

Supporting Information

Microwave-assisted synthesis of shell-core structural CoO@Co coupled with N-doped reduced graphene oxide as superior multifunctional electrocatalysts for Hydrogen Evolution, Oxygen Reduction and Oxygen Evolution Reaction

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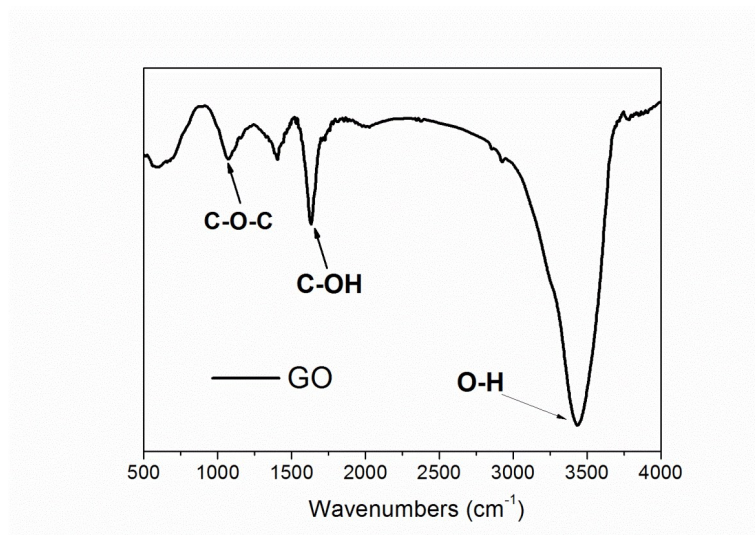


