Supporting Information

Promotional effect on multiple active sites in Fe-based oxygen reduction electrocatalysts for zinc-air battery

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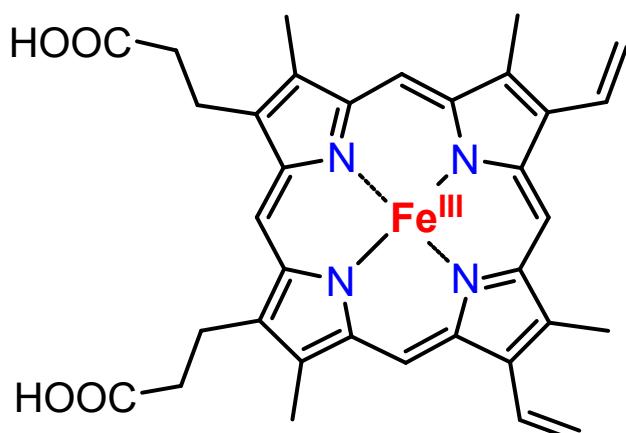
Scheme S1. The molecular structure of Hemin, which is a Fe-centered natural macrocyclic compound.

II. Supporting figures
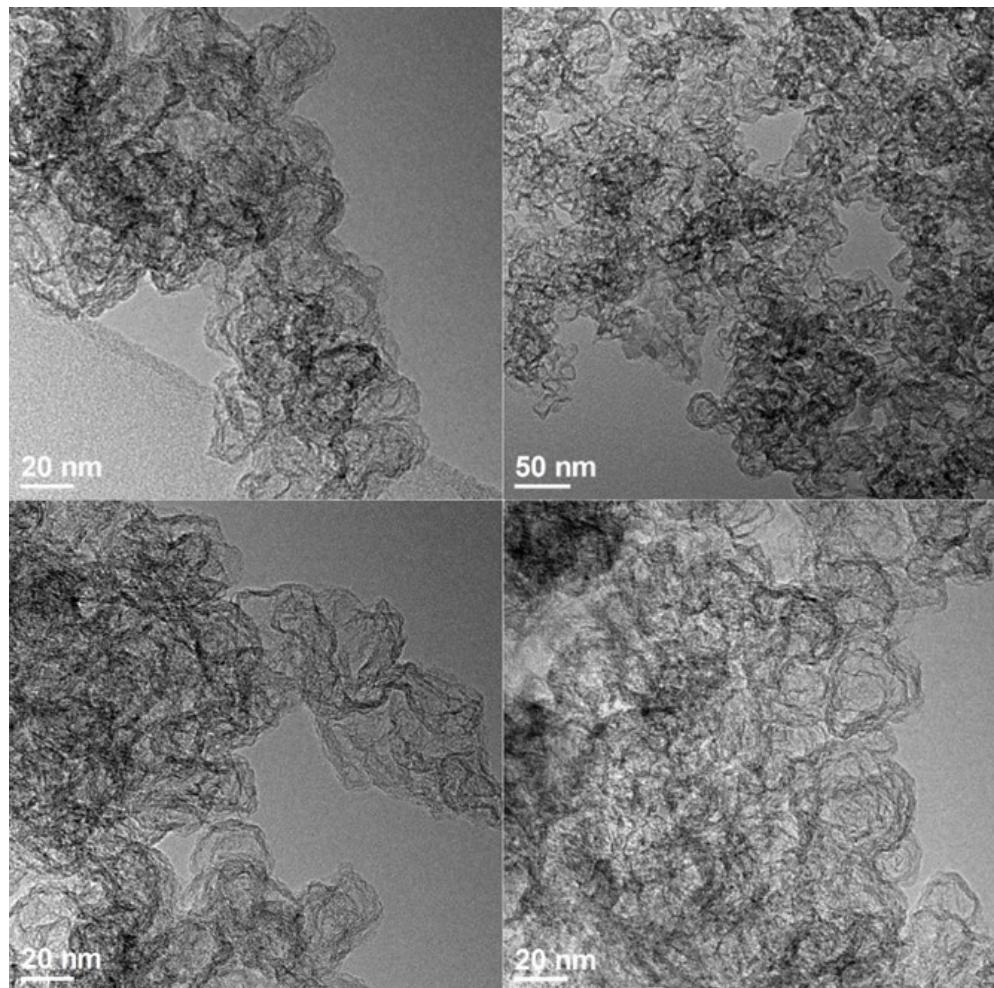

Fig. S1. TEM images of Hm/Cy@C-900.
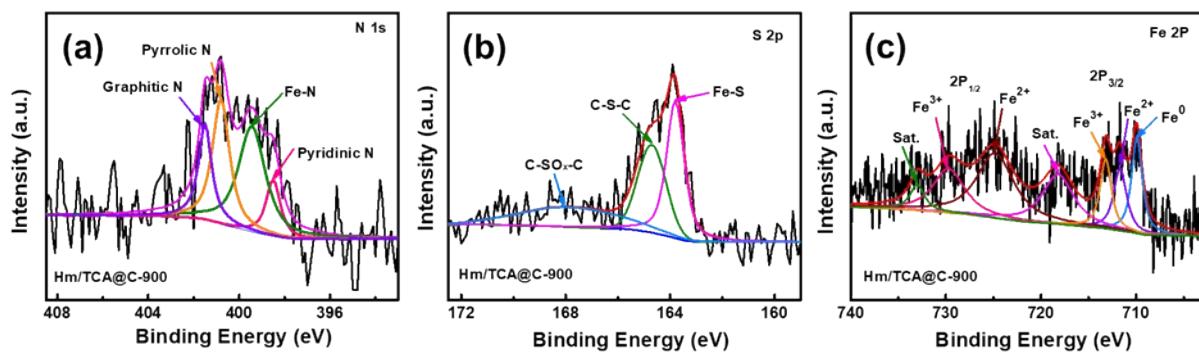
Fig. S2. XPS spectra of Hm/TCA@C-900 sample: (a) N 1s, (b) S 2p, and (c) Fe 2p.

