Supplementary Information

Core@Shell Structured Co-CoO@NC Nanoparticles Supported on Nitrogen Doped Carbon with High Catalytic Activity for Oxygen Reduction Reaction

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Content

1. Element mapping

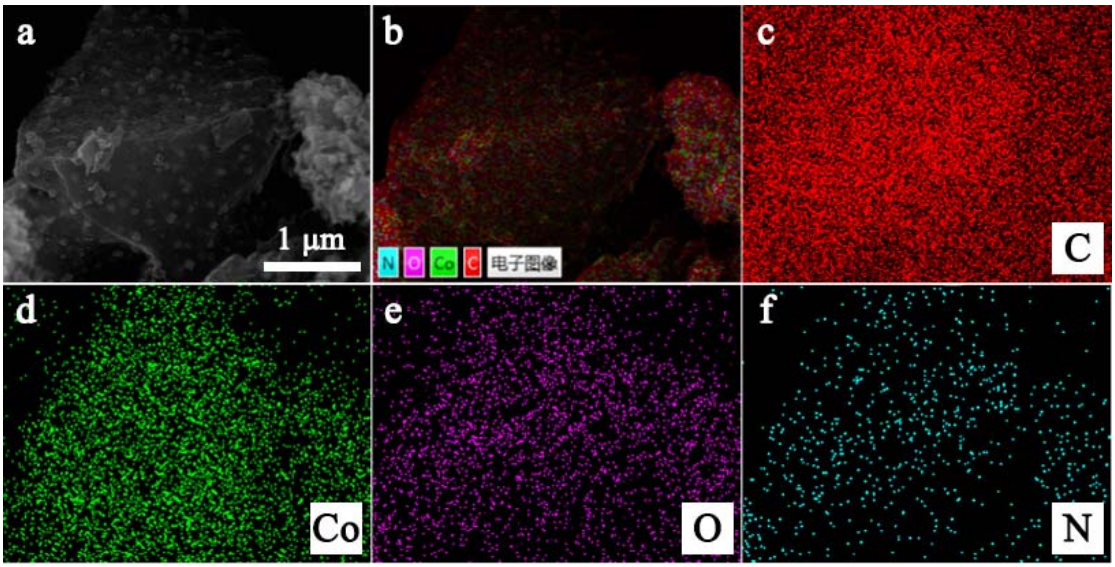


Figure S1. The SEM image and corresponding elemental mapping images of Co-CoO@NC/NC-800.

2. TGA curve

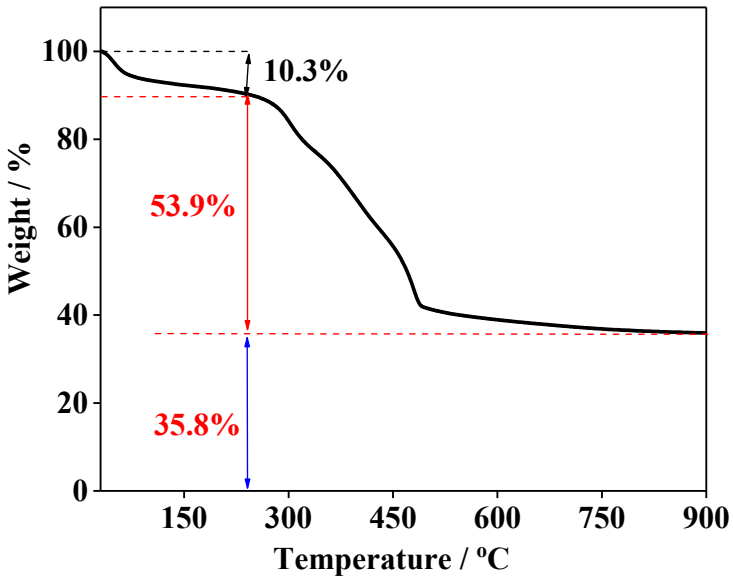


Figure S2. TGA curve of the Co-CoO@NC/NC-800.