Figure S1. FTIR spectra of GO

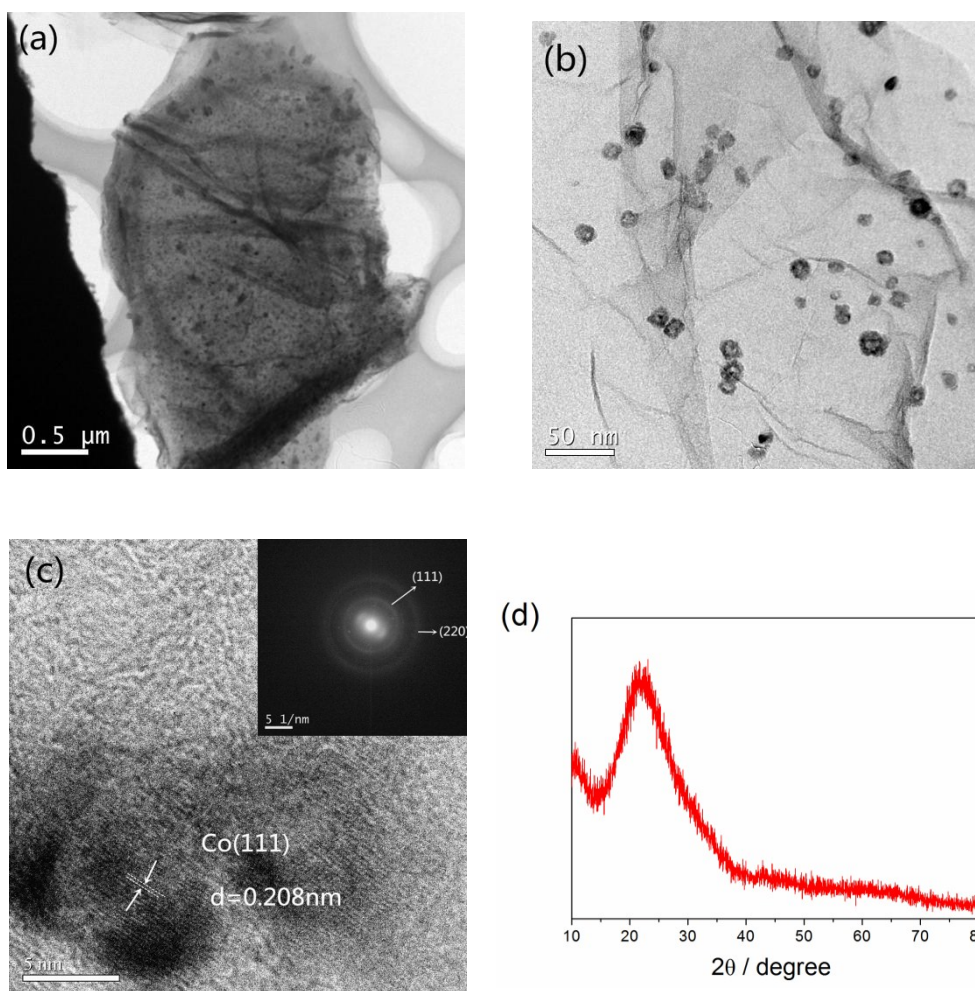


Figure S2. TEM images (a) and (b) of the intermediate products (Co/GO) with different magnifications. (c) HRTEM images of an individual Co/GO nanoparticle with the inset showing the corresponding SADE images. (d) XRD patterns of Co/GO.

Figure S2a-b shows a typical TEM image of Co/GO, the formed Co-related nanoparticles with the size of more than a dozen nanometers have been well-dispersed on the oxidized graphene (GO) through a rapid microwave-polyol method. GO containing abundant oxygen-containing functional groups probably provides efficient anchoring points for the nucleation of Co cluster. A high-resolution TEM (HRTEM) image indicates that the observed lattice fringes spacing of 0.208 nm matches well with the (111) planes of Co (Figure S2c). The corresponding selected area electronic diffraction (SAED) investigations further verify the dark particle being Co nanoparticles. But, we only observed the diffraction peak of GO in the XRD patterns of Co/GO composite (Figure S2d). No obvious diffraction peak of Co has been found in the XRD patterns, which probably attributes to that most of the Co particles in the intermediate products (Co/GO) have smaller size and bad crystalline structure before thermal treatment.

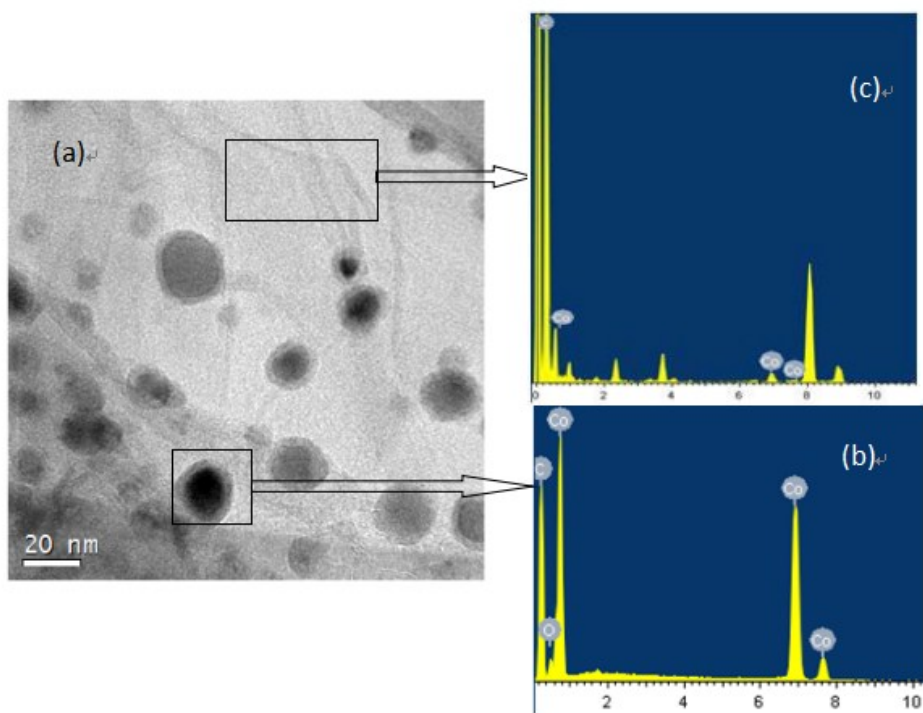


Figure S3. (a) TEM image of CoO@Co/N-rGO. EDX analysis on the areas with (b) and without (c) large particles.

