Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information for

Metallic Cobalt/Cobalt Sulfide Hetero-nanostructures Embedded within N-doped Graphitic Carbon Nanocage for Hydrogen Evolution Reaction

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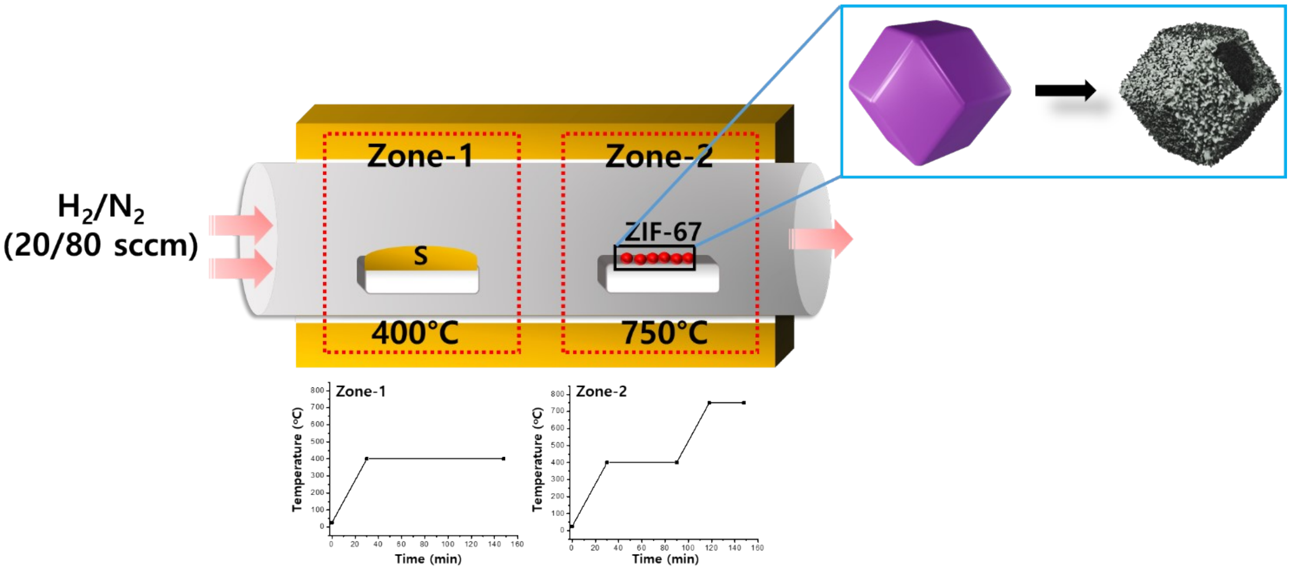

Figure S1. Schematic of fabrication of hollow nanocages composed of metallic cobalt/cobalt sulfide heterostructures embedded within N-doped graphitic carbon (Co/Co_xS_y@NC-750) through thermal annealing at 750 °C in the presence of H_2 and S.