The weight loss below 200 ºC could be attributed to the vaporization of physically adsorbed water, which accounts for 10.3 wt.% of the Co-CoO@NC/NC-800. The weight loss

at the temperature higher than 200ºC could be attributed to the decomposition of the Co-CoO@NC/NC-800 with association of the transformation of Co and CoO to Co_3O_4. Assuming that the atomic ratio of $Co^{(0)}$: $Co^{(II)}$=3:2 (estimated from the XPS result), the weight percentage of Co-CoO in the Co-CoO@NC/NC-800 could be calculated as follows:

$$wt.\ \%\ of\ Co-CoO = 35.8\% / \left(0.6 \times \frac{MW_{Co_3O_4}}{MW_{CoO}} + 0.4 \times \frac{MW_{Co_3O_4}}{MW_{CoO}}\right) = 28.7\%$$

3. TEM images

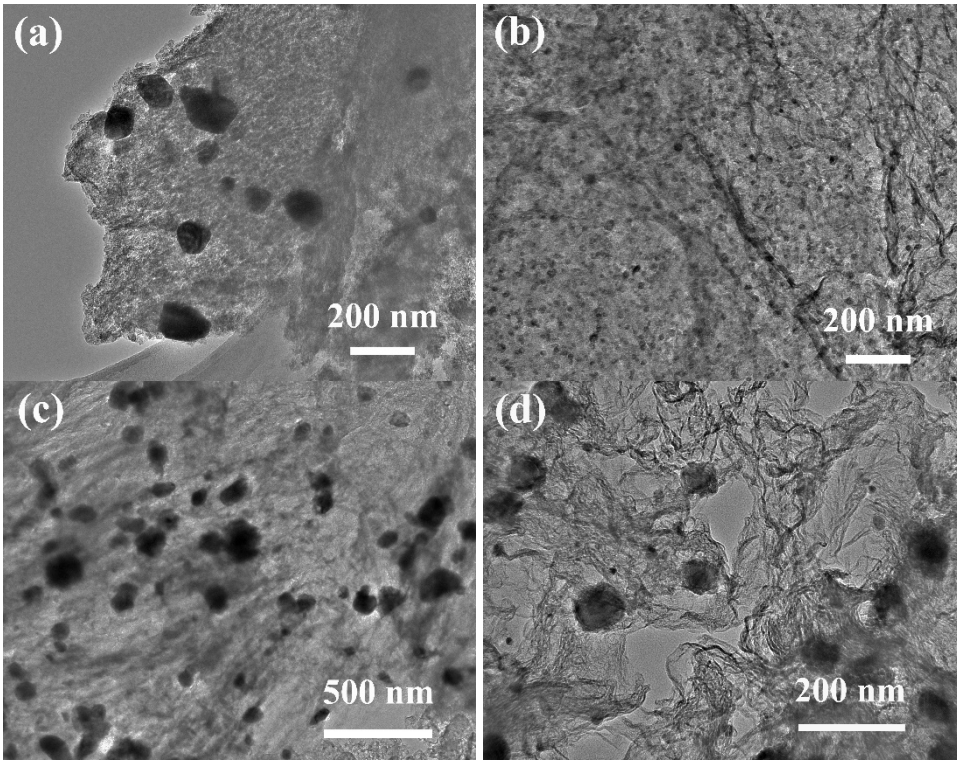


Figure S3. TEM images of (a) the Co-CoO@C/C-800, (b) the Co-CoO@NC/NC-700, (c) the Co-CoO@NC/NC-900, (d) the Co-CoO@NC/NC-800 synthesized without the drying at 200ºC.