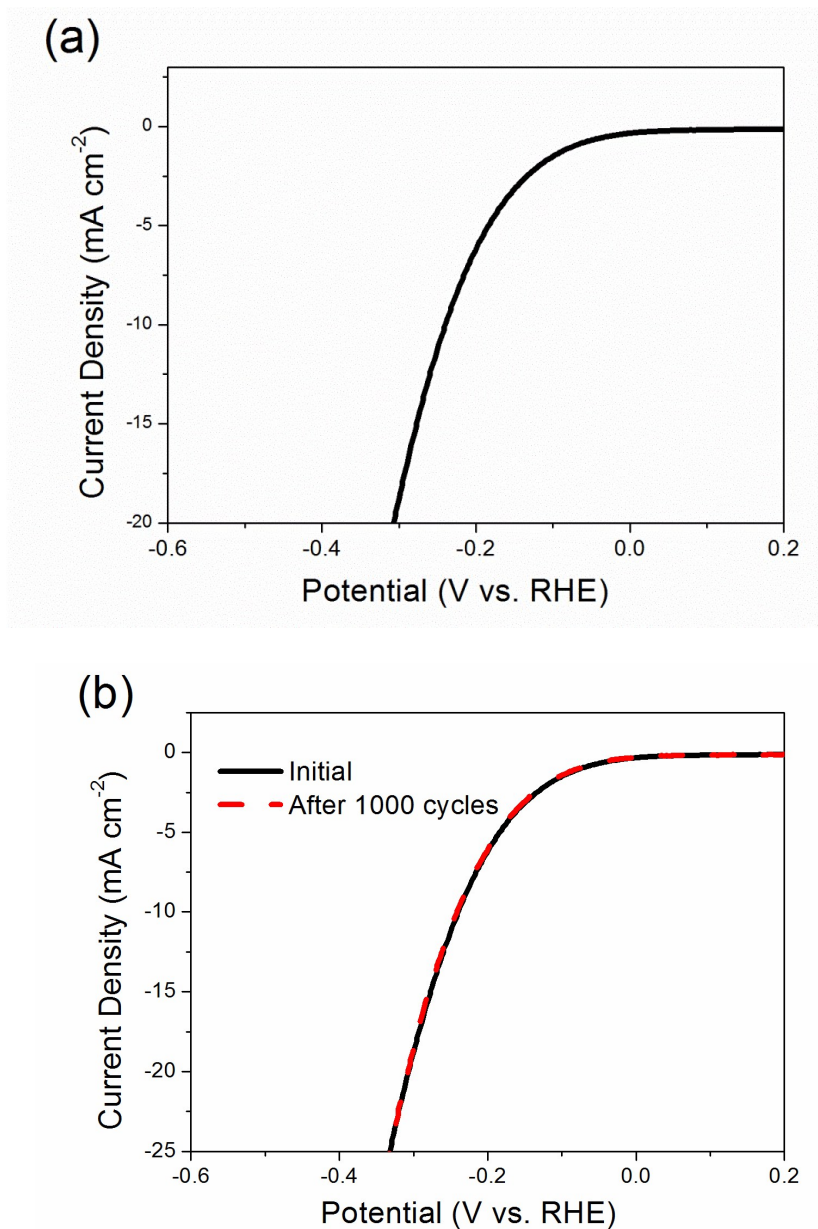


Figure S4. (a) Polarization curves of the CoO@Co/N-rGO at 5 mV s⁻¹ in N₂-saturated 0.1 M KOH solution (rotation speed 1600rpm). (b) Durability test for the CoO@Co/N-rGO (V) by CV scanning at 1000th cycles in N₂-saturated 0.1 M KOH solution.