In view of the Fe 2p XPS spectra in Fig. S2c, the Fe^{2+} and Fe^{3+} species and metallic Fe^0 particles were found, meaning the presence of metallic Fe, Fe_3C, FeN_x, FeS_x, or Fe_3O_4 species in the electrocatalysts.
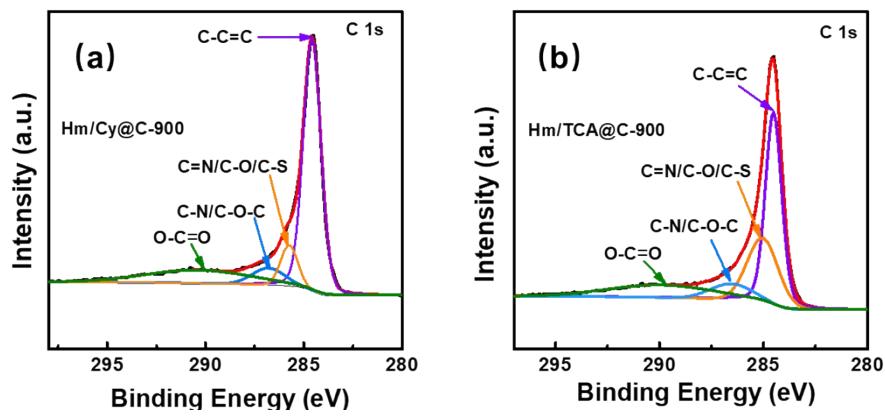
Fig. S3. C 1s XPS spectra of (a) Hm/Cy@C-900 and (b) Hm/TCA@C-900 samples.

C 1s XPS was deconvoluted into four peaks, locating at 284.6, 285.7, 286.8, and 290.3 eV, matching with the C-C=C, C=N/C-O/C-S, C-N/C-O-C, and O-C=O species, respectively.[1, 2] The prominent peak at 284.6 eV, attributed to sp^2-hybridized C, suggests a high degree of graphitization.
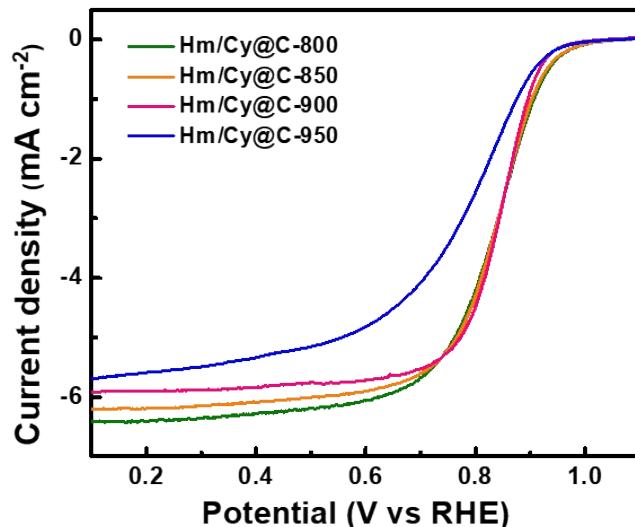

