

### Supplementary Information

#### **Highly dispersed Co nanoparticles decorated on N-doped defective carbon nano-framework for hybrid Na-Air battery**

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Table S1. Performance of bifunctional catalysts derived from Co-MOF for ORR and OER.

Catalysts	Electrolyte	Onset Potential (V)	Half-wave potential (V)	J at 1.6 V (mA cm <sup>-2</sup> )	Ref.
BNPC-1100	0.1 M KOH	0.894	0.793	4.7	[1]
Co@N-CNTF-2	0.1 M KOH	0.91	0.81	10	[2]
CoZn-NC-700	0.1 M KOH	0.97	0.84	6.0	[3]
MnO@Co/N-C	0.1 M KOH	0.88	0.83	2.4	[4]
Co-CoP-HNC	0.1 M KOH	0.94	0.83	140	[5]
Co-CoO-C	0.1 M KOH	0.90	0.82	4.0	[6]
Co-N-C-0	0.1 M KOH	0.85	0.81	1.5	Present work
Co-N-C-0.2	0.1 M KOH	0.87	0.80	2.5	Present work
Co-N-C-0.5	0.1 M KOH	0.92	0.82	4.4	Present work

Table S2. The atomic percentage of fitted peaks of N 1s in Co-N-C catalysts

Catalysts	Pyridine N (at %)	Pyrrolic N (at %)	CoN <sub>x</sub> (at %)
Co-N-C-0	0.13	0.09	0.11
Co-N-C-0.2	0.08	0.17	0.13
Co-N-C-0.5	0.14	0.13	0.30

Table S3. Atomic ratio of  $\text{Co}^{3+}$ ,  $\text{Co}^{2+}$ , and  $\text{Co}^0$  in Co-N-C catalysts calculated by XPS

Catalysts	$\text{Co}^{3+}$ (at %)	$\text{Co}^{2+}$ (at %)	$\text{Co}^0$ (at %)
Co-N-C-0	0.06	0.06	0.01
Co-N-C-0.2	0.07	0.05	0.01
Co-N-C-0.5	0.07	0.02	0.01

Table S4. Discharge–charge performance of hybrid sodium-air batteries with different catalysts

Catalysts	Discharge voltage (V)	Charge voltage (V)	Voltage gap (V)	Current densities	Roundtrip efficiency (%)	Ref.
Mn <sub>3</sub> O <sub>4</sub> /C	2.60	3.51	0.91	1 mA·cm <sup>-2</sup>	74.07	[7]
Co <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	2.82	3.41	0.59	0.01 mA·cm <sup>-2</sup>	82.70	[8]
<i>dp</i> -MnCo <sub>2</sub> O <sub>4</sub> /N-rGO	2.75	3.14	0.39	0.13 mA·cm <sup>-2</sup>	87.58	[9]
Pt/C	2.85	3.38	0.53	0.025 mA·cm <sup>-2</sup>	84.32	[10]
Carbon paper	2.6	3.59	0.99	0.025 mA·cm <sup>-2</sup>	72.42	[10]
Carambol a-shaped VO <sub>2</sub>	2.81	3.45	0.64	0.01 mA·cm <sup>-2</sup>	81.45	[11]
Pt/C	2.94	3.55	0.61	0.01 mA·cm <sup>-2</sup>	82.82	[11]
Pt/C	2.69	3.20	0.51	0.1 mA·cm <sup>-2</sup>	84.06	Present work
Co-N-C-0	2.60	3.17	0.57	0.1 mA·cm <sup>-2</sup>	82.02	Present work

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Co-N-C-	2.79	3.12	0.33	0.1 mA·cm <sup>-2</sup>	89.42	Present
0.2						work
Co-N-C-	2.80	3.11	0.38	0.1 mA·cm <sup>-2</sup>	90.03	Present
0.5						work