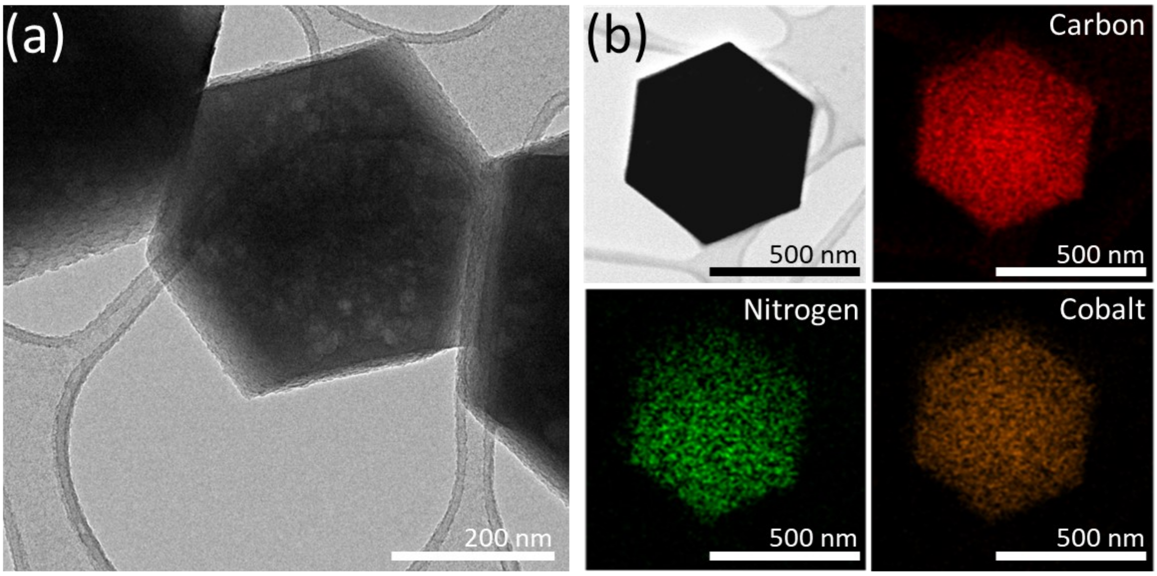

Figure S2. (a) TEM and (b) EDX mapping of ZIF-67 with C (red), N (green), and Co (orange).

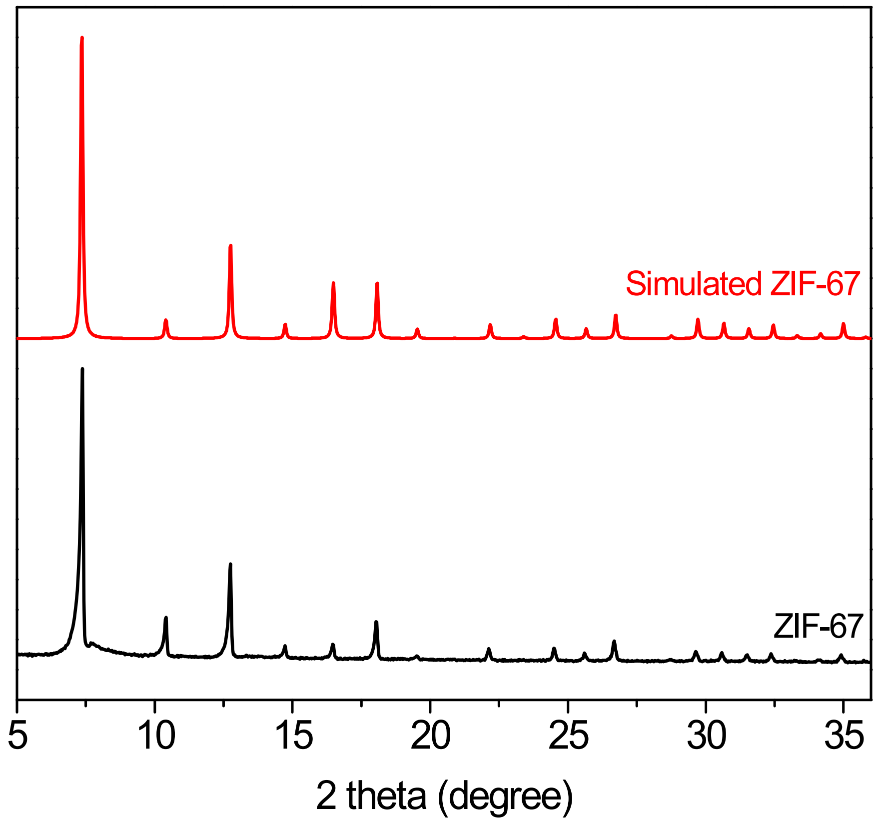

Figure S3. PXRD of ZIF-67 and its simulated pattern. The simulated PXRD data using Mercury 3.3 program.