4. XPS survey spectra

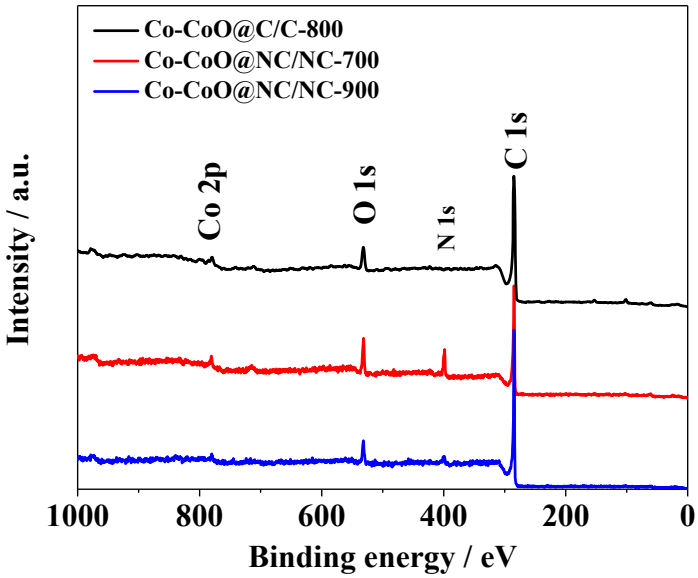


Figure S4. XPS survey spectra of the Co-CoO@C/C-800, the Co-CoO@NC/NC-700, the Co-CoO@NC/NC-900.

5. XRD patterns

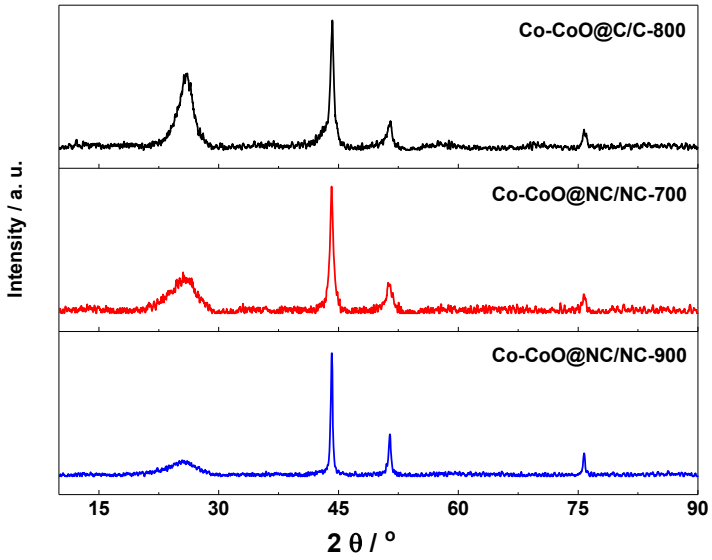


Figure S5. XRD patterns of the Co-CoO@C/C-800, the Co-CoO@NC/NC-700, the Co-CoO@NC/NC-900.

