

Supporting Information

## **Carbon aerogels with atomic dispersion of binary iron-cobalt sites as effective oxygen catalysts for flexible zinc-air batteries**

Yang Chen,<sup>a</sup> Shengqiang Hu,<sup>b</sup> Forrest Nichols,<sup>c</sup> Frank Bridges,<sup>d</sup> Shuting Kan,<sup>a</sup> Ting He,<sup>a,\*</sup> Yi Zhang<sup>a,\*</sup> and Shaowei Chen,<sup>c,\*</sup>

<sup>a</sup> College of Chemistry and Chemical Engineering, Central South University, Changsha, Henan 410083, China

<sup>b</sup> State Key Laboratory for the Chemistry and Molecular Engineering of Medicinal Resources, College of Chemistry and Pharmacy, Guangxi Normal University, Guilin, Guangxi 541004, China

<sup>c</sup> Department of Chemistry and Biochemistry, University of California, 1156 High Street, Santa Cruz, CA 95064, USA

<sup>d</sup> Department of Physics, University of California, 1156 High Street, Santa Cruz, CA 95064, USA

**Table S1.** Porosity of NCAG/Fe-Co, NCAG/Fe, and NCAG/Co samples.

Sample	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	Pore volumes ( $\text{cm}^3 \text{g}^{-1}$ )	Micropore (%)	Mesopore (%)	Macropore (%)
NCAG/Fe-Co	748.2	0.84	32.1	66.7	1.2
NCAG/Co	822.7	1.05	25.7	72.4	1.9
CACG/Fe	893.3	1.15	27.8	69.6	2.6

**Table S2.** Metal contents determined by ICP-OES measurements.

Sample	Fe (wt.%)	Co (wt.%)
NCAG/Fe	0.6	
NCAG/Fe-Co	0.7	1.1
NCAG/Co		1.0

**Table S3.** Elemental contents of the various catalysts determined by XPS.

Sample	C (wt.%)	O (wt.%)	N (wt.%)	Fe (wt.%)	Co (wt.%)
NCAG/Fe	89.0	5.9	4.1	1.0	
NCAG/Fe-Co	89.3	4.8	5.0	0.9	1.0
NCAG/Co	89.4	4.7	4.6		1.3

**Table S4.** Binding energies and contents of various nitrogen dopants in the series of carbon aerogels.

Sample	pridinic N	M-N	graphitic N
NCAG/Fe	398.14 eV	<b>398.80 eV</b>	401.02 eV
	0.4 wt.%	0.8 wt.%	2.9 wt.%
NCAG/Fe-Co	398.16 eV	<b>398.86 eV</b>	401.00 eV
	0.4 wt.%	1.4 wt.%	3.2 wt.%
NCAG/Co	398.25 eV	<b>399.03 eV</b>	401.07 eV
	0.5 wt.%	1.1 wt.%	2.9 wt.%

**Table S5.** Binding energies of Co and Fe 2p electrons in the series of carbon aerogels.

Sample	Co (eV)	Fe <sup>2+</sup> (eV)	Fe <sup>3+</sup> (eV)
NCAG/Fe-Co	780.4	710.5	715.0
NCAG/Fe		710.0	714.7
NCAG/Co	780.6		

**Table S6** EXAFS fitting results of FePc.

Bond	Coordination number	r (Å)	$\sigma^2$ (Å <sup>2</sup> )
Fe-N	4	1.962	0.0052
Fe-C	8	2.985	0.0045
Fe-N	4	3.214	0.0036

**Table S7** Atomic positions of FeN<sub>3</sub>CoN<sub>3</sub> as depicted in Figure 3d.

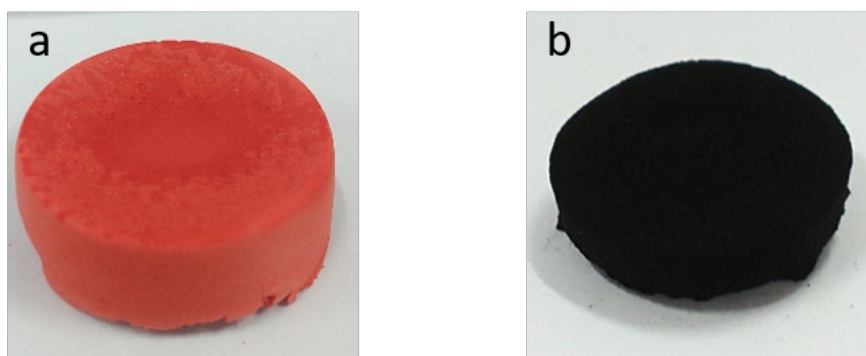
Atom	x	y	z
Fe	0	0	0
N	-1.803	0	0
Co	2.787	0	0
N	0	1.947	0
N	0	-1.947	0
N	1.75	0	1.64
N	1.75	0	-1.64
N	4.59	0	0