Fig. S4.ORR polarization curves of Hm/Cy@C-T (T: 800, 850, 900 and 950 °C) at 5 mV s^{-1} in O$_2$-saturated 0.1 M KOH solution. Thus, Hm/Cy@C-900 exhibited the best ORR activity, based on the value of E$_{1/2}$.
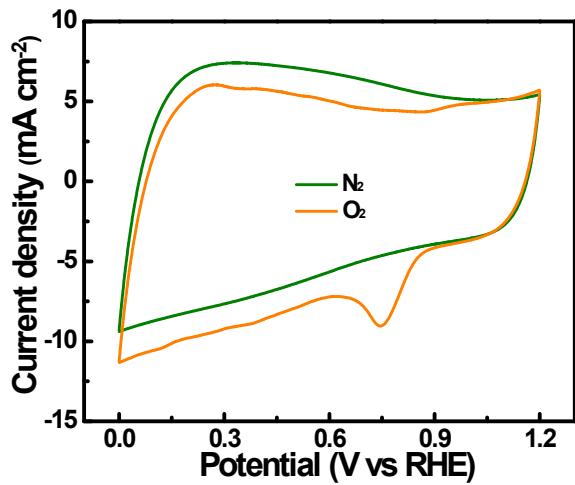
Fig. S5. CV curves in O_2- or N_2-saturated 0.1 M KOH solution of Hm/Cy@C-900 at 100 mV s^{-1}. The reduction peak observed at ~ 0.78 V (vs RHE) suggested that Hm/Cy@C-900 is effective in ORR.
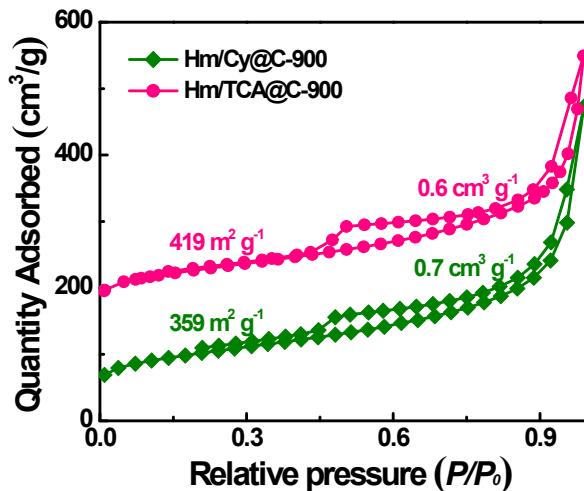
Fig. S6. N_2 adsorption-desorption isotherms of Hm/Cy@C-900 and Hm/TCA@C-900 samples. The isotherm for Hm/TCA@C-900 was offset vertically by 100 cm^3 g^{-1}.
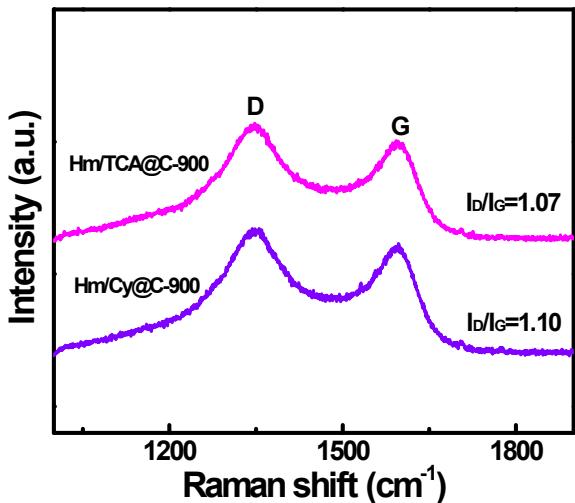
Fig. S7. Raman spectra of Hm/Cy@C-900 and Hm/TCA@C-900 samples.