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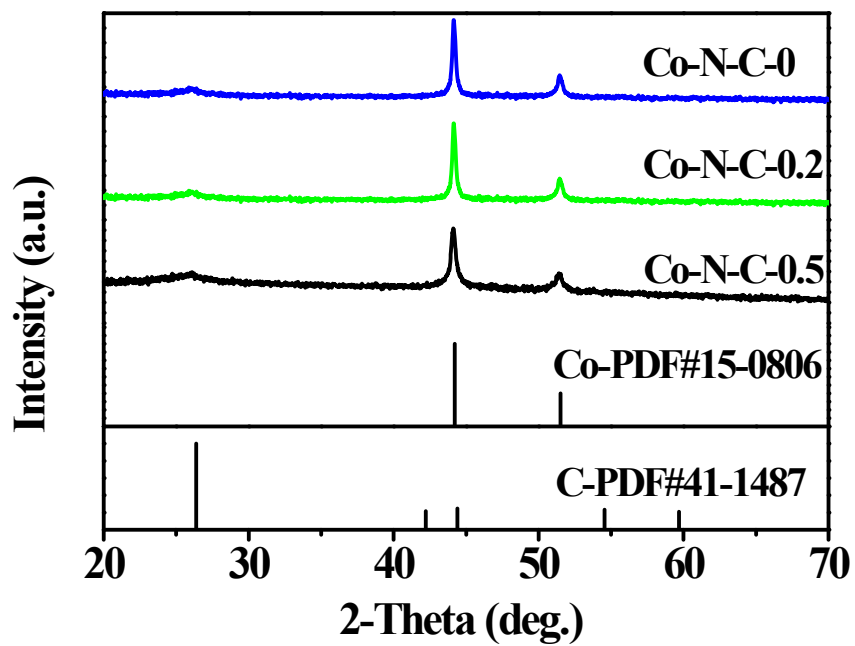


Figure S1. XRD patterns of Co-N-C-0, Co-N-C-0.2, and Co-N-C-0.5.

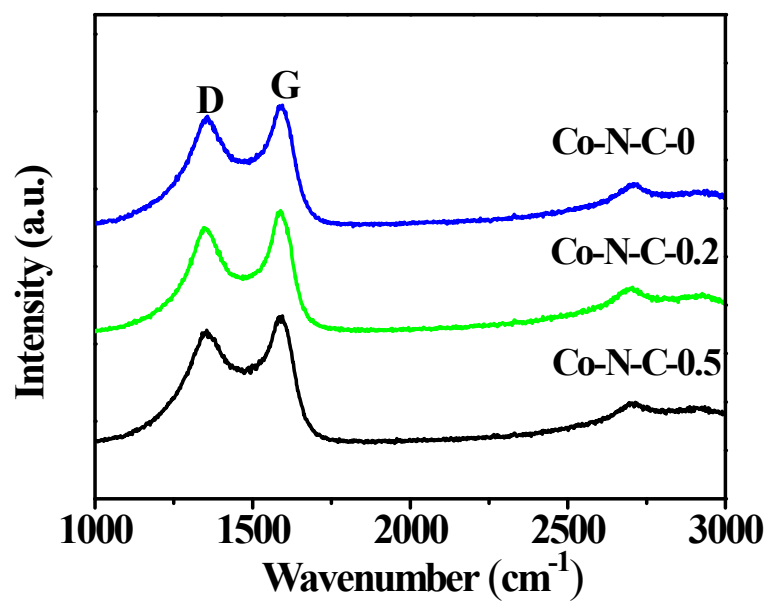


Figure S2. Raman spectra of Co-N-C-0, Co-N-C-0.2, and Co-N-C-0.5.



