Electronic Supplementary Information

Cobalt and nitrogen-codoped ordered mesoporous carbon as

highly efficient bifunctional catalysts for oxygen reduction and

hydrogen evolution reactions

Xiaojun Liu,^{a,b} Wenyue Li^a and Shouzhong Zou^a*

^aDepartment of Chemistry, American University, Washington, DC 20016, USA. ^bPresent address: Department of Chemistry, Oakland University, Rochester, MI 48309, USA E-mail: szou@american.edu (S. Z.)

Table S1. Comparison of ORR activity of different samples

Sample	Onset potential	Half wave potential	Limiting current	Electron transfer
	(V vs RHE)	(V vs RHE)	density at +0.4 V	number (n, 0 to
			(mA cm ⁻²)	+0.9 V))
Co,N-C700	+0.82	+0.65	2.79	1.0-3.1
Co,N-C800	+0.94	+0.83	4.86	2.8-3.8
Co,N-C900	+0.97	+0.85	5.82	3.7-4.0
Co,N-C1000	+0.92	+0.81	4.64	3.0-3.8
Pt/C	+0.97	+0.88	5.68	3.8-3.9

Table S2.	Comparison	of catalytic	performances	of Co,N-C900	and Co-based	carbon	materials i	in the
literature								

Catalysts	Catalyst loading (mg cm ⁻²)	BET area (m ² g ⁻¹)	E _{onset} (V) ^a	n (at E/V) ^b	E _{1/2} (V) ^c	i _l (mA cm ⁻²) ^d
This work	0.24	413.0	+0.97	3.71-3.99 (0~0.90)	0.85	5.82
rGO/ cobalt porphyrin ¹	0.10	na	-0.18e	~3.85 (-0.3 ~-0.5)	-0.22 ^e	4.0
CoP-CMP800 ²	0.60	~480	-0.12 ^e	~3.85 (- 0.45 to - 0.55)	-0.18e	4.6
Co@Co ₃ O ₄ @C core@bishell nanoparticles ³	0.10	~616	+ 0.93	~3.96 (+0.35 to +0.75)	0.81	4.7
Nitrogen-doped graphene/cobal t-embedded porous carbon ⁴	0.70	375	+ 0.97	3.90–3.94 (+0.4 to +0.6)	na	na

Co _x Zn _{100-x} – ZIF-8 ⁵	0.28	~1700	-0.05e	3.8-4.0 (- 0.3 ~ -0.6)	-0.12 ^e	5.0
N,Co,P- codoped porous carbon ⁶	0.10	1225	-0.04 ^e	~3.9 (-0.25 ~-0.45)	-0.12 ^e	6.0
Co/CoO nanoparticles immobilized on Co–N-doped carbon ⁷	0.60	647.7	-0.05 ^e	~3.8 (-0.3 to -0.45)	-0.17°	5.5
Cobalt- embeded N- doped graphene aerogel ⁸	0.28	466.6	+ 0.90	3.99 (+0.3 to +0.6)	0.81	6.0
Co-N-doped mesoporous carbon hollow spheres ⁹	0.28	342.3	+ 0.94	3.7 (+0.6 to +0.75)	0.85	4.7

- a. Onset potential in V vs RHE, unless otherwise noted
- b. Number of electron transfer at the specified potential range. The potential scale is identical to the E_{onset} .
- c. Half wave potential in V vs RHE, unless otherwise noted.
- d. Limiting current density
- e. V vs Ag/AgCl



Figure S1. (a) Corresponding EDS of Co,N-C900 and TEM images of (b) Co,N-C700, (c) Co,N-C800 and (d) Co,N-C1000.



Figure S2. RDE voltammograms for ORR of Co,N-C900 and 20 wt% Pt/C at 1600 rpm with a scan rate of 10 mV s⁻¹ in O_2 -saturated 0.1 M HClO₄.

Table S3. BET specific surface area and total pore volume of N,Co-codoped porous carbon prepared at different heat treatment temperatures.

Sample	S _{BET} (m ² g ⁻¹)	Pore volumes (cm ³
		g ⁻¹)
Co,N-C700	173.8	1.61
Co,N-C800	326.6	2.69
Co,N-C900	413.1	5.32
Co,N-C1000	274.5	1.93

Table S4. BET specific surface area and total pore volume of Co,N-NTC900, Co,N-C900 and N-C900.

Sample	S _{BET} (m ² g ⁻¹)	Pore volumes (cm ³
		g ⁻¹)
Co,N-NTC900	90.2	0.65
Co,N-C900	413.1	5.32
N-C900	361.3	3.26



Figure S3. RDE voltammograms for ORR of Co,N-NTC900, N-C900 and Co,N-C900 in O_2 -saturated 0.1 M KOH at the electrode rotation rate of 1600 rpm and potential scan rate of 10 mV s⁻¹.



Figure S4. Peak deconvolutions of the N1s spectra of (a) Co, N-C700, (b) Co, N-C800 and (c) Co, N-C1000.

measurenne	1110								
1 .	С	0	Ν	Со	Pyrinidic	Co-	Pyrrolic	Graphitic	Oxide
sample	(at.%)	(at.%)	(at.%)	(at.%)	Ν	Ν	Ν	Ν	Ν
Co,N-	77 62	10.77	10.0	0.70	2.25	0.66	2.07	2.09	1.04
C700	//.63	10.77	10.9	0.70	2.25	0.00	5.97	2.98	1.04
Co,N-	<u>80 86</u>	0.51	8 67	1.01	1.61	0.82	2.40	2.05	0.65
C800	80.80	.80 9.51	8.02	1.01	1.01	0.82	2.49	3.05	0.05
Co,N-	84 71	7.80	6 27	1 1 2	1 20	0.07	0.50	2 40	0.61
C900	84.71	7.80	0.57	1.12	1.29	0.97	0.50	5.40	0.01
Co,N-	87.00	7 44	1 26	1 21	0.97	0.63	0.20	1 30	0.08
C1000	67.09	7.44	4.20	1.21	0.97	0.05	0.29	1.39	0.90