6. Raman spectra

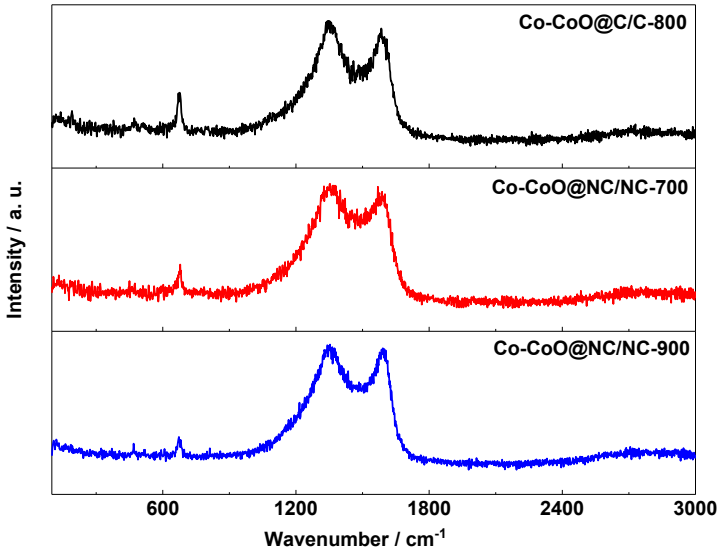
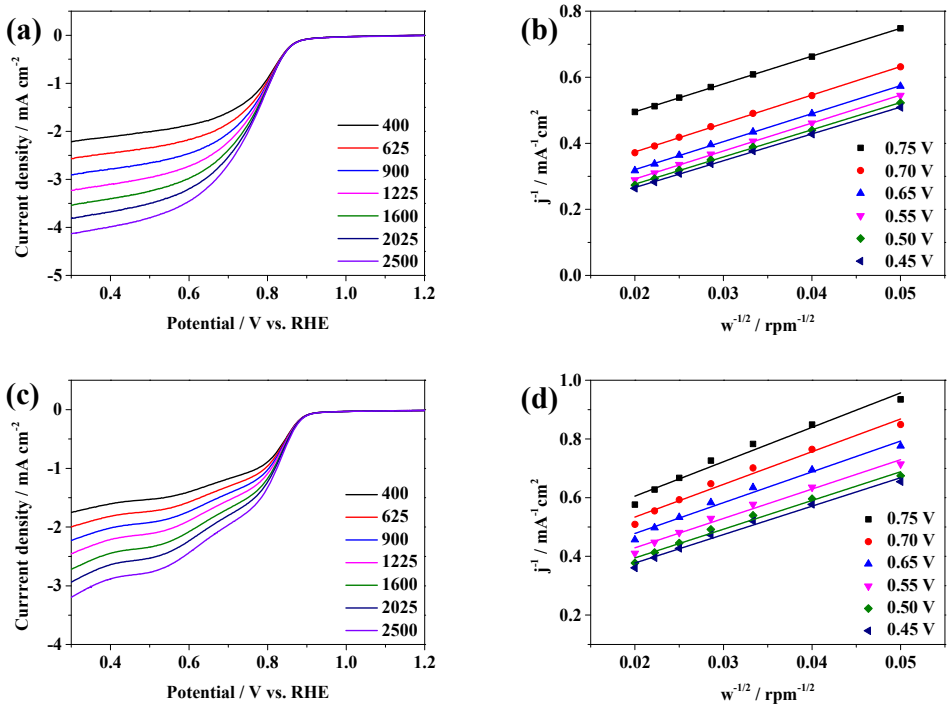


Figure S6. Raman spectra of the Co-CoO@C/C-800, the Co-CoO@NC/NC-700, the Co-CoO@NC/NC-900.