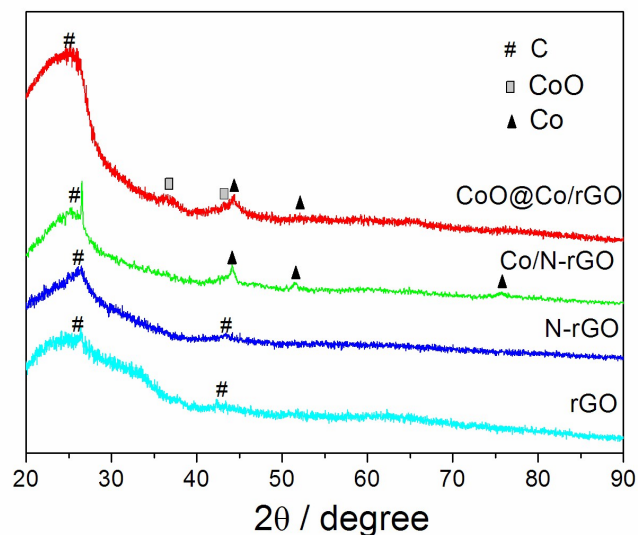


Figure S5. XRD patterns of rGO, N-rGO, Co/N-rGO and CoO@Co/rGO

As can be seen from all the XRD results (Figure S5), the broad diffraction peak at $25.5 \pm 0.5^\circ$ suggests the GO has been reduced into the graphene. The diffraction peaks at 44.2° , 51.5° , 75.8° which present in the CoO@Co/rGO and Co/N-rGO correspond to (111), (200), (220) crystal facets of metallic Co with a face-centered cubic (fcc) crystal structure. And the peaks at 36.5° , 42.4° which present in the CoO@Co/rGO match well with the planes of CoO at (111), (200) respectively. The XRD results indicate the existence of Co and CoO in our samples.

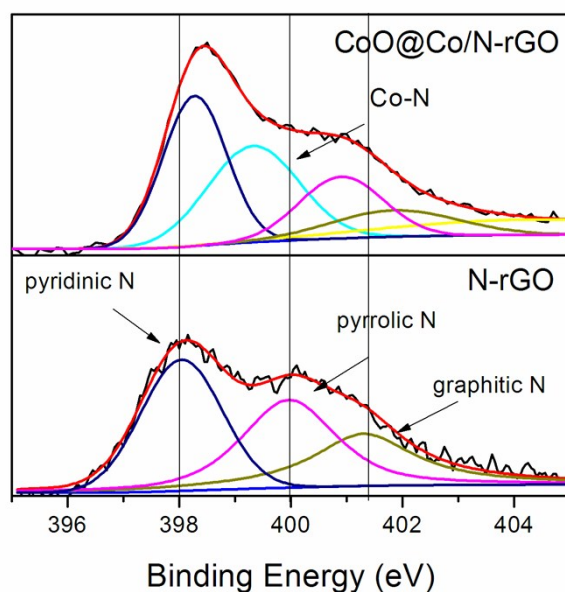
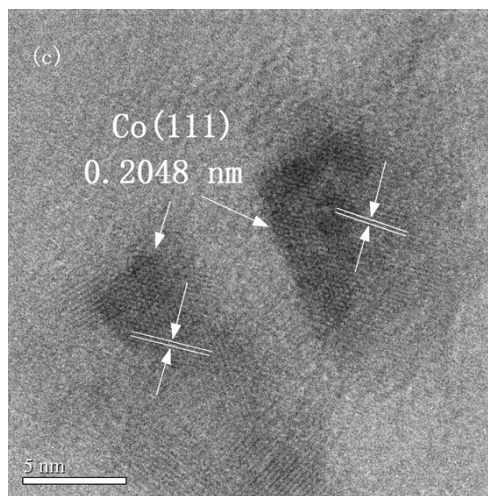
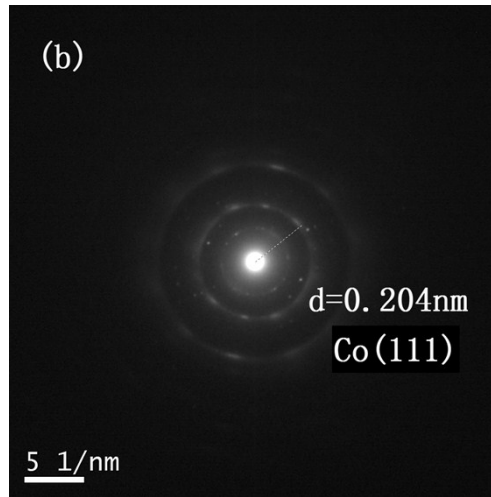
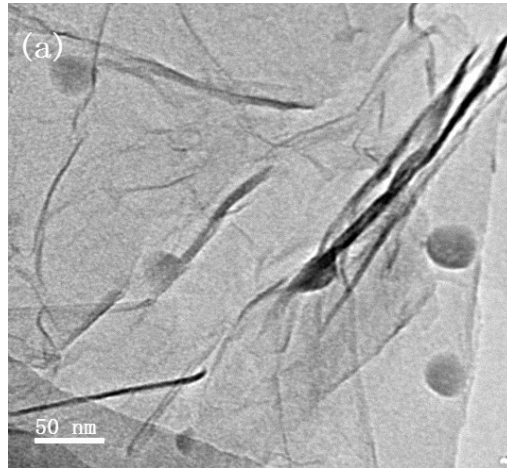


