

## Electronic Supplementary Information

# **Unusual Formation of Tetragonal Microstructure from Nitrogen-Doped Carbon Nanocapsules with Cobalt Nanocores as a Bi-Functional Oxygen Electrocatalyst**

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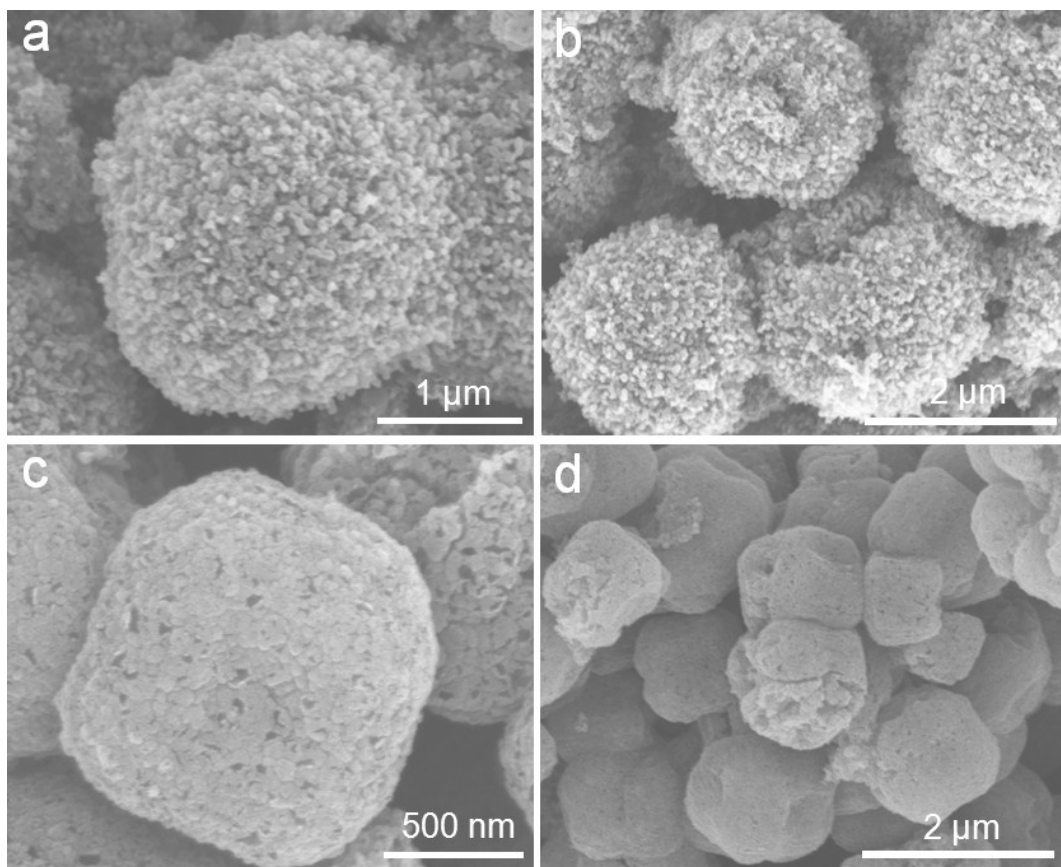
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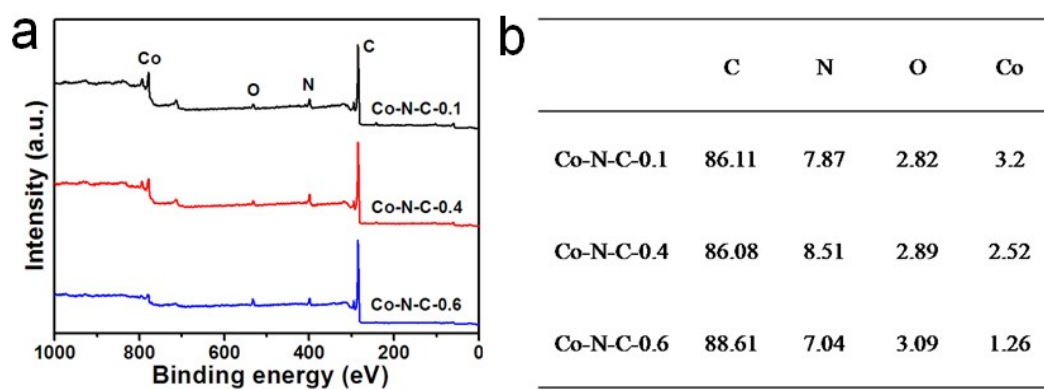
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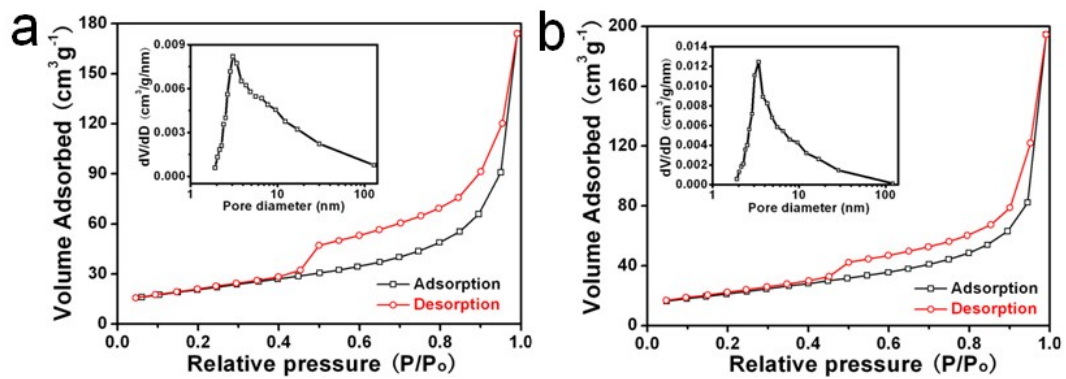
<sup>1</sup>These authors contributed equally to this work.