7. LSVs and K-L plots



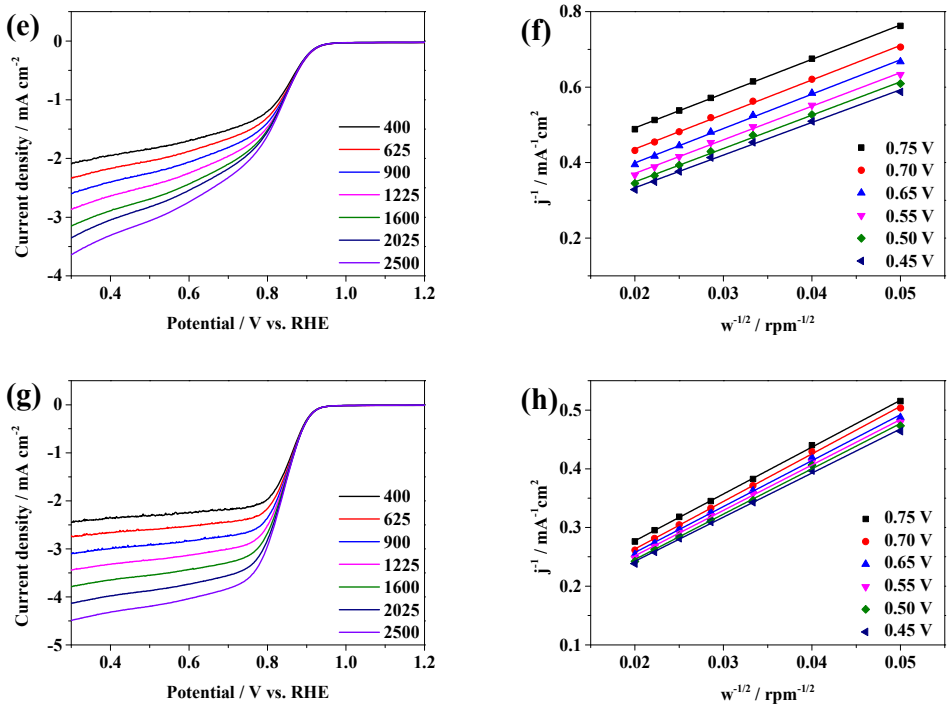


Figure S7. LSVs and K-L plots for the ORR by (a, b) the NC, (c, d) the Co-CoO@C/C-800, (e, f) the Co-CoO@NC/NC-700, (g, h) the Co-CoO@NC/NC-900 in an O_2-saturated 0.1 M KOH solution at various rotation rates at a scan rate of 5 mV/s.

8. Elemental composition

Table S1. Relative atomic percentages of the elements in the Co-CoO@NC/NC-800, the NC, the Co-CoO@C/C-800, the Co-CoO@NC/NC-700, and the Co-CoO@NC/NC-900.

Samples	Co	C	N	O
Co-CoO@NC/NC-800	1.7	82.6	10.2	5.5
NC	0	82.4	11.9	5.7
Co-CoO@C/C-800	1.1	87.6	3.8	7.5
Co-CoO@NC/NC-700	3.32	71.52	13.75	11.41
Co-CoO@NC/NC-900	2.12	85.02	5.63	7.24

9. Performance comparison

Table S2. Comparison of the ORR onset potential of the Co-CoO@NC/NC-800 with those of the catalysts reported.

Catalyst	Mass Loading / mg cm^{-2}	Onset potential / V vs. RHE[a]	Half-wave potential / V vs. RHE	Reference
Co-CoO@NC/NC-800	0.102	0.961	0.868	This work
N-C@Co-2	0.213	0.895		[1]
Co-N-GN	0.1	0.864	0.800	[2]
g-VB12	0.6	0.925	0.833	[3]
Co/NrGO	0.2	0.902		[4]
Co-NCA5	0.2	0.842	0.802	[5]
Co-N-GC-800	0.2	0.900	0.810	[6]
Co-NMCV	0.153	0.832	0.783	[7]
Co-C@NWCs	0.1	0.939	0.83	[8]
Co_3O_4−SP/NGr-24h	1	0.896	0.756	[9]
Co/N-C-800	0.25	0.834		[10]
CNCNT	0.1	0.900		[11]
Co@CoO@N–C/C	0.42	0.92	0.81	[12]
Co/CoO@Co–N-C-800	0.2	0.913	0.793	[13]
MOFs-800	0.335	0.90	0.80	[14]
Fe_3C@NG800	0.2	0.98	0.87	[15]
G–Co/CoO	0.1	0.882	0.786	[16]
NCA_CZ_FeCo	0.21	0.95	0.888	[17]
N-CoO	0.07	0.773	0.653	[18]
HP-Co-NCNFs	0.306	0.907		[19]
$CoFe_2O_4$ /NG	0.283	0.932	0.818	[20]
$Co(OH)_x$-NCNT	0.1	0.87		[21]
$Co_{0.5}Fe_{0.5}S$@N-MC	0.8	0.913	0.808	[22]
CoO/NCW	0.244	0.85	0.78	[23]
BNC/Co_2P-2	0.213	0.893	0.813	[24]
CoO/MC-1.5	0.510	0.882		[25]
Co−S/G-3	0.08	0.89	0.82	[26]

[a] The ORR onset potential is defined at which the current density reaches to 0.1 mA cm^{-2}.

References

1. C. Han, X. Bo, Y. Zhang, M. Li, A. Nsabimana and L. Guo, *Nanoscale*, 2015, **7**, 5607-5611.
2. S. Jiang, C. Zhu and S. Dong, *J. Mater. Chem. A*, 2013, **1**, 3593-3599.

