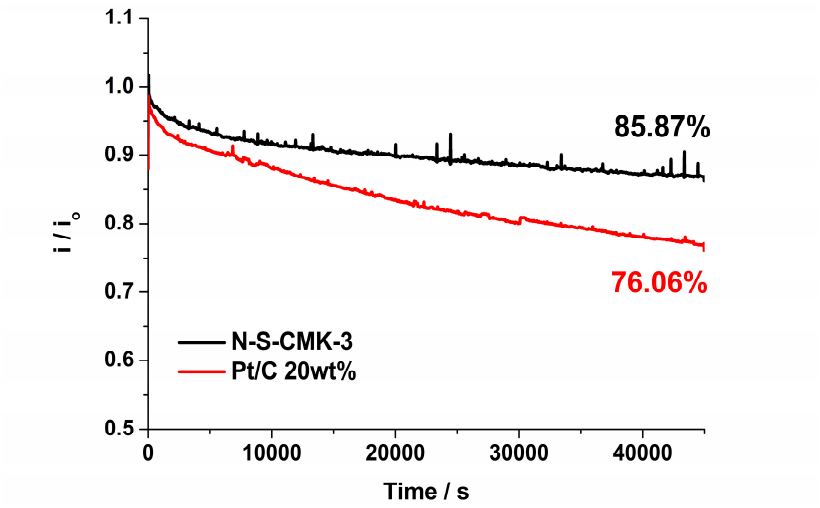


Fig. S12 Time-drifting stability of the N-S-CMK-3 800 °C and commercial Pt/C at 0.5 V vs. RHE for 45000 s with a rotating rate of 1600 rpm.

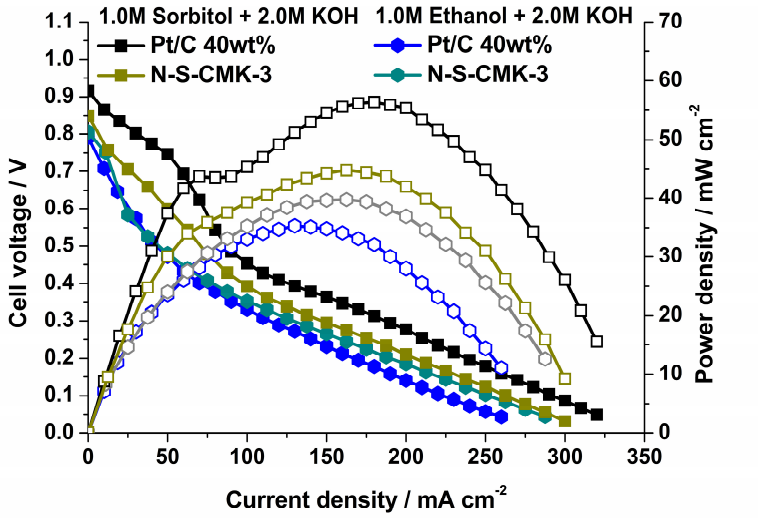


Fig. S13 Polarization and power density curves of direct biorenewable alcohol fuel cell with the N-S-CMK-3 800 °C (loading 2.0 mg cm^{-2}) and commercial Pt/C (loading 1.0 mg_{Pt} cm^{-2}) cathode fed by 1.0 M ethanol + 0.1 M KOH or 1.0 M sorbitol + 0.1 M KOH at 50 °C.

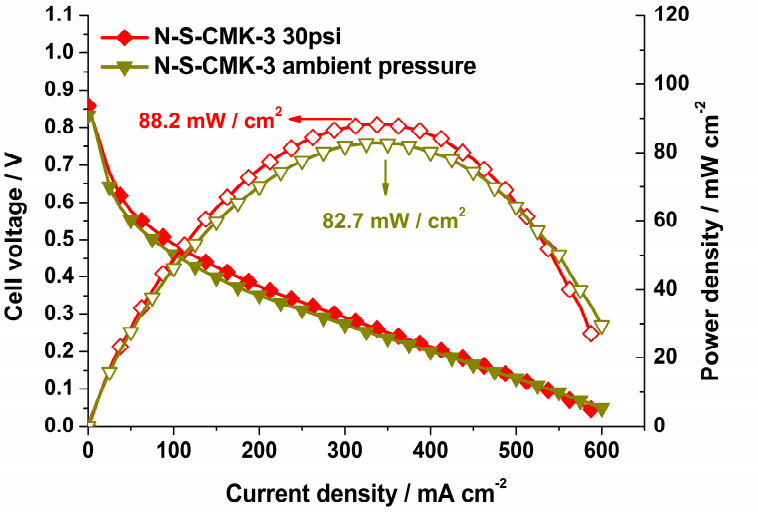
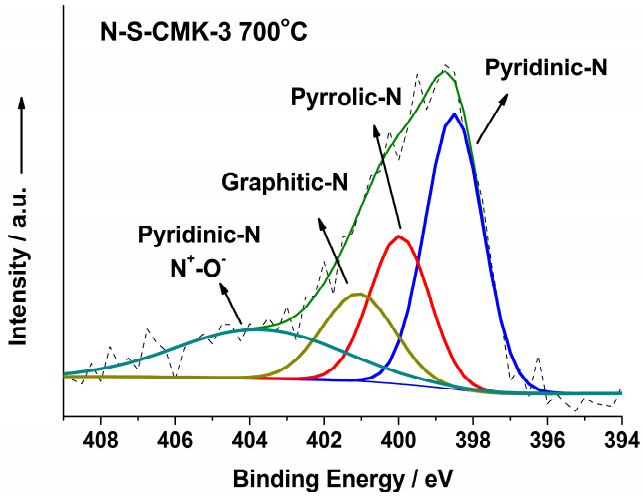
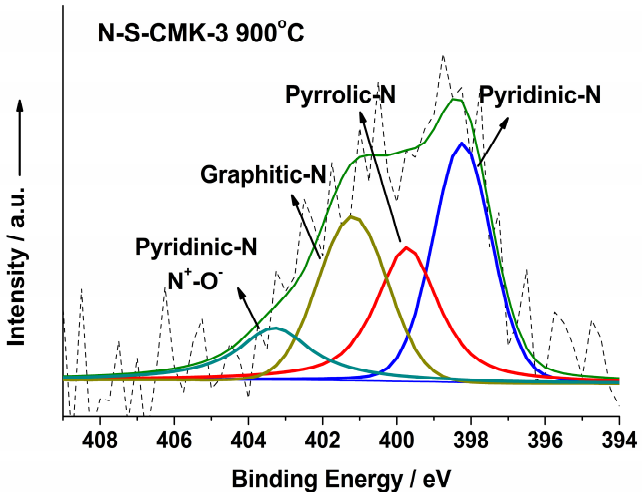