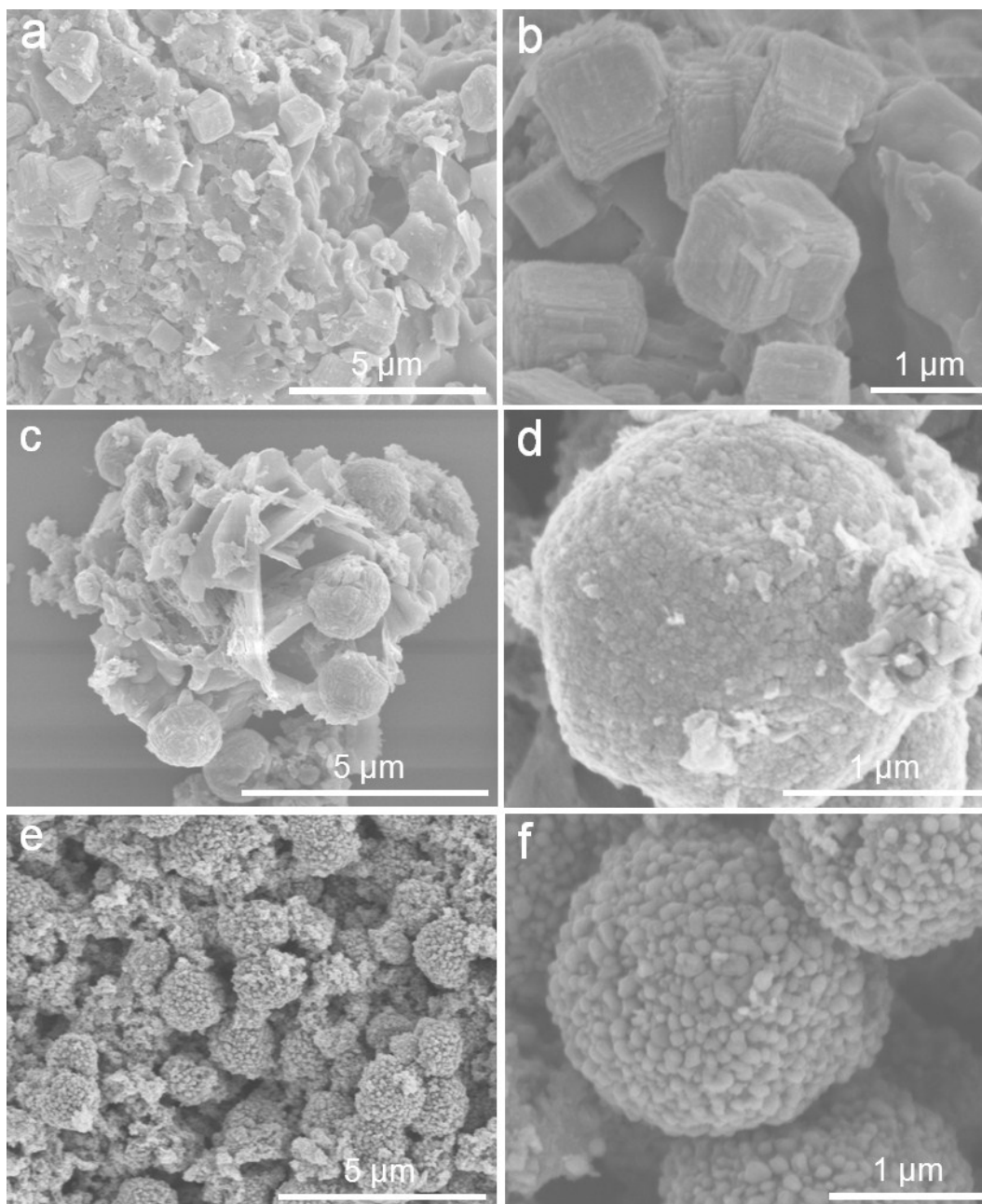
**Fig. S1** SEM images of the as-prepared samples: (a) and (b) Co-N-C-0.1. (c) and (d) Co-N-C-0.6.