**Table S8.** EXAFS fitting results of NCAG/Fe-Co.

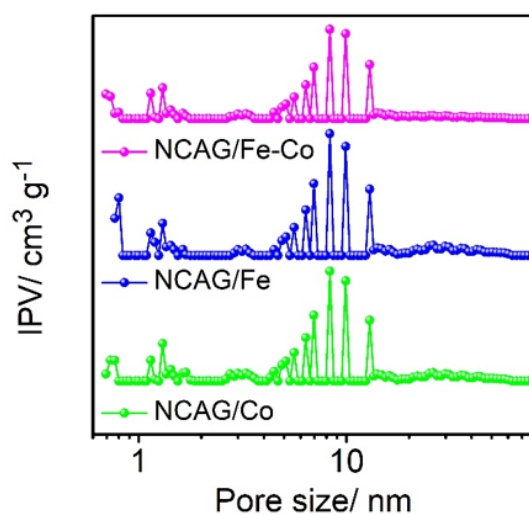
Bond	Coordination number	r (Å)	$\sigma^2$ (Å <sup>2</sup> )
Fe-N <sub>1</sub>	1	1.803	0.0013
Fe-N <sub>2</sub>	2	1.947	0.0015
Fe-N <sub>3</sub>	2	2.394	0.0017
Fe-Co	1	2.787	0.0023

**Table S9.** Comparison of the performance of flexible Zn-air batteries based on relevant oxygen catalysts.

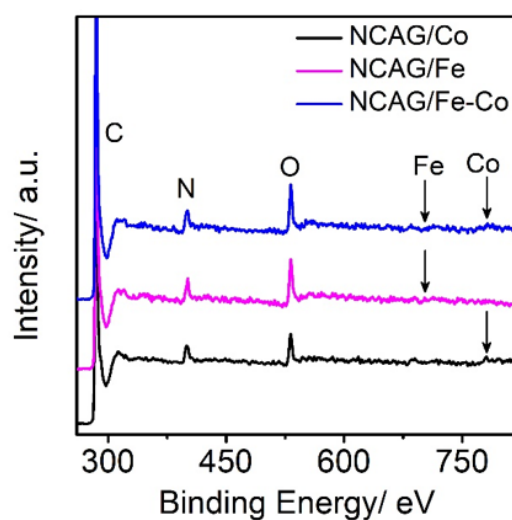
Catalyst	Power density (mW cm <sup>-2</sup> )	OCV (V)	Ref.
NCAG/FeCo	117	1.47	This work
N-doped Ni <sub>2</sub> CoO <sub>4</sub>	30		1
FeCoNi/carbon nanotube	85	1.45	2
Fe-Co <sub>4</sub> N@N-C	72	1.34	3
Co <sub>3</sub> O <sub>4</sub> /carbon fiber		1.33	4
FeCo alloy/N-carbon	98	1.25	5
Zn, Co-N <sub>x</sub> -C-S <sub>y</sub>	15	1.56	6
Co/carbon nanotube	63	1.34	7



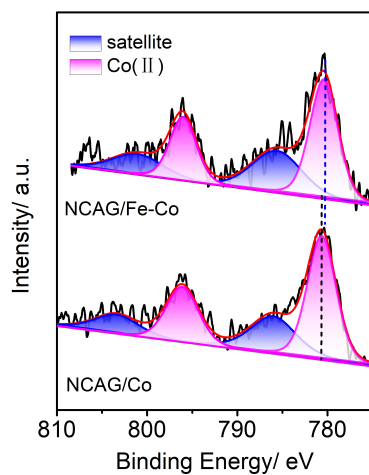
**Figure S1.** Digital photos of (a) freeze-dried  $G_{\text{Si-Zn}}/\text{Fe@CoPM}$  hydrogel and (b) NCAG/Fe-Co aerogel.