Fig. S14 Polarization and power density curves of direct glycerol fuel cell with the N-S-CMK-3 800 °C cathode (loading 2.0 mg cm^{-2}) at 50 °C and different O_2 back pressures.



(a)



(b)

Fig. S15 High-resolution spectra of N_{1s} for (a) N-S-CMK-3 700 °C and (b) N-S-CMK-3 900 °C

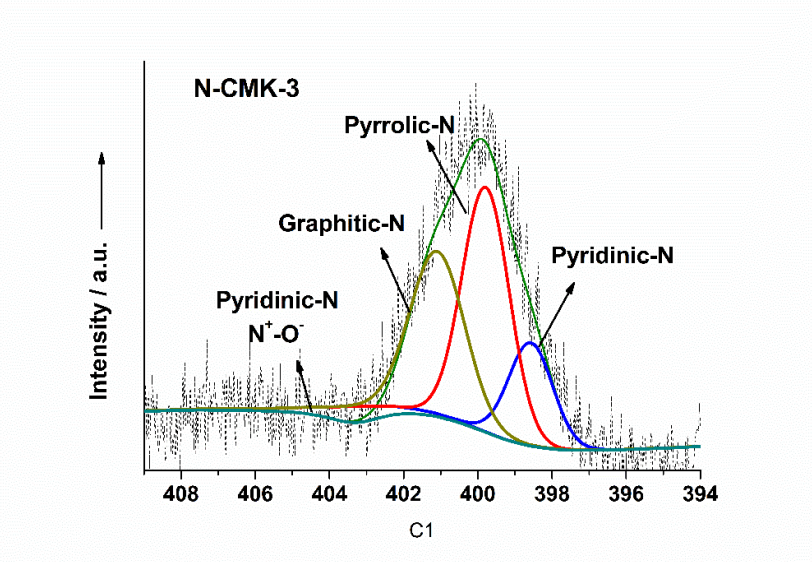


Fig. S16 High-resolution spectra of N_{1s} for N-CMK-3

Table S1 The textural parameters and element atomic concentrations of different catalysts.

Catalyst	BET surface area / $m^2 g^{-1}$	Total pore volume / $cm^3 g^{-1}$	Element atomic concentration / atom %				
			C	N	S	O	Fe
CMK-3	1126	1.215	96.51	N/A	N/A	3.33	N/A
N-S-CMK-3 700 °C	784	0.821	90.12	6.40	1.11	2.29	0.08
N-S-CMK-3 800 °C	1023	0.973	94.07	3.84	0.83	1.14	0.12
N-S-CMK-3 900 °C	921	0.701	97.64	1.27	0.20	0.87	0.02
N-CMK-3 800 °C	N/A	N/A	93.31	4.88	N/A	1.77	0.04
S-CMK-3 800 °C	N/A	N/A	97.07	N/A	1.21	1.57	0.15

From the high-resolution XPS spectum, slight Si signal was observed on CMK-3. For element atomic concentration calculations, Si was eliminated from catalysts except the CMK-3.

Table S2 Comparison of the ORR activity of N-S-CMK-3 with other electrocatalysts.

Catalysts	ORR onset potential (vs. RHE)	ORR Tafel slope ($mV\ dec^{-1}$)	Potential at -3 $mA\ cm^{-2}$ (vs. RHE)	Catalysts loading ($mg\ cm^{-2}$)	Electron transfer number (n) at 0.5V vs. RHE	Electrolyte	Ref.
800 °C N-S-CMK-3	0.92	68	0.78	0.306	3.96	0.1M KOH	This work
N-S-G	0.91	N.A	N.A.	~0.2	3.6	0.1M KOH	1
PCN-CFP	0.94	122.3	N.A.	~0.2	3.9	0.1M KOH	2
N-S doped graphene/CNT	0.85	N.A.	0.72	0.407	3.8	0.1M KOH	3
Fe-N/C	0.92	N.A	0.81	0.1	4.0	0.1M KOH	4
$FeSO_4$-PEI	0.79	58	0.68	0.4	3.8	0.1M KOH	5
Mn_3O_4/pGC	0.75	~85	~0.7	~0.0001	4.0	0.1M KOH	6