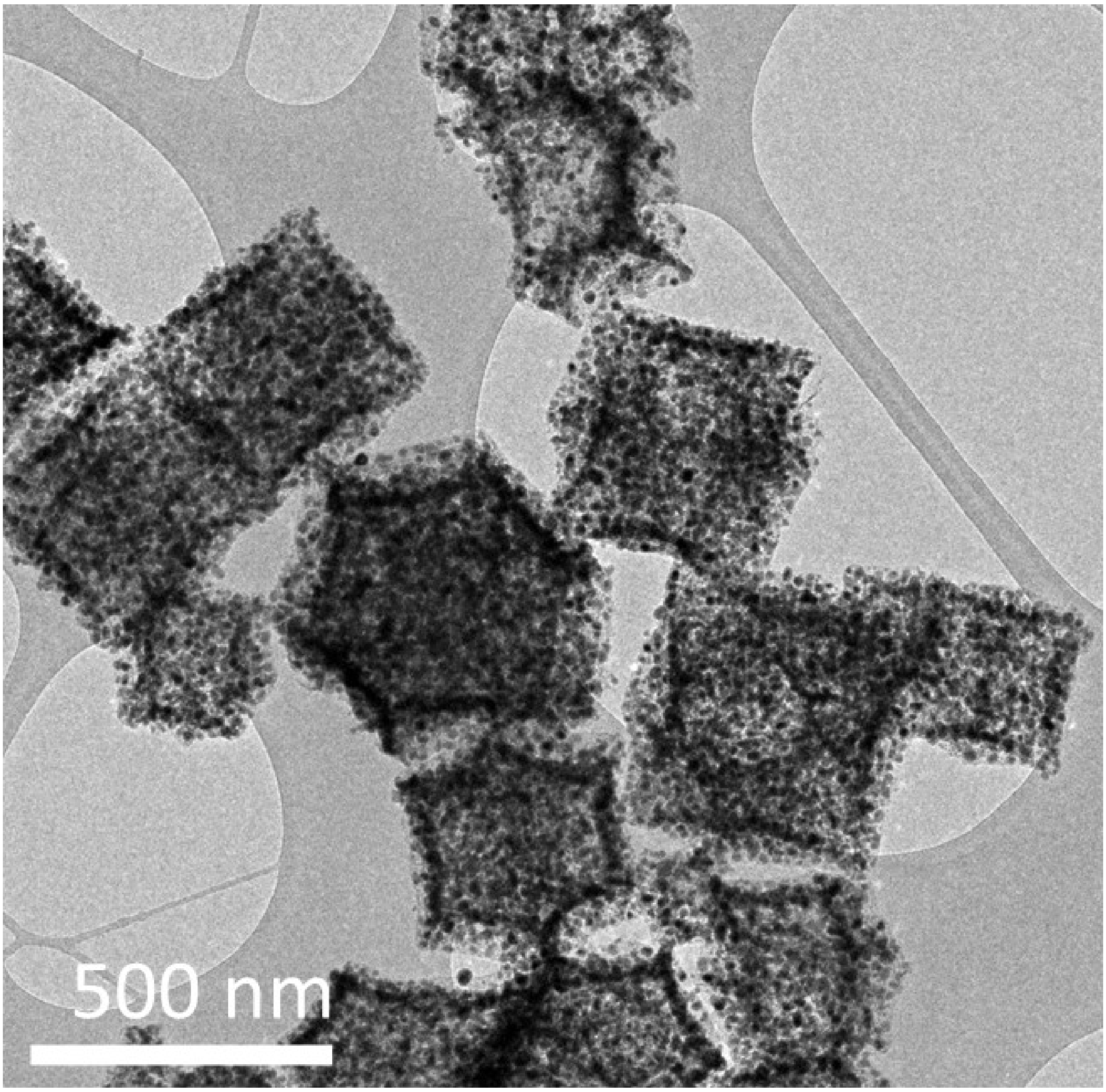

Figure S4. TEM of Co/Co_xS_y@NC-750.