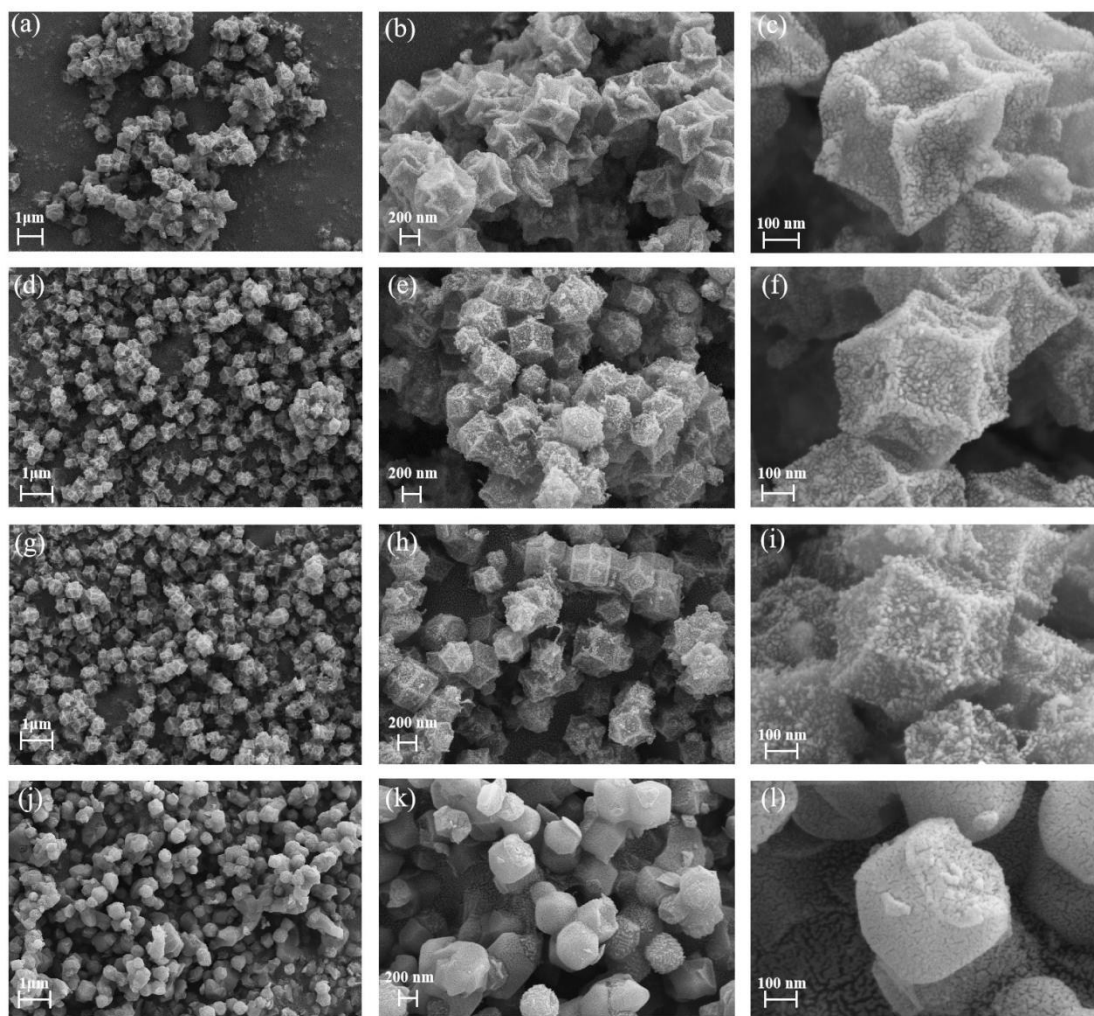


Figure S3. FESEM images of (a, b, c) Co-N-C-0; (d, e, f) Co-N-C-0.2; (g, h, i) Co-N-C-0.5; (j, k, l) Co-N-C-1.0.

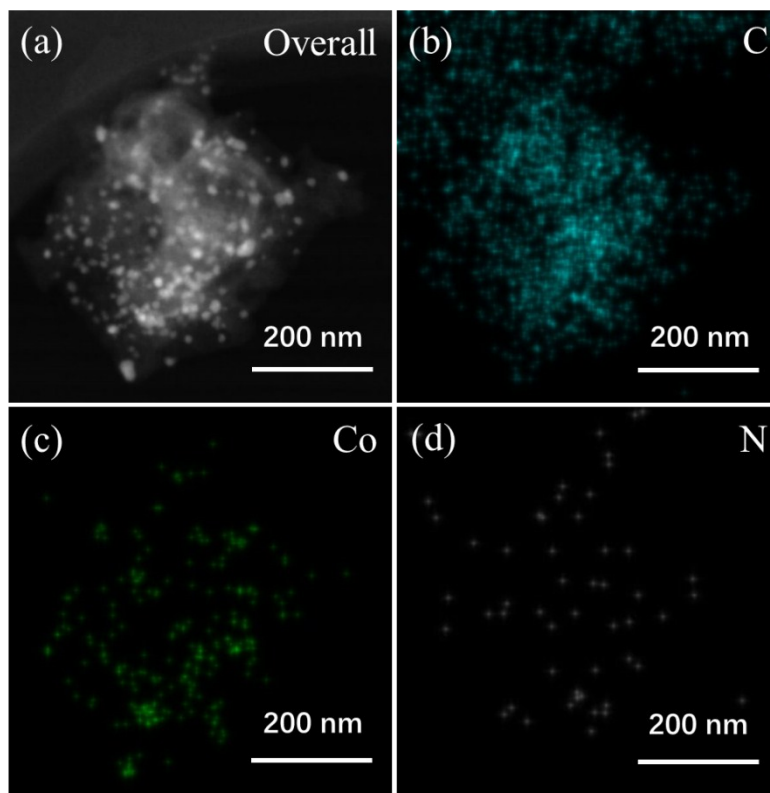


Figure S4. EDS elemental maps of Co-N-C-0.5.