Figure S6. High-resolution XPS spectra of N 1s for CoO@Co/N-rGO and N-rGO

The N 1s XPS spectra of CoO@Co/N-rGO sample and N-rGO without Co sample were prepared for comparison in Figure S6. Three types of nitrogen coordination can be attributed to the presence of N atoms in both two samples, which respectively are pyridinic-N, pyrrolic-N and graphitic-N. From these spectra, one could observe that the binding energy of N 1s peak on CoO@Co/N-rGO shifts to higher direction compared with that on N-rGO.



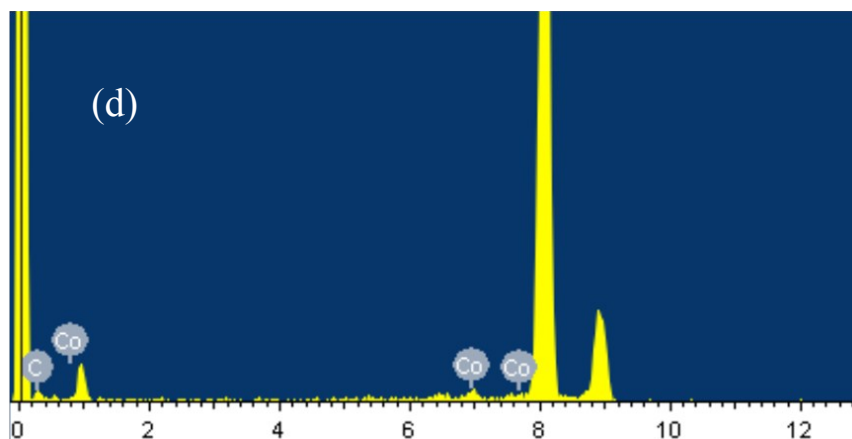


Figure S7. (a) TEM images of Co/N-rGO. (b) The corresponding SADE images of Co/N-rGO. (c) HRTEM images of an individual Co nanoparticle in Co/N-rGO. (d) EDX analysis on the areas with Co nanoparticle of Co/N-rGO.

Figure S7a shows a typical TEM image of Co/N-rGO, the formed Co-related nanoparticles are uniformly dispersed on the graphene. The corresponding selected area electronic diffraction (SAED) and the high-resolution TEM (HRTEM) image investigations verified the dark particles attached on the graphene being Co nanoparticles (Figure S7b-c). In addition, the energy dispersive X-ray spectroscopy (EDX) analysis of the nanoparticles shows only cobalt signal without oxygen which further verified that the Co nanoparticles have not been oxidized.

Table S1. Comparison of the HER performance of different catalysts.

Author	Catalyst	Current density (J)	Over potential at the corresponding J	Electrolyte
This work	CoO@Co/N-rGO	10 mA cm ⁻²	146 mV	0.5 M H ₂ SO ₄
This work	CoO@Co/N-rGO	10 mA cm ⁻²	237 mV	0.1M KOH
Yang Hou ¹	N/Co-doped PCP//NRGO	10 mA cm ⁻²	229 mV	0.5 M H ₂ SO ₄
X. Zou ²	Co-NRCNTs	10 mA cm ⁻²	260 mV	0.5 M H ₂ SO ₄
J. Deng ³	FeCo@NCNTs	10 mA cm ⁻²	320 mV	1.0 M H ₂ SO ₄
D. Merki ⁴	Amorphous MoS _x	10 mA cm ⁻²	540 mV	0.5 M H ₂ SO ₄
M. Ledendecker ⁵	MnNi	10 mA cm ⁻²	360 mV	0.5 M H ₂ SO ₄
T. F. Jaramillo ⁶	Double-gyroid MoS ₂	10 mA cm ⁻²	270 mV	0.5 M H ₂ SO ₄
Z. B. Chen ⁷	MoO ₃ -MoS ₂	10 mA cm ⁻²	275 mV	1.0 M H ₂ SO ₄
D. Voiry ⁸	WS ₂ nanosheets	10 mA cm ⁻²	230 mV	0.5 M H ₂ SO ₄
Y. Zheng ⁹	N,P-graphene	10 mA cm ⁻²	422 mV	0.5 M H ₂ SO ₄
M. Gong ¹⁰	NiO/CNT	20 mA cm ⁻²	490 mV	0.1M KOH
B. F. Cao ¹¹	Ni ₂ P	20 mA cm ⁻²	250 mV	0.1M KOH
R. Subbaraman ¹²	δ-MoN	10 mA cm ⁻²	400 mV	0.1M KOH
M. A. McArthur ¹³	Ni/MWCNT	10 mA cm ⁻²	350 mV	1M KOH
H. Vrubel ¹⁴	Co-NRCNTs	10 mA cm ⁻²	370 mV	0.1M KOH