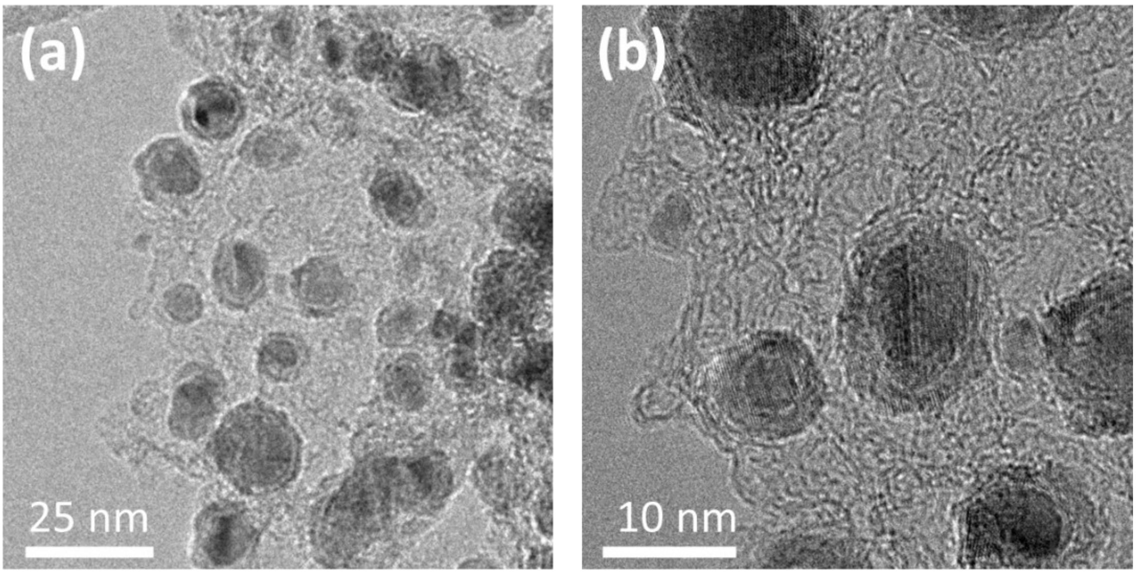

Figure S5. Higher-magnification TEM images of Co/Co_xS_y@NC-750.

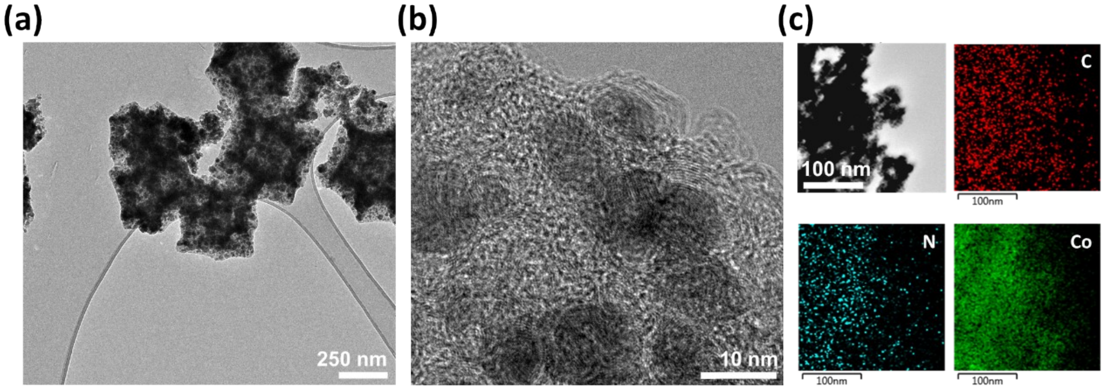

Figure S6. (a, b) TEM images and (c) EDX mapping of Co@NC. C (red), N (blue), and Co (green).