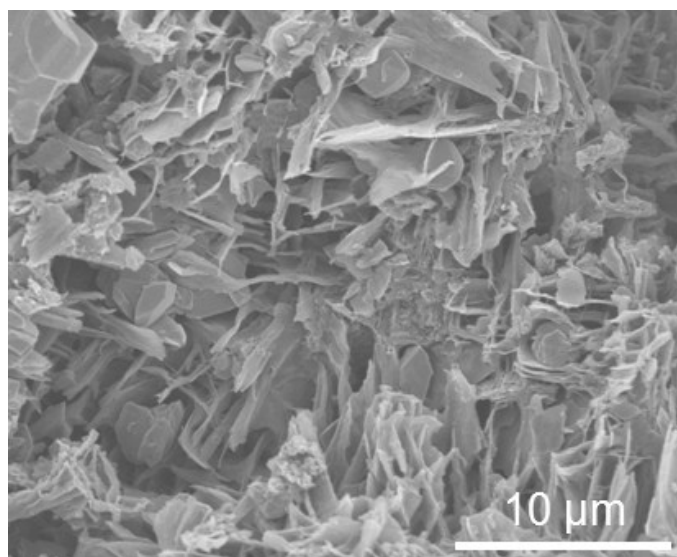
**Fig. S2** XPS analysis results of the as-prepared samples: **(a)** XPS spectra. **(b)** Elemental composition (atomic percentage) obtained from XPS analysis.



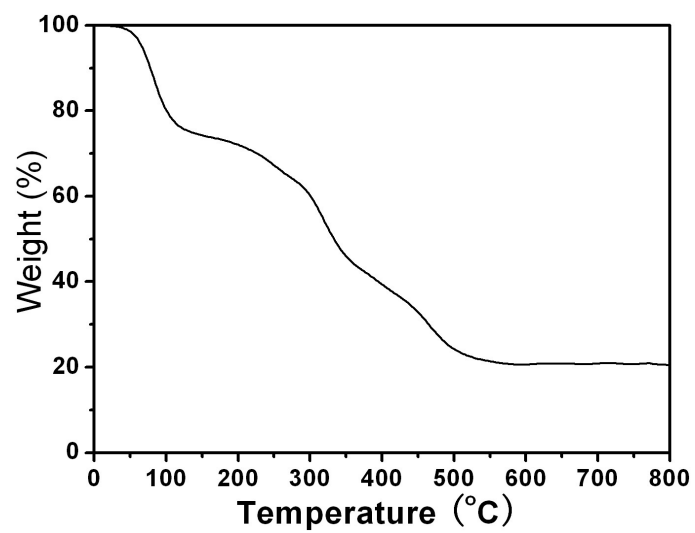
**Fig. S3** N<sub>2</sub> adsorption-desorption isotherms of the as-prepared samples: (a) Co-N-C-0.1, (b) Co-N-C-0.6.



**Fig. S4** SEM images of the as-prepared sample Co-N-C-0.4 after annealing at different temperatures: (a) and (b) at 300 °C. (c) and (d) at 400 °C. (e) and (f) at 500 °C.



**Fig. S5** SEM image of the as-prepared g-C<sub>3</sub>N<sub>4</sub>.



**Fig. S6** TGA curve of the mixture of 0.1 g g-C<sub>3</sub>N<sub>4</sub> and 0.4 g Co(CH<sub>3</sub>COO)<sub>2</sub>•4H<sub>2</sub>O.