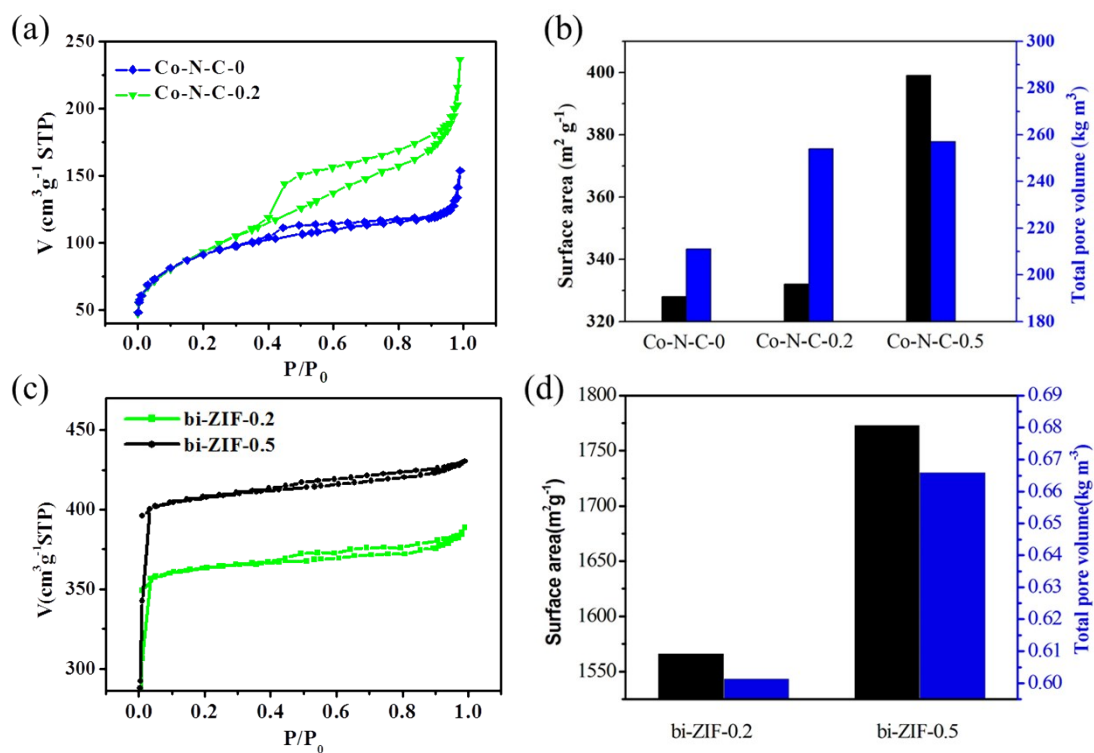


Figure S5. (a)  $N_2$  adsorption-desorption isotherms of Co-N-C-0 and Co-N-C-0.2; (b) surface area and total pore volume of Co-N-C-0, Co-N-C-0.2, and Co-N-C-0.5; (c)  $N_2$  adsorption-desorption isotherms of bi-ZIF-0.2 and bi-ZIF-0.5; (d) surface area and total pore volume of bi-ZIF-0.2 and bi-ZIF-0.5.