Table S2. Comparison of the ORR performance of different catalysts.

Author	Catalyst	Half wave Potential (V)	Onset potential (V)	Number of electron transfer (n)	Electrolyte
this work	CoO@Co/N-rGO	0.81	0.95	3.97~4.0	0.1 M KOH
Y. Hou ¹	N/Co-doped PCP//NRGO	0.86	0.97	3.90~3.94	0.1 M KOH
D. K. Huang ¹⁵	Cobalt oxide@cobalt/N-C	0.82	0.97	about 4	0.1 M KOH
X. Liu ¹⁶	Co-CoO/N-rGO	0.78	0.88	3.7~3.9	0.1 M KOH
Z. Y. Liu ¹⁷	N-doped nanoporous carbon	0.73	0.82	3.23 at 0.3 V	0.1 M KOH
Y. Liang ¹⁸	Co ₃ O ₄ -N-rmGO	0.83	-	4.0	0.1 M KOH
Y. Hu ¹⁹	Fe ₃ C/C-800	0.83	1.05	3.8~4.0	0.1 M KOH
L. Lin ²⁰	Fe-N/C-800	0.81	0.92	3.96	0.1 M KOH
J. Ryu ²¹	C@Co-P/C	0.80	0.87	-	0.1 M KOH
R. Huo ²²	Co/CoO/CoFe ₂ O ₄ /G	0.69	0.77	3.70~3.84	0.1 M KOH
B. Cao ²³	Co _{0.50} Mo _{0.50} O _y N _z /C	0.76	0.92	3.85~3.9	0.1 M KOH
H. Dai ²⁴	CoO/NCNT	-	0.93	3.9	1 M KOH
S. Mao ²⁵	N-CG-CoO	0.81	0.9	4.0	1 M KOH

Table S3. Comparison of the OER performance of different catalysts.

Author	Catalyst	Current density (J)	Over potential at the corresponding J	Electrolyte
This work	CoO@Co/N-rGO	10 mA cm⁻²	165mV	0.1 M KOH
Y. Hou ¹	N/Co-doped PCP//NRGO	10 mA cm ⁻²	166 mV	0.1 M KOH
X. Liu ¹⁶	Co-CoO/N-rGO/Ni foam	10 mA cm ⁻²	163mV	0.1M KOH
S. Q. Ci ²⁶	crumpled graphene/CoO	10 mA cm ⁻²	165mV	0.1M KOH
J. Masa ²⁷	Co _x O _y /NC	10 mA cm ⁻²	166 mV	0.1M KOH
J. Masa ²⁷	Mn _x O _y /NC	10 mA cm ⁻²	168 mV	0.1M KOH
Y. Lee ²⁸	IrO ₂	10 mA cm ⁻²	168mV	0.1M KOH
M. R. Gao ²⁹	Mn ₃ O ₄ /CoSe ₂	10 mA cm ⁻²	168 mV	0.1M KOH
Y. T. Meng ³⁰	α-MnO ₂ -SF	10 mA cm ⁻²	172 mV	0.1M KOH
Y. Gorlin ³¹	CaMn ₄ O _x	10 mA cm ⁻²	177 mV	0.1M KOH

Table S4. Comparison of the bifunctional oxygen electrode activities of different catalysts.