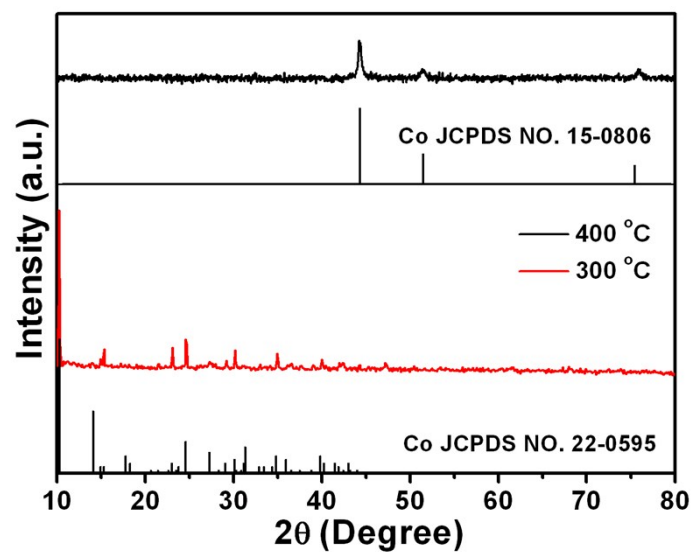
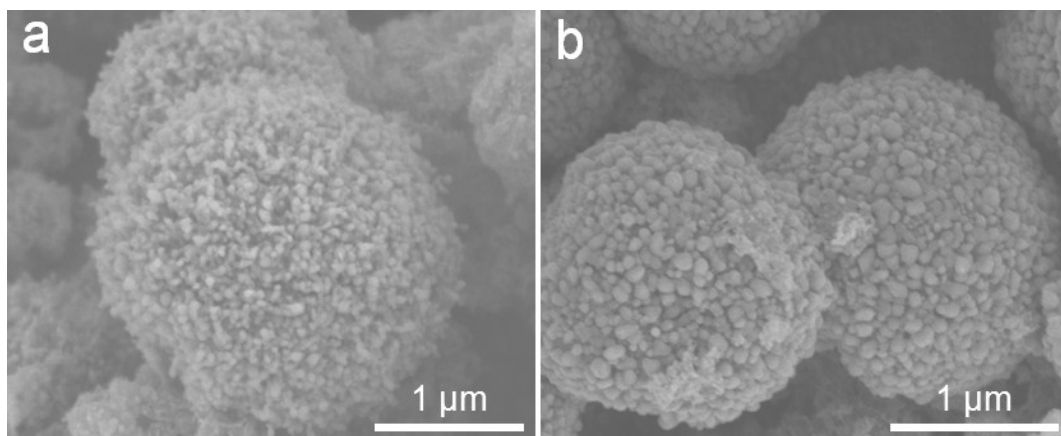
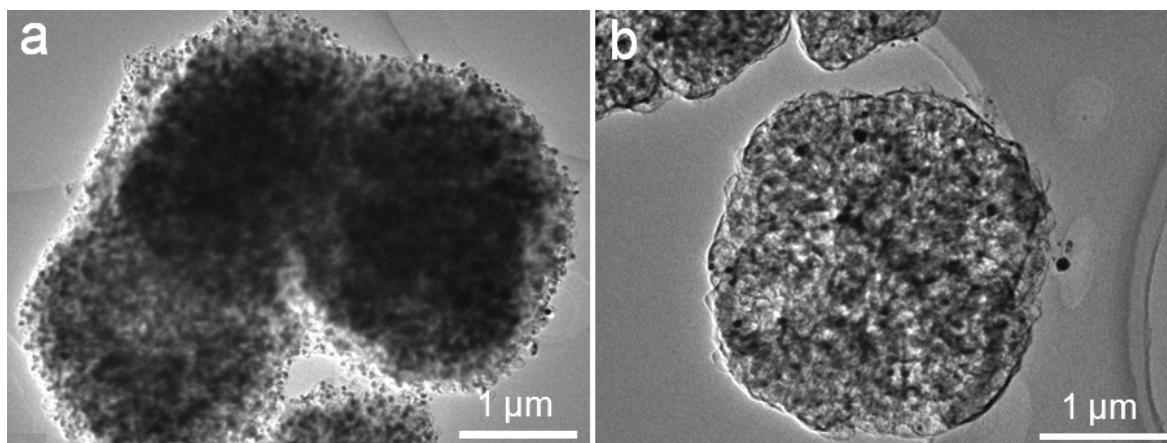


Fig. S7 XRD patterns of the Co-N-C-0.4 obtained at different temperature.