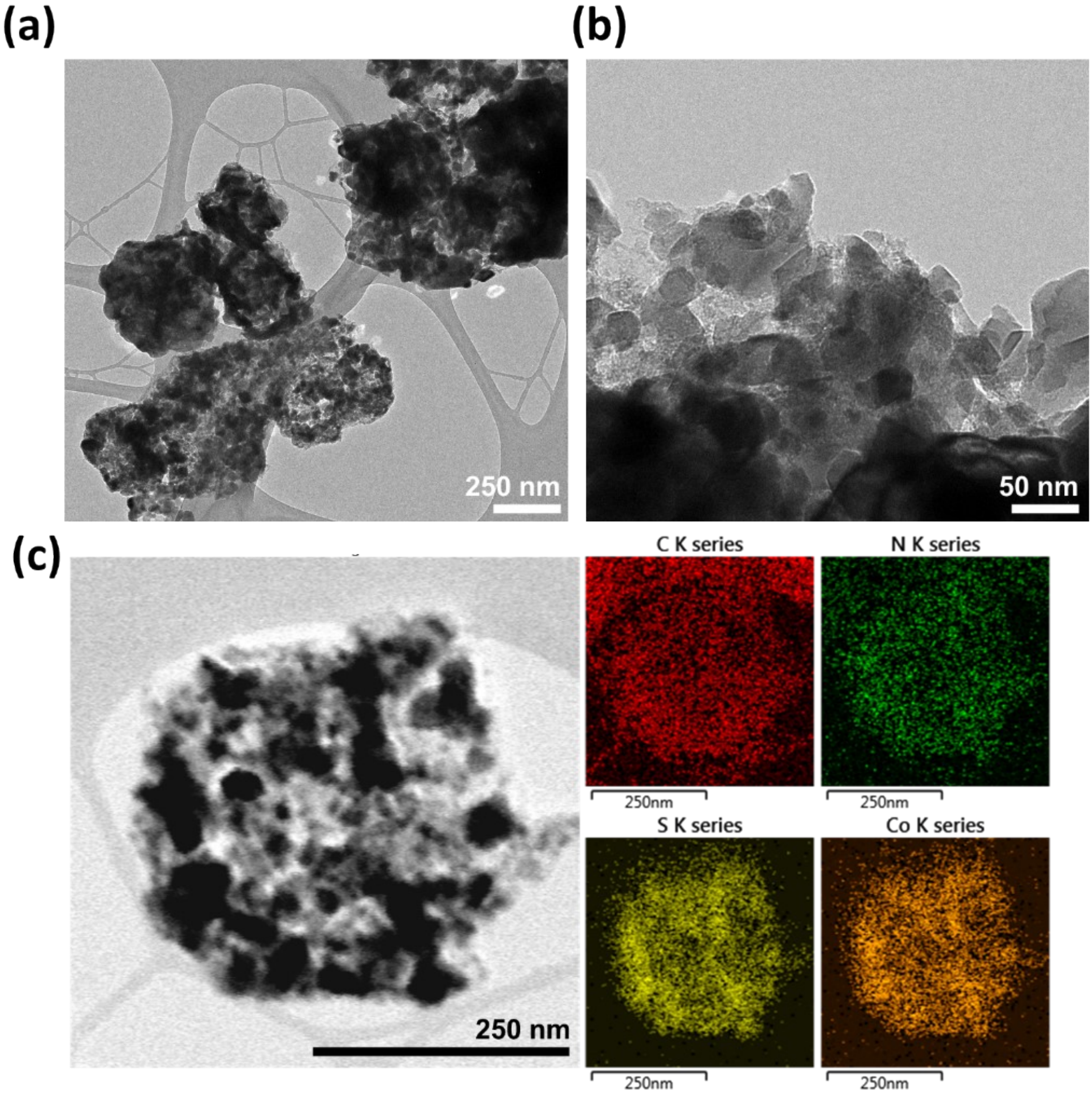

Figure S7. (a, b) TEM images and (c) EDX mapping of Co_xS_y@NC. C (red), N (green), S (yellow), and Co (orange).