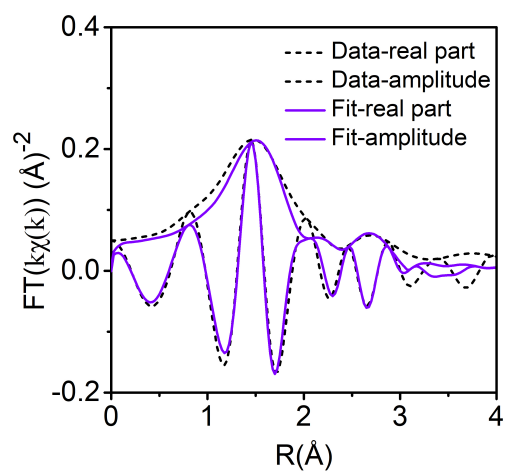
**Figure S2.** Pore-size distributions of NCAG/Fe-Co, NCAG/Fe, and NCAG/Co.



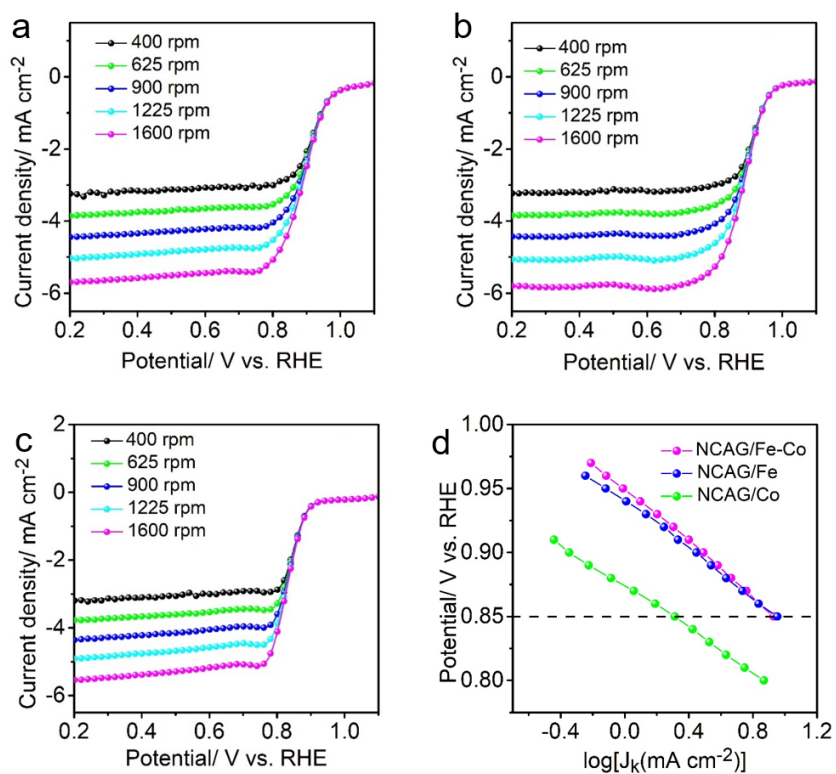
**Figure S3.** XPS survey spectra of NCAG/Co, NCAG/Fe, and NCAG/Fe-Co.



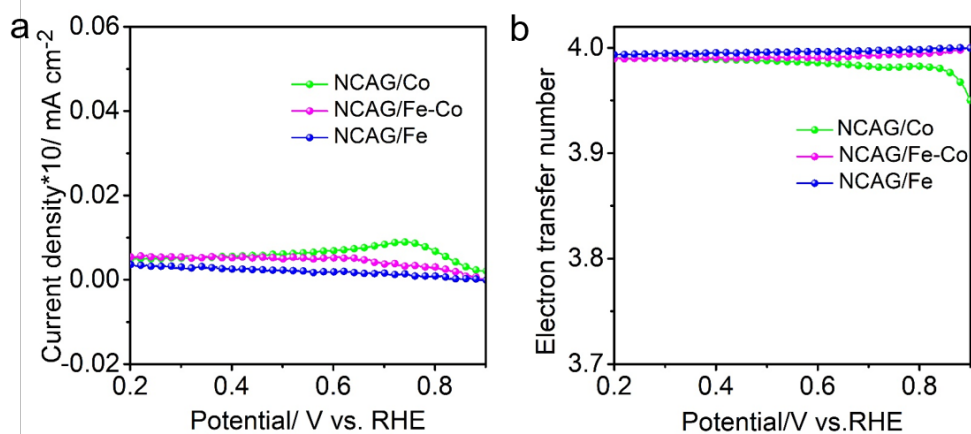
**Figure S4.** High-resolution XPS scan of the Co 2p electrons of NCAG/Fe-Co and NCAG/Co. Black curves are experimental data and shaded peaks are deconvolution fits.