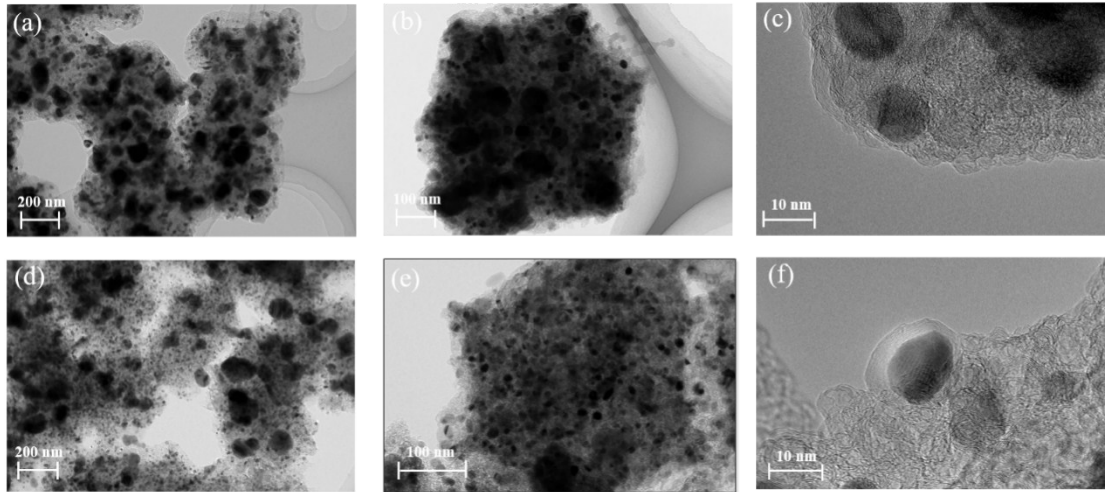


Figure S6. TEM images of (a,b,c) Co-N-C-0 and (d,e,f) Co-N-C-0.2.

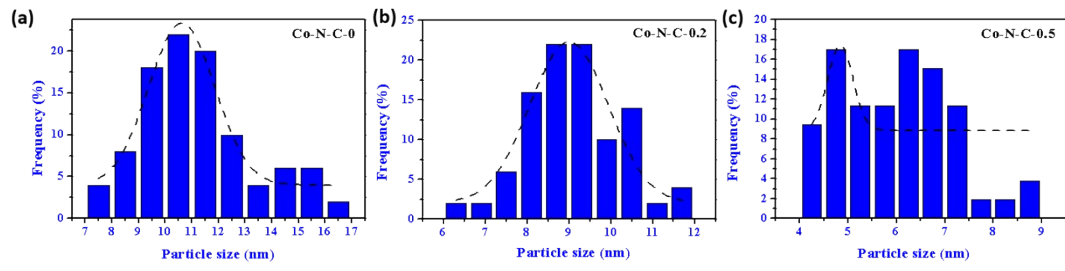


Figure S7. The size distribution of (a) Co-N-C-0; (b) Co-N-C-0.2; (c) Co-N-C-0.5.