Two typical peaks at 1344 (D band) and 1596 cm^{-1} (G band) stand for the disordered carbon (the defects) and sp^2-hybridization carbon species (graphitization), respectively.[3] The I_D/I_G value of Hm/Cy@C-900 (1.10) is higher than that of Hm/TCA@C-900 (1.07), demonstrating that Hm/Cy@C-900 has more defect carbon and disordered carbon matrix, which is conducive to ORR.[4]

III. Supporting tables

Table S1. The fitting parameters of high-resolution XPS N1s spectra of Hm/Cy@C-900 and Hm/TCA@C-900 samples.

Catalysts	Binding energy of N species (eV) and content (%)				N relative to C (at%)
	Pyridinic N	Fe-N	Pyrrolic N	Graphitic N	
Hm/Cy@C-900	398.4	399.3	400.7	401.7	2.4
	(37.3)	(18.1)	(34.1)	(10.5)	
Hm/TCA@C-900	398.5	399.4	400.8	401.5	1.9
	(11.4)	(39.6)	(30.1)	(18.9)	

Table S2. The fitting parameters of high-resolution XPS S 2p spectra of Hm/Cy@C-900 and Hm/TCA@C-900 samples.

Catalysts	Binding energy of S species (eV) and content (%)		
	Fe-S	C-S-C	C-SOx-C
Hm/Cy@C-900	163.8	164.8	167.5
	(38.1)	(39.4)	(22.5)
Hm/TCA@C-900	163.8	164.7	167.8
	(40.4)	(32.6)	(27.0)

Table S3. Fitting parameters of ^{57}Fe Mössbauer spectrum for Hm/Cy@C-900 catalyst.

Site	δ_{iso} (mms^{-1})	ΔE_Q	FWHM (mms^{-1})	Area (%)	Assignment
Doublet 1	0.29	0.74	0.58	8.55	Fe^{III}N$_4$ (five fold)
Doublet 2	0.40	2.81	0.58	7.18	Fe^{III}N$_4$ (six fold)
Sextet 1	0.19	0.00	0.38	53.51	Fe$_3$C
Sextet 2	0.77	-0.16	0.33	14.96	FeS$_x$
Sextet 3	0.10	-0.23	0.42	6.46	α-Fe
Sextet 4	0.42	-0.11	0.58	9.34	FeS$_x$

Table S4. Fitting parameters of ^{57}Fe Mössbauer spectrum for Hm/TCA@C-900 catalyst.

Site	δ_{iso} (mms^{-1})	ΔE_Q	FWHM (mms^{-1})	Area (%)	Assignment
Doublet 1	0.28	-0.07	0.38	6.22	Fe_3O_4 (+3.0)
Doublet 2	0.56	0.10	0.68	12.43	Fe_3O_4 (+2.5)
Sextet 1	-0.02	0.01	0.31	18.84	α-Fe
Sextet 2	0.17	0.01	0.35	41.41	Fe_3C
Sextet 3	0.29	0.83	0.58	6.92	$Fe^{III}N_4$ (five fold)
Sextet 4	0.52	1.65	0.58	4.83	$Fe^{II}N_4$ (four fold)
Sextet 5	0.75	-0.26	0.58	9.35	FeS_x

Table S5. Comparison of the ORR performances of Hm/Cy@C-900 and presentative reported Fe-based NNMEs in a O_2-saturated 0.1 M KOH solution in recent five years.

Catalyst	Carbon source	E_{onset} (V)	$E_{1/2}$ (V)	J_L (mA cm^{-2})	Ref.
Hm/Cy@C-900	carbon ECP	0.93	0.845	5.76	This work
Fe$_1$-HNC-500-850	glucose	0.93	0.842	5.80	[5]
Fe/N/S-PCNT	polypyrrole	0.96	0.840	--	[6]
Fe$_3$C@NCNTs	g-C$_3$N$_4$	0.92	0.840	5.80	[7]
Fe–N–C/MXene	C$_3$N$_4$	0.92	0.840	--	[8]
Fe/OES	2-methylimidazole	1.00	0.850	--	[9]
Fe-SAC/NC	adenine	0.95	0.840	--	[10]
OM-NCNF-FeN$_x$	PAN, branched silica nanoaggregates	0.905	0.836	5.6	[11]
Fe/Mn-N-C	dopamine hydrochloride	1.02	0.880	5.7	[12]
Ni-N$_4$/GHSs/Fe-N$_4$	graphene oxide	0.93	0.83	--	[13]
PtFeNC	2-methylimidazole	1.05	0.895	6.20	[14]

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