3. Y. Jiang, Y. Lu, X. Wang, Y. Bao, W. Chen and L. Niu, *Nanoscale*, 2014, **6**, 15066-15072.
4. T. Kottakkat and M. Bron, *ChemElectroChem*, 2014, **1**, 2163-2171.
5. K. Kreek, A. Sarapuu, L. Samolberg, U. Joost, V. Mikli, M. Koel and K. Tammeveski, *ChemElectroChem*, 2015, **2**, 2079-2088.
6. C. Li, Z. Han, Y. Yu, Y. Zhang, B. Dong, A. Kong and Y. Shan, *RSC Adv.*, 2016, **6**, 15167-15174.
7. M. Li, X. Bo, Y. Zhang, C. Han, A. Nsabimana and L. Guo, *J. Mater. Chem. A*, 2014, **2**, 11672-11682.
8. Y. Li, F. Cheng, J. Zhang, Z. Chen, Q. Xu and S. Guo, *Small*, 2016, **12**, 2839-2845.
9. S. K. Singh, V. M. Dhavale and S. Kurungot, *ACS Appl. Mater. Interfaces*, 2015, **7**, 21138-21149.
10. J. Masa, W. Xia, I. Sinev, A. Zhao, Z. Sun, S. Grutzke, P. Weide, M. Muhler and W. Schuhmann, *Angew. Chem. Int. Ed.*, 2014, **53**, 8508-8512.
11. Z. Wang, S. Xiao, Z. Zhu, X. Long, X. Zheng, X. Lu and S. Yang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 4048-4055.
12. Z. Wu, J. Wang, L. Han, R. Lin, H. Liu, H. L. Xin and D. Wang, *Nanoscale*, 2016, **8**, 4681-4687.
13. X. Zhang, R. Liu, Y. Zang, G. Liu, G. Wang, Y. Zhang, H. Zhang and H. Zhao, *Chem. Commun.*, 2016, **52**, 5946-5949.
14. H. Zhong, Y. Luo, S. He, P. Tang, D. Li, N. Alonso-Vante and Y. Feng, *ACS Appl. Mater. Interfaces*, 2017, **9**, 2541-2549.
15. H. Jiang, Y. Yao, Y. Zhu, Y. Liu, Y. Su, X. Yang and C. Li, *ACS Appl. Mater. Interfaces*, 2015, **7** 21511–21520.
16. S. Guo, S. Zhang, L. Wu and S. Sun, *Angew. Chem. Int. Ed.*, 2012, **51**, 11770-11773.
17. K. Elumeeva, J. Ren, M. Antonietti and T.-P. Fellinger, *ChemElectroChem*, 2015, **2**, 584-591.

18. H. Yu, Y. Li, X. Li, L. Fan and S. Yang, *Chem. Eur. J.*, 2014, **20**, 3457-3462.

19. S. Wang, Z. Cui and M. Cao, *Chem. Eur. J.*, 2015, **21**, 2165-2172.

20. L. Lu, Q. Hao, W. Lei, X. Xia, P. Liu, D. Sun, X. Wang and X. Yang, *Small*, 2015, **11**, 5833-5843.

21. J. E. Kim, J. Lim, G. Y. Lee, S. H. Choi, U. N. Maiti, W. J. Lee, H. J. Lee and S. O. Kim, *ACS Appl. Mater. Interfaces*, 2016, **8**, 1571-1577.

22. M. Shen, C. Ruan, Y. Chen, C. Jiang, K. Ai and L. Lu, *ACS Appl. Mater. Interfaces*, 2015, **7**, 1207-1218.

23. J. Xu, Q. Yu, C. Wu and L. Guan, *J. Mater. Chem. A*, 2015, **3**, 21647-21654.

24. C. Han, X. Bo, Y. Zhang, M. Li, A. Wang and L. Guo, *Chem. Commun.*, 2015, **51**, 15015-15018.

25. P. Li, R. Ma, Y. Zhou, Y. Chen, Q. Liu, G. Peng and J. Wang, *RSC Adv.*, 2016, **6**, 70763-70769.

26. T. Odedairo, X. Yan, J. Ma, Y. Jiao, X. Yao, A. Du and Z. Zhu, *ACS Appl. Mater. Interfaces*, 2015, **7**, 21373-21380.