Author	Catalyst	E_{ORR} (V) at $J = -3 \text{ mA cm}^{-2}$	E_{OER} (V) at $J = 10 \text{ mA cm}^{-2}$	Oxygen Electrode ΔE (V) = $E_{\text{OER}} - E_{\text{ORR}}$
This work	CoO@Co/N-rGO	0.73	1.64	0.91
Y. Gorlin ³²	20 wt% Ir/C	0.69	1.61	0.92
Y. Gorlin ³²	20 wt% Ru/C	0.61	1.62	1.01
Y. Gorlin ³²	20 wt% Pt/C Mn-oxide	0.86	2.02	1.16
Y. Gorlin ³²	Mn-oxide	0.73	1.77	1.04
W. G. Hardin ³³	LaNiO ₃ /NC	0.64	1.66	1.02
Q. Liu ³⁴	NiCo ₂ S ₄ @N/S-rGO	0.76	1.70	0.94
D. Wang ³⁵	Co ₃ O ₄ /2.7Co ₂ MnO ₄	0.68	1.77	1.09
D. U. Lee ³⁶	NiCo ₂ O ₄ /G	0.54	1.67	1.13
C. Jin ³⁷	NiCo ₂ O ₄	0.75	1.72	0.97

1. Y. Hou, Z. H. Wen, S. M. Cui, S. Q. Ci, S. Mao and J. H. Chen, *Advanced Functional Materials*, 2015, **25**, 872-882.
2. X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmeková and T. Asefa, *Angewandte Chemie*, 2014, **126**, 4461-4465.
3. J. Deng, P. J. Ren, D. H. Deng, L. Yu, F. Yang and X. H. Bao, *Energy & Environmental Science*, 2014, **7**, 1919-1923.
4. D. Merki, S. Fierro, H. Vrubel and X. L. Hu, *Chemical Science*, 2011, **2**, 1262-1267.
5. M. Ledendecker, G. Clavel, M. Antonietti and M. Shalom, *Advanced Functional Materials*, 2015, **25**, 393-399.
6. T. F. Jaramillo, K. P. Jorgensen, J. Bonde, J. H. Nielsen, S. Horch and I. Chorkendorff, *Science*, 2007, **317**, 100-102.
7. Z. B. Chen, D. Cummins, B. N. Reinecke, E. Clark, M. K. Sunkara and T. F. Jaramillo, *Nano Letters*, 2011, **11**, 4168-4175.
8. D. Voiry, H. Yamaguchi, J. W. Li, R. Silva, D. C. B. Alves, T. Fujita, M. W. Chen, T. Asefa, V. B. Shenoy, G. Eda and M. Chhowalla, *Nature Materials*, 2013, **12**, 850-855.