Table S5. Elemental contents and concentrations of N species in carbon catalysts determined by XPS measurements

Table S6. Comparison of HER performances of Co,N-C900 and Co-based carbon materials in literature

Catalysts	Loading amount (mg cm ⁻²)	Onset potential (V)	Overpotential @10mA cm ⁻² (V)	Tafel slope
This work	0.28	-0.04	-0.106	49
N-graphene/ cobalt-				
embedded	0.357	-0.058	-0.229	126
porous carbon ⁴				
Co-embedded				
Nitrogen-rich carbon	0.28	-0.05	-0.26	69
nanotubes 10				
Fe and Co				
Encapsulated N	0.32	0.07	-0.28	72
doped carbon	0.32	-0.07		12
nanotube 11				
CoS ₂ microwires ¹²	unknown	-0.075	-0.158	58
CoS ₂ nanowires ¹³	unknown	-0.075	-0.145	51.6
Co ₂ P nanorods ¹⁴	1.02	-0.07	-0.134	71
CoSe ₂ nanowires	1.30	-0.085	-0.130	32
CoSe ₂ film ¹⁵	0.037	-0.045	-0.17	40
MoS_2 /reduced	0.285	0.010	0.16	41
graphene ¹⁶	0.283	-0.010	-0.10	41
$MoS_2/CoSe_2$	0.28	0.011	0.068	36
hybrid ¹⁷	0.20	-0.011	-0.000	50



Figure S5. Polarization curves for HER in 0.1 M KOH at Co,N-C900 and 20 wt% Pt/C. Potential sweep rate 5 mV s⁻¹.



Figure S6. Electrochemical impedance spectra of Co, N-C700, Co, N-C800, Co, N-C900 and Co, N-C1000 for HER in 0.5 M H_2SO_4 at -0.2 V.



Figure S7. LSV curves of Co,N-NTC900, N-C900 and Co,N-C900 for HER in 0.5 M H₂SO₄. Potential sweep rate: 5 mV s⁻¹.



Figure S8. Cyclic voltammograms of (a) Co, N-C700, (c) Co, N-C800, (e) Co, N-900 and (g) Co, N-C1000 taken in N₂-saturated 0.5 M H_2SO_4 and the capacitive currents at 0.05 V vs. RHE as a function of scan rate for (b) Co, N-C700, (d) Co, N-C800, (f) Co, N-900 and (h) Co, N-C1000.

Reference

- 1. H. Tang, H. Yin, J. Wang, N. Yang, D. Wang and Z. Tang, *Angewandte Chemie*, 2013, **125**, 5695-5699.
- 2. Z. S. Wu, L. Chen, J. Liu, K. Parvez, H. Liang, J. Shu, H. Sachdev, R. Graf, X. Feng and K. Müllen, *Advanced materials*, 2014, **26**, 1450-1455.
- 3. W. Xia, R. Zou, L. An, D. Xia and S. Guo, *Energy & Environmental Science*, 2015, **8**, 568-576.
- 4. Y. Hou, Z. Wen, S. Cui, S. Ci, S. Mao and J. Chen, *Advanced Functional Materials*, 2015, **25**, 872-882.
- 5. S. Gadipelli, T. Zhao, S. A. Shevlin and Z. Guo, *Energy & Environmental Science*, 2016, **9**, 1661-1667.
- Y. Z. Chen, C. Wang, Z. Y. Wu, Y. Xiong, Q. Xu, S. H. Yu and H. L. Jiang, *Advanced Materials*, 2015, 27, 5010-5016.
- 7. X. Zhang, R. Liu, Y. Zang, G. Liu, G. Wang, Y. Zhang, H. Zhang and H. Zhao, *Chemical Communications*, 2016, **52**, 5946-5949.
- 8. Z. Zhu, Y. Yang, Y. Guan, J. Xue and L. Cui, *Journal of Materials Chemistry A*, 2016, **4**, 15536-15545.
- 9. F. Hu, H. Yang, C. Wang, Y. Zhang, H. Lu and Q. Wang, *Small*, 2017, **13**, 1602507.
- 10. X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmeková and T. Asefa, *Angewandte Chemie*, 2014, **126**, 4461-4465.
- 11. J. Deng, P. Ren, D. Deng, L. Yu, F. Yang and X. Bao, *Energy & Environmental Science*, 2014, **7**, 1919-1923.
- 12. M. S. Faber, R. Dziedzic, M. A. Lukowski, N. S. Kaiser, Q. Ding and S. Jin, *Journal of the American Chemical Society*, 2014, **136**, 10053-10061.
- 13. Z. Huang, Z. Chen, Z. Chen, C. Lv, M. G. Humphrey and C. Zhang, *Nano Energy*, 2014, **9**, 373-382.
- 14. Q. Liu, J. Shi, J. Hu, A. M. Asiri, Y. Luo and X. Sun, *ACS applied materials & interfaces*, 2015, **7**, 3877-3881.
- 15. D. Kong, J. J. Cha, H. Wang, H. R. Lee and Y. Cui, *Energy & Environmental Science*, 2013, **6**, 3553-3558.
- 16. Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong and H. Dai, *Journal of the American Chemical Society*, 2011, **133**, 7296-7299.
- 17. M.-R. Gao, J.-X. Liang, Y.-R. Zheng, Y.-F. Xu, J. Jiang, Q. Gao, J. Li and S.-H. Yu, *Nature communications*, 2015, **6**, 5982.