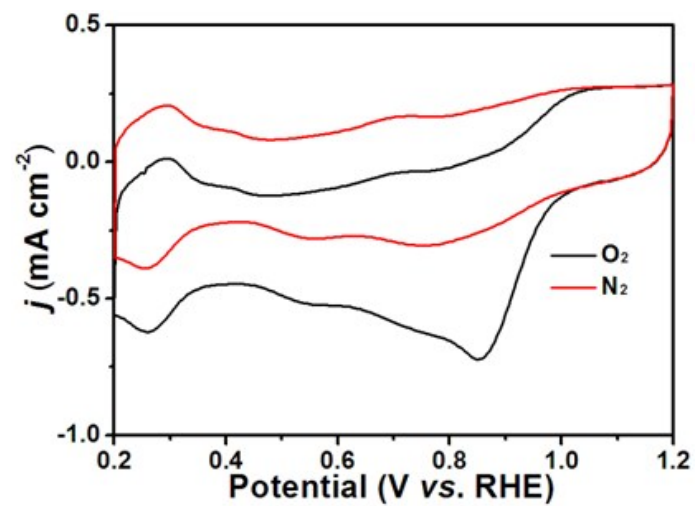




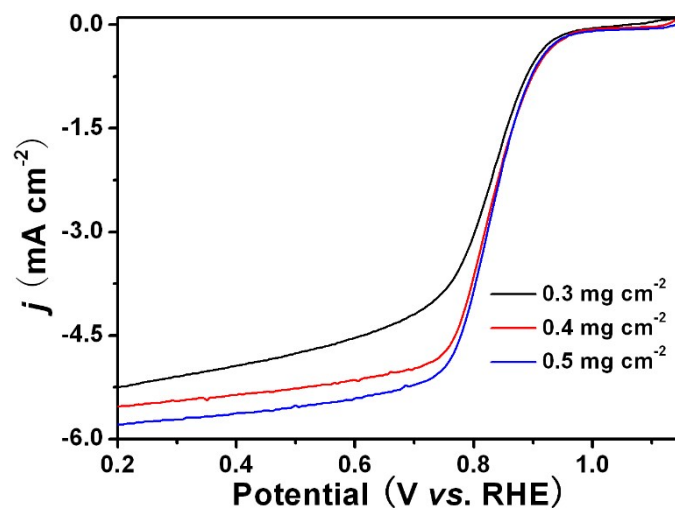
**Fig. S8** SEM images of the as-prepared samples: (a) Co-N-C-0.1. (b) Co-N-C-0.4 without acid leaching treatment.



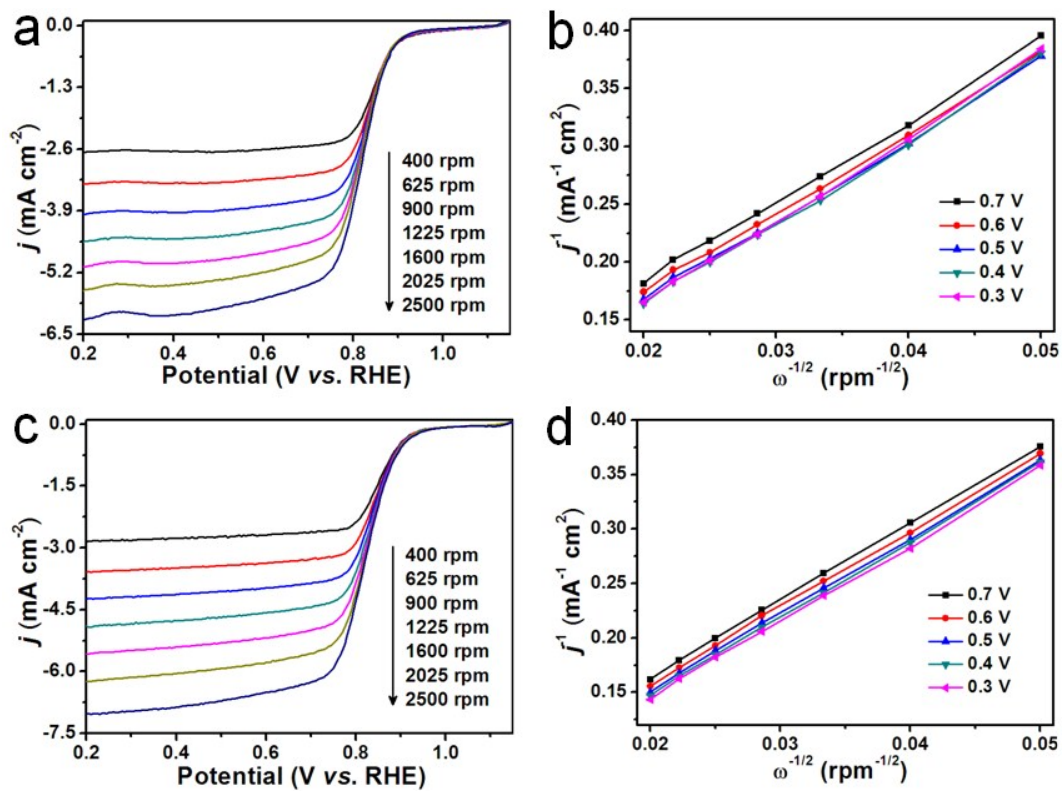
**Fig. S9** TEM images of the as-prepared samples: (a) Co-N-C-0.1. (b) Co-N-C-0.6.