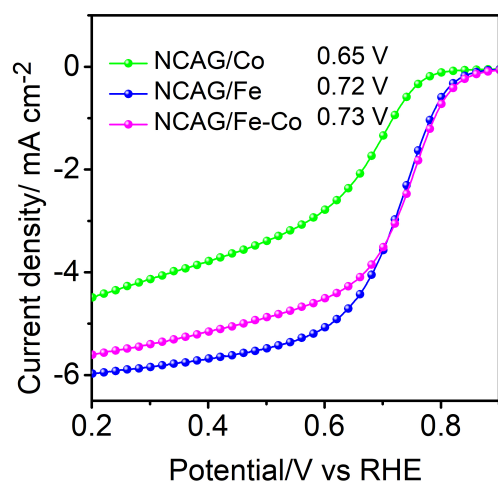
**Figure S5** Fe K-edge EXFAS of FePc and the fitting curve. The fitting result is summarized in Table S6.



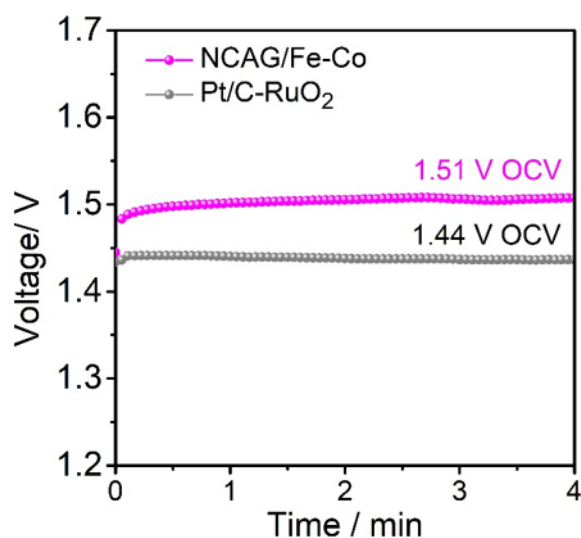
**Figure S6.** (a-c) ORR polarization curves of (a) NCAG/Fe-Co, (b) NCAG/Fe, and (c) NCAG/Co at various rotation speeds and (d) the corresponding Tafel plots.



**Figure S7.** (a) Current density at the ring electrode during RRDE measurements, and (b) electron transfer number of NCAG/Co, NCAG/Fe, and NCAG/Fe-Co.



**Figure S8.** LSV curves of the ORR catalysts at 1600 rpm and  $5 \text{ mV s}^{-1}$  in  $0.1 \text{ HClO}_4$ . The half-wave potentials ( $E_{1/2}$ ) of NCAG/Co, NCAG/Fe and NCAG/Fe-Co are +0.65, +0.72 and +0.73 V, respectively.



**Figure S9.** Open circuit voltage of liquid Zn-air battery using either NCAG/Fe-Co or Pt/C-RuO<sub>2</sub> mixture as the cathode catalyst.

## References

- 1 J. Bian, X. Cheng, X. Meng, J. Wang, J. Zhou, S. Li, Y. Zhang and C. Sun, *ACS Appl. Energy Mater.*, 2019, **2**, 2296-2304.
- 2 Z. Wang, J. Ang, B. Zhang, Y. Zhang, X. Y. D. Ma, T. Yan, J. Liu, B. Che, Y. Huang and X. Lu, *Appl. Catal., B*, 2019, **254**, 26-36.
- 3 Q. Xu, H. Jiang, Y. Li, D. Liang, Y. Hu and C. Li, *Appl. Catal., B*, 2019, **256**, 117893.
- 4 X. Chen, B. Liu, C. Zhong, Z. Liu, J. Liu, L. Ma, Y. Deng, X. Han, T. Wu and W. Hu, *Adv. Energy Mater.*, 2017, **7**, 1700779.
- 5 C.-Y. Su, H. Cheng, W. Li, Z.-Q. Liu, N. Li, Z. Hou, F.-Q. Bai, H.-X. Zhang and T.-Y. Ma, *Adv. Energy Mater.*, 2017, **7**, 1602420.
- 6 D. Liu, B. Wang, H. Li, S. Huang, M. Liu, J. Wang, Q. Wang, J. Zhang and Y. Zhao, *Nano Energy*, 2019, **58**, 277-283.
- 7 D. Ji, L. Fan, L. Li, N. Mao, X. Qin, S. Peng and S. Ramakrishna, *Carbon*, 2019, **142**, 379-387.