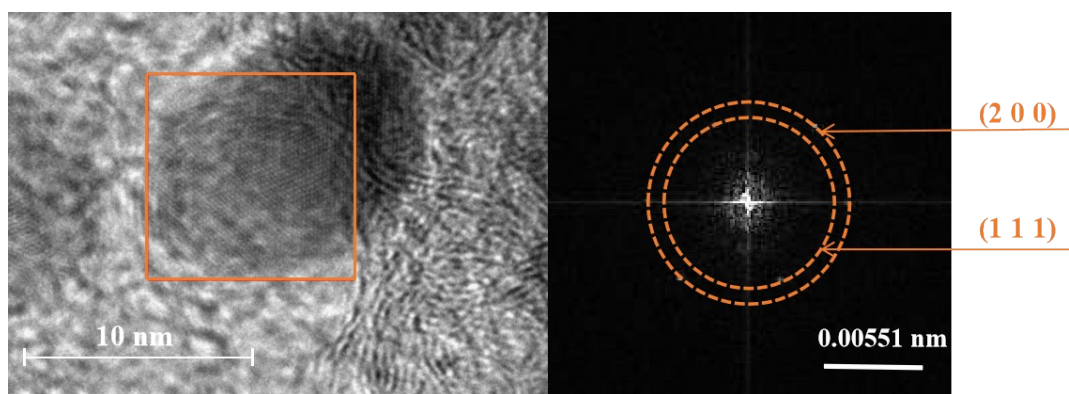


Figure S8. SAED of Co-N-C-0.5

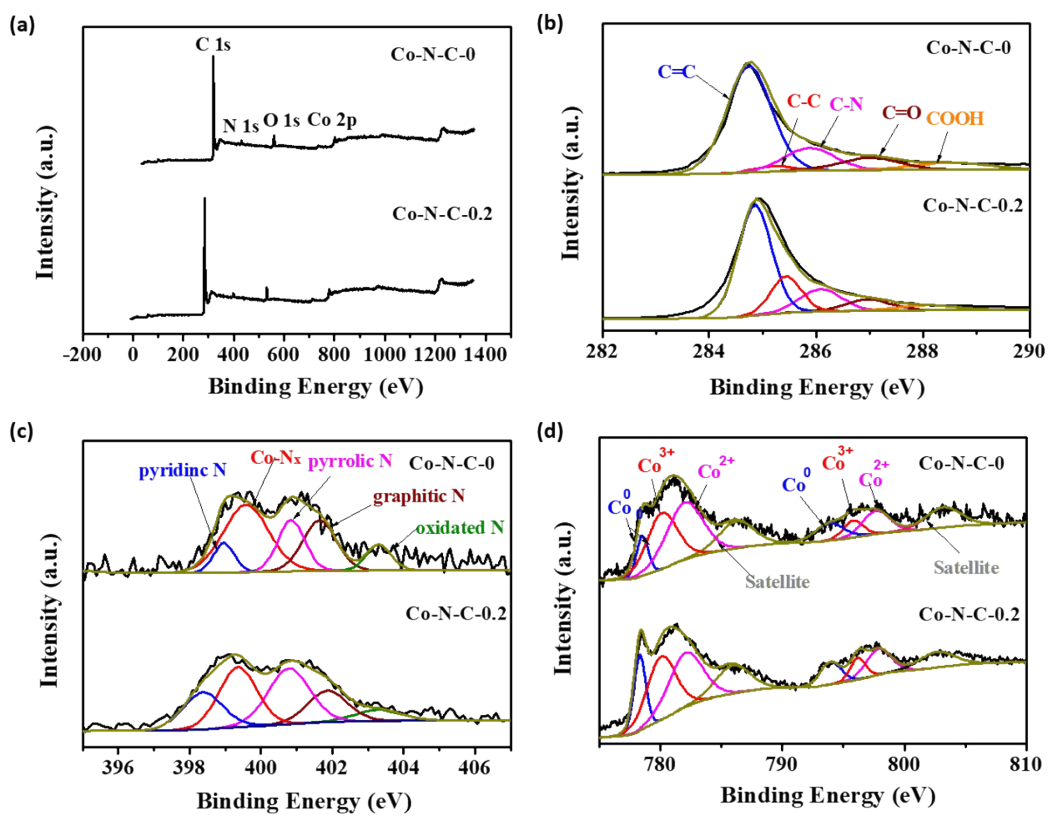


Figure S9. (a) XPS survey spectra and high-resolution spectra of (b) C 1s, (c) N 1s and (d) Co 2p of Co-N-C-0 and Co-N-C-0.5 catalysts.

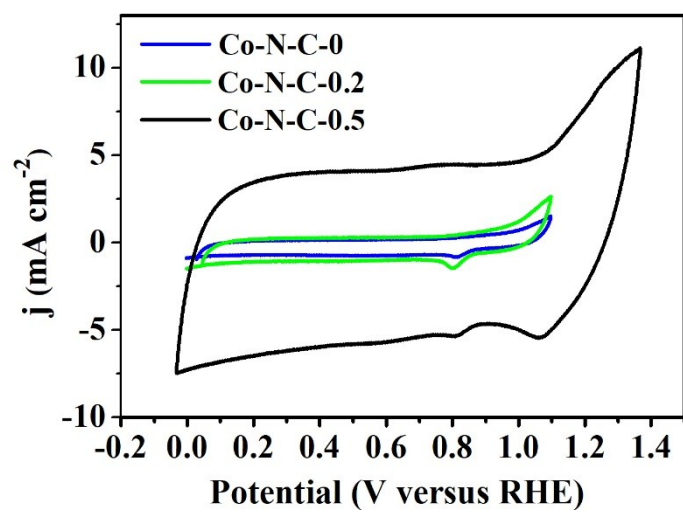


Figure S10. CV curves of different catalysts.



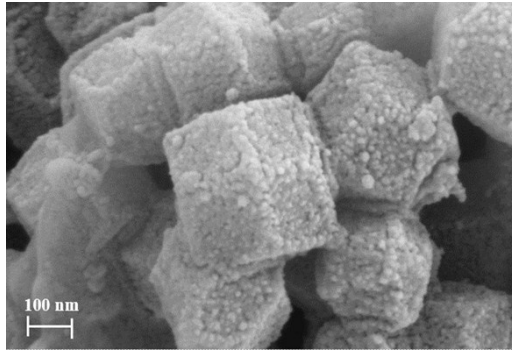


Figure S11. FESEM images of Co-N-C-0.5 after 20 cycles.

## Reference

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