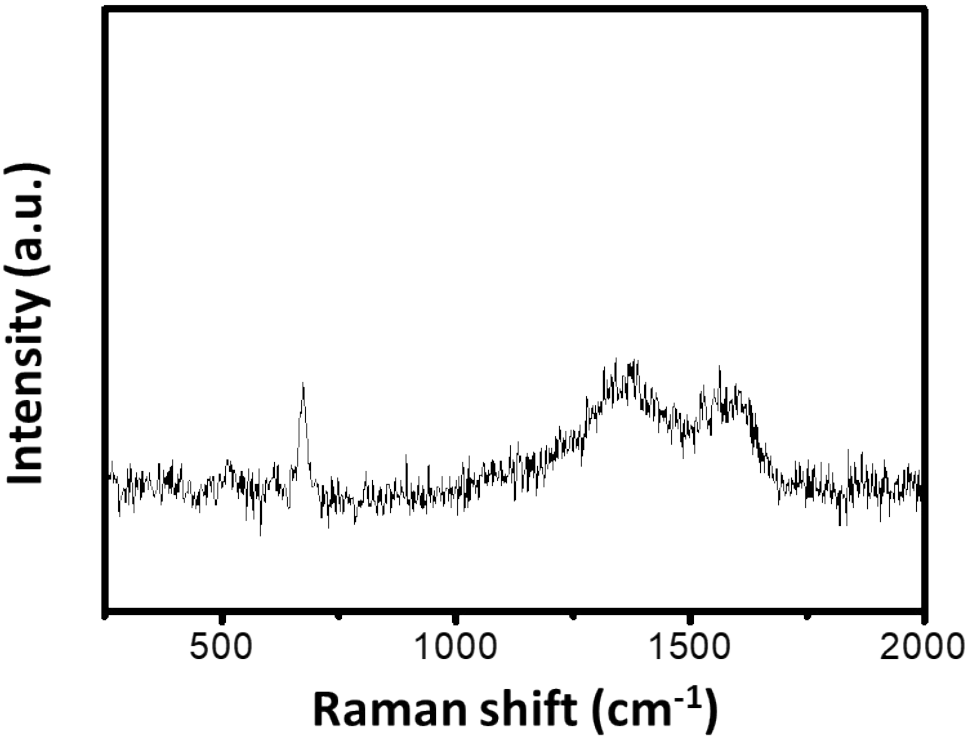

Figure S8. Raman spectrum of Co_3O_4 prepared by calcinating ZIF-67 in the air.