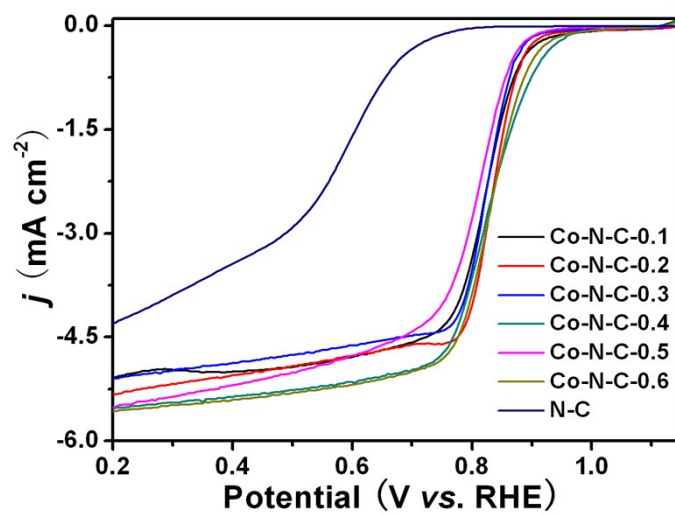
**Fig. S10** CV profiles of the Pt/C in O<sub>2</sub>(black curve) and N<sub>2</sub> (red curve) saturated 0.1 M KOH solution at 1600 rpm with a scan rate of 20 mV s<sup>-1</sup>.



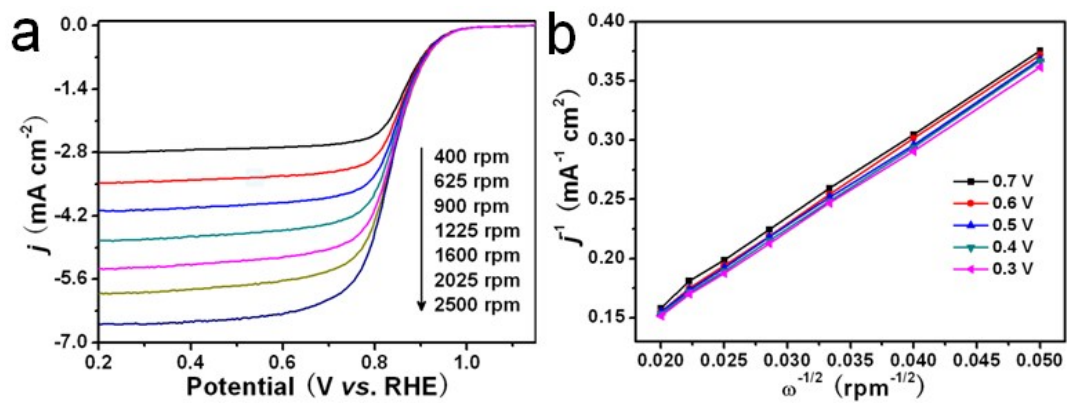
**Fig. S11** LSV results of the as-prepared Co-N-C-0.4 catalyst with different loading amount. (in O<sub>2</sub> saturated 0.1 M KOH solution at a rotation rate of 1600 rpm)



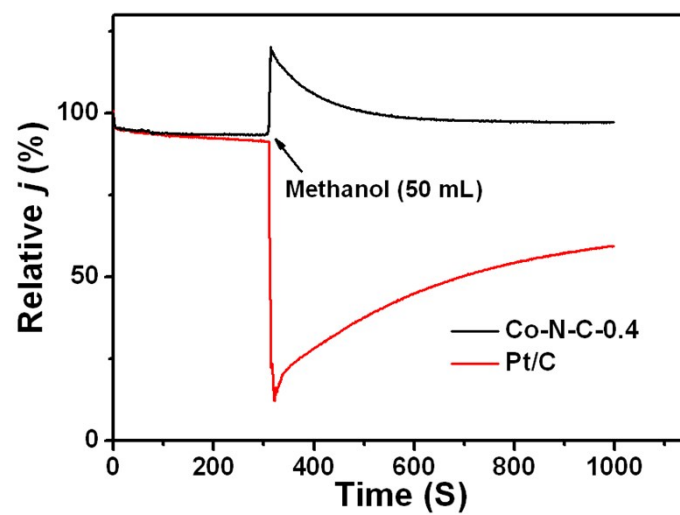
**Fig. S12** (a) and (c) LSV results of Co-N-C-0.1 (a) and Co-N-C-0.6 (c) at different rotation rates. (b) and (d) the corresponding K-L plots.