9. Y. Zheng, Y. Jiao, L. H. Li, T. Xing, Y. Chen, M. Jaroniec and S. Z. Qiao, *Acs Nano*, 2014, **8**, 5290-5296.
10. M. Gong, W. Zhou, M. C. Tsai, J. G. Zhou, M. Y. Guan, M. C. Lin, B. Zhang, Y. F. Hu, D. Y. Wang, J. Yang, S. J. Pennycook, B. J. Hwang and H. J. Dai, *Nature Communications*, 2014, **5**.
11. B. F. Cao, G. M. Veith, J. C. Neufeind, R. R. Adzic and P. G. Khalifah, *Journal of the American Chemical Society*, 2013, **135**, 19186-19192.
12. R. Subbaraman, D. Tripkovic, K. C. Chang, D. Strmcnik, A. P. Paulikas, P. Hirunsit, M. Chan, J. Greeley, V. Stamenkovic and N. M. Markovic, *Nature Materials*, 2012, **11**, 550-557.
13. M. A. McArthur, L. Jorge, S. Coulombe and S. Omanovic, *Journal of Power Sources*, 2014, **266**, 365-373.
14. H. Vrubel and X. L. Hu, *Angewandte Chemie-International Edition*, 2012, **51**, 12703-12706.
15. D. K. Huang, Y. P. Luo, S. H. Li, B. Y. Zhang, Y. Shen and M. K. Wang, *Nano Research*, 2014, **7**, 1054-1064.
16. X. Liu, W. Liu, M. Ko, M. Park, M. G. Kim, P. Oh, S. Chae, S. Park, A. Casimir, G. Wu and J. Cho, *Advanced Functional Materials*, 2015, **25**, 5799-5808.
17. Z. Y. Liu, G. X. Zhang, Z. Y. Lu, X. Y. Jin, Z. Chang and X. M. Sun, *Nano Research*, 2013, **6**, 293-301.
18. Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier and H. Dai, *Nat Mater*, 2011, **10**, 780-786.
19. Y. Hu, J. O. Jensen, W. Zhang, L. N. Cleemann, W. Xing, N. J. Bjerrum and Q. Li, *Angew Chem Int Ed Engl*, 2014, **53**, 3675-3679.
20. L. Lin, Q. Zhu and A. W. Xu, *J Am Chem Soc*, 2014, **136**, 11027-11033.
21. J. Ryu, N. Jung, D. H. Lim, D. Y. Shin, S. H. Park, H. C. Ham, J. H. Jang, H. J. Kim and S. J. Yoo, *Chemical communications*, 2014, **50**, 15940-15943.
22. R. Huo, W. J. Jiang, S. Xu, F. Zhang and J. S. Hu, *Nanoscale*, 2014, **6**, 203-206.
23. B. Cao, G. M. Veith, R. E. Diaz, J. Liu, E. A. Stach, R. R. Adzic and P. G. Khalifah, *Angew Chem Int Ed Engl*, 2013, **52**, 10753-10757.
24. Y. Y. Liang, H. L. Wang, P. Diao, W. Chang, G. S. Hong, Y. G. Li, M. Gong, L. M. Xie, J. G. Zhou, J. Wang, T. Z. Regier, F. Wei and H. J. Dai, *Journal of the American Chemical Society*, 2012, **134**, 15849-15857.
25. S. Mao, Z. Wen, T. Huang, Y. Hou and J. Chen, *Energy Environ. Sci.*, 2014, **7**, 609-616.
26. S. Q. Ci, S. Mao, T. Z. Huang, Z. H. Wen, D. A. Steeber and J. H. Chen, *Electroanalysis*, 2014, **26**, 1326-1334.
27. J. Masa, W. Xia, I. Sinev, A. Q. Zhao, Z. Y. Sun, S. Grutzke, P. Weide, M. Muhler and W. Schuhmann, *Angewandte Chemie-International Edition*, 2014, **53**, 8508-8512.
28. Y. Lee, J. Suntivich, K. J. May, E. E. Perry and Y. Shao-Horn, *Journal of Physical Chemistry Letters*, 2012, **3**, 399-404.
29. M. R. Gao, Y. F. Xu, J. Jiang, Y. R. Zheng and S. H. Yu, *Journal of the American Chemical Society*, 2013, **135**, 6378-6378.
30. Y. T. Meng, W. Q. Song, H. Huang, Z. Ren, S. Y. Chen and S. L. Suib, *Journal of the American Chemical Society*, 2014, **136**, 11452-11464.
31. Y. Gorlin, B. Lassalle-Kaiser, J. D. Benck, S. Gul, S. M. Webb, V. K. Yachandra, J. Yano and T. F. Jaramillo, *Journal of the American Chemical Society*, 2013, **135**, 8525-8534.

32. Y. Gorlin and T. F. Jaramillo, *Journal of the American Chemical Society*, 2010, **132**, 13612-13614.
33. W. G. Hardin, D. A. Slanac, X. Wang, S. Dai, K. P. Johnston and K. J. Stevenson, *Journal of Physical Chemistry Letters*, 2013, **4**, 1254-1259.
34. Q. Liu, J. T. Jin and J. Y. Zhang, *Acs Applied Materials & Interfaces*, 2013, **5**, 5002-5008.
35. D. D. Wang, X. Chen, D. G. Evans and W. S. Yang, *Nanoscale*, 2013, **5**, 5312-5315.
36. D. U. Lee, B. J. Kim and Z. W. Chen, *Journal of Materials Chemistry A*, 2013, **1**, 4754-4762.
37. C. Jin, F. L. Lu, X. C. Cao, Z. R. Yang and R. Z. Yang, *Journal of Materials Chemistry A*, 2013, **1**, 12170-12177.