**Fig. S13** LSV results of the as-prepared samples. (in O<sub>2</sub> saturated 0.1 M KOH solution at a rotation rate of 1600 rpm)

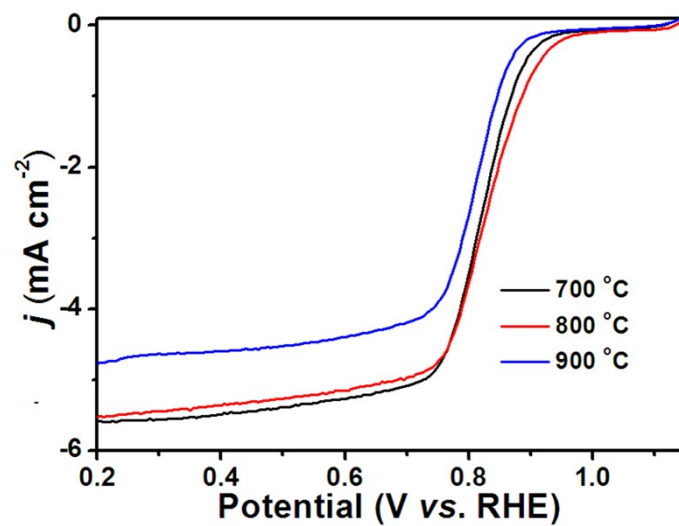


**Fig. S14** (a) LSV results of the commercial Pt/C at different rotation rates. (b) corresponding K-L plots.

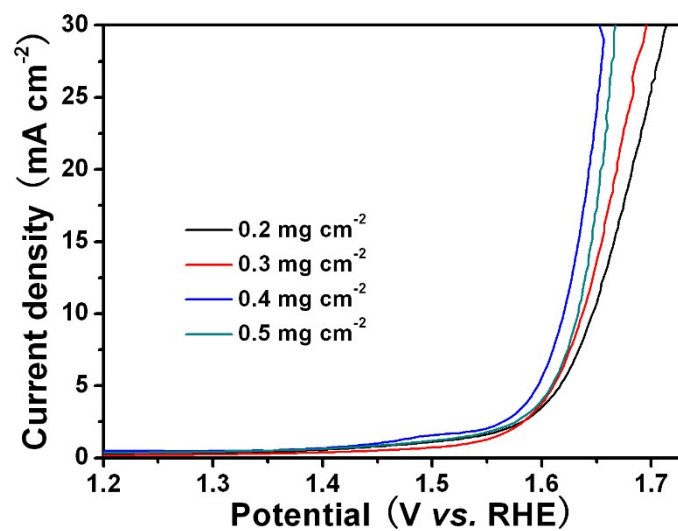


**Fig. S15** Chronoamperometric response at 0.6 V in  $O_2$  saturated 0.1 M KOH solution with the adding of 50 ml methanol.

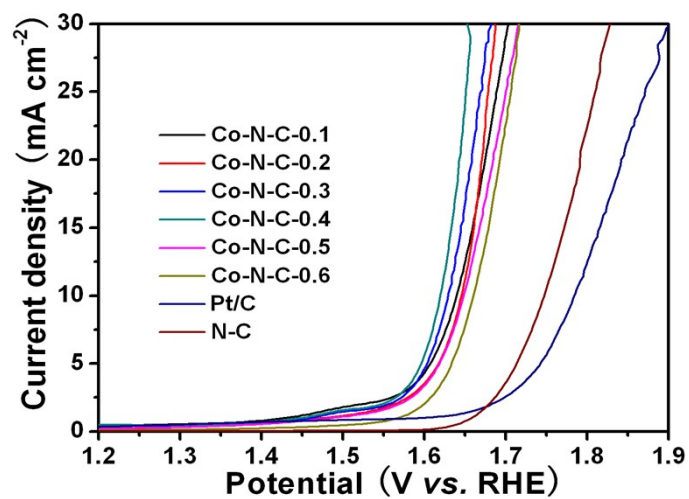




**Fig. S16** LSV curves of the as-prepared Co-N-C-0.4 obtained at different temperatures. (in O<sub>2</sub> saturated 0.1 M KOH solution at a rotation rate of 1600 rpm).



**Fig. S17** LSV results of the as-prepared Co-N-C-0.4 catalyst with different loading amount. (in O<sub>2</sub> saturated 0.1 M KOH solution at a rotation rate of 1600 rpm)



**Fig. S18** LSV results of the as-prepared catalyst. (in O<sub>2</sub> saturated 0.1 M KOH solution at a rotation rate of 1600 rpm)

**Table S1** Comparison of various carbon based materials for ORR.

Catalysts	Loading ( $\text{mg cm}^{-2}$ )	Onset potential (V)	Half-wave potential (V)	n	References
N/Co-doped PCP//NRGO	0.714	0.97	0.86	3.9	<i>Adv. Funct. Mater.</i> <b>2015</b> , 25, 872
N/Co-doped PCP-RGO	0.714	0.94	N/A	3.3	<i>Adv. Funct. Mater.</i> <b>2015</b> , 25, 872
$\text{Fe}_3\text{C}/\text{C}$	0.6	1.05	0.83	3.9	<i>Angew. Chem. Int. Ed.</i> <b>2014</b> , 53, 3675
$\text{FeN}_x/\text{C}$ catalyst	0.6	0.94	0.82	N/A	<i>J. Am. Chem. Soc.</i> <b>2014</b> , 136, 10882
$\text{Co}_3\text{O}_4/\text{N-rmGO}$	0.17	0.88	0.83	3.9	<i>Nat. Mater.</i> <b>2011</b> , 10, 780
Co@NG	1.08	0.9	0.83	3.9	<i>Adv. Funct. Mater.</i> <b>2016</b> , 26, 4397
Co/N-CNTs	0.2	0.94	0.84	3.9	<i>J. Mater. Chem. A</i> , <b>2016</b> , 4, 1694
Fe/N-CNTs	0.2	0.96	0.82	3.8	<i>J. Mater. Chem. A</i> , <b>2016</b> , 4, 1694
Co-N-C	0.283	0.98	0.87	4.0	<i>ACS Catal.</i> <b>2015</b> , 5, 7068
Fe-N-CC	0.1	0.94	0.83	3.7	<i>ACS Nano</i> , <b>2016</b> , 10, 5922
LDH@ZIF-67-800	0.2	0.94	0.83	4.0	<i>Adv. Mater.</i> <b>2016</b> , 28, 2337
Co@ $\text{Co}_3\text{O}_4$ @C-CM	0.1	0.93	0.81	3.8	<i>Energy Environ. Sci.</i> <b>2015</b> , 8, 568
N-Carbon nanotube frameworks	0.2	0.97	0.87	3.97	<i>Nat. Energy.</i> <b>2016</b> , 1, 15006.
N,P-codoped ordered mesoporous carbon	0.3	0.95	0.82	3.7	<i>Angew. Chem. Int. Ed.</i> <b>2015</b> , 54, 9230
$\text{Co}_x\text{Zn}_{100-x}$ -NPCs	0.1	0.9	N/A	3.9	<i>ACS Appl. Mater. Interfaces.</i> <b>2015</b> , 7, 4048
Co-N-C	0.25	0.98	0.84	3.9	This work

**Table S2** Comparison of various carbon based materials for OER.

Catalysts	Loading (mg cm <sup>-2</sup> )	Onset Potential (V)	Tafel (mV decade <sup>-1</sup> )	Potential (V) @ 10 mA cm <sup>-2</sup>	References
N/Co-doped MOF derived carbon/NRGO	0.36	N/A	292	1.66	<i>Adv. Funct. Mater.</i> <b>2015</b> , 25, 872
ZIF-derived carbon	0.36	N/A	393	1.75	<i>Adv. Funct. Mater.</i> <b>2015</b> , 25, 872
Ni-Co mixed oxide porous cubes	N/A	N/A	59	1.66	<i>Adv. Mater.</i> <b>2016</b> , 28, 4601
Mn <sub>3</sub> O <sub>4</sub> /CoSe <sub>2</sub>	0.2	N/A	49	1.68	<i>J. Am. Chem. Soc.</i> <b>2012</b> , 134, 2930
N- CNT/graphen e	0.24	1.52	82	1.63	<i>Small</i> <b>2014</b> , 10, 2251
N, O-dual dopedCNTs	1.75	1.55	141	1.8 @ 14.8 mA cm <sup>-2</sup>	<i>Adv. Mater.</i> <b>2014</b> , 26, 2925
N-Carbon nanotube frameworks	0.2	1.47	93	1.60	<i>Nat. Energy.</i> <b>2016</b> , 1, 15006.
Co(OH) <sub>2</sub>	0.1	N/A	62	1.68	<i>ACS Appl. Mater. Interfaces</i> 2015, 7, 12930
Co-N-C	0.4	1.55	110	1.62	This work