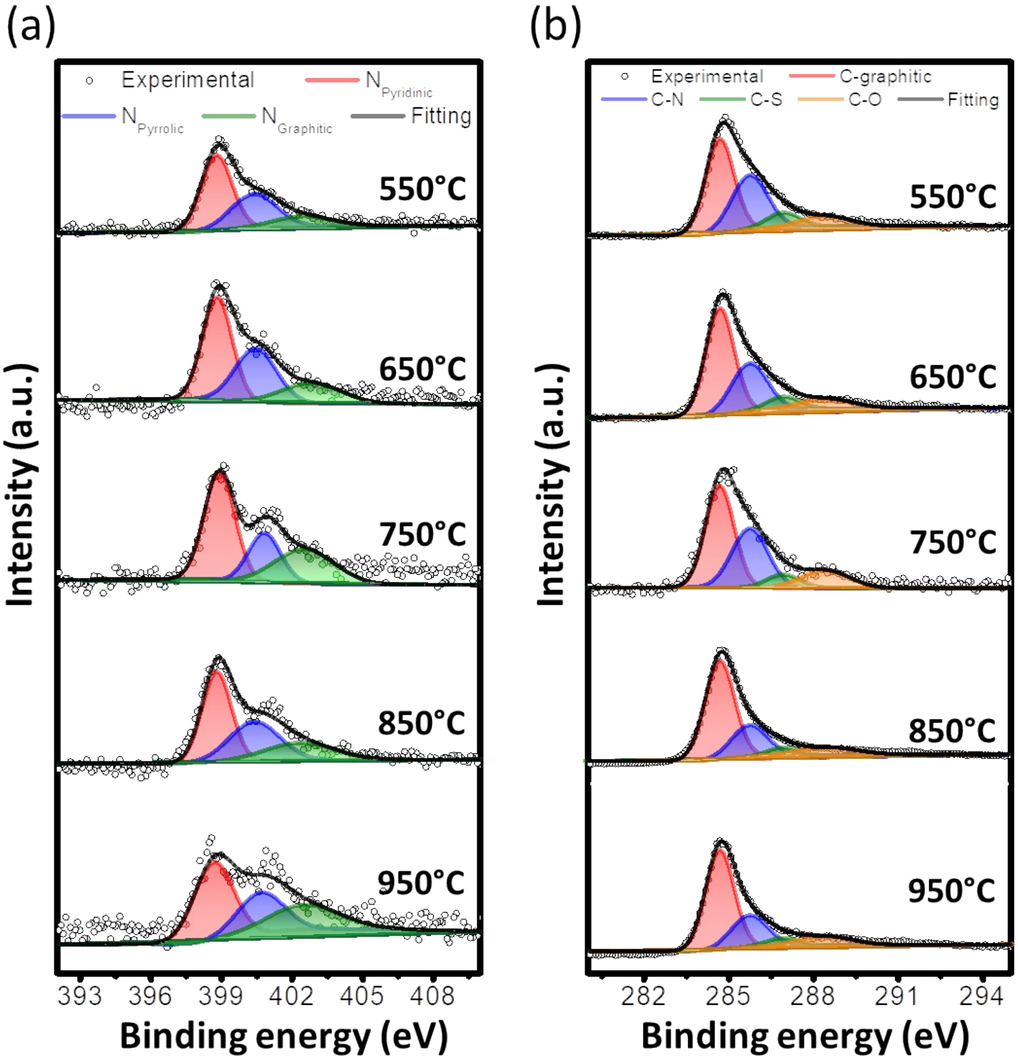

Figure S9. XPS spectra of (a) N 1s and (b) C 1s of S-*T* samples.

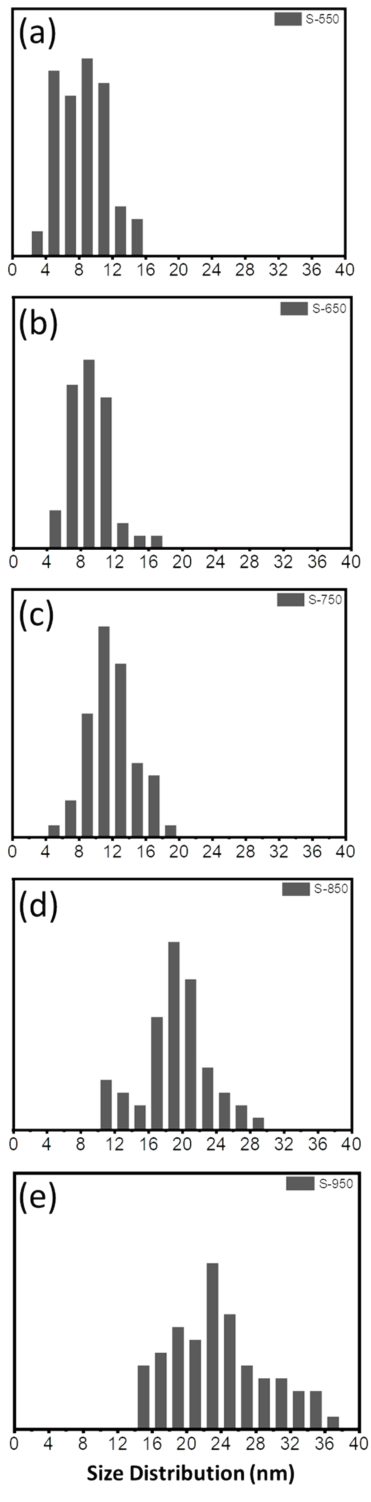

Figure S10. Size distribution of S-T sample synthesized at (a) 550 °C, (b) 650 °C, (c) 750 °C; (d) 850 °C, and (e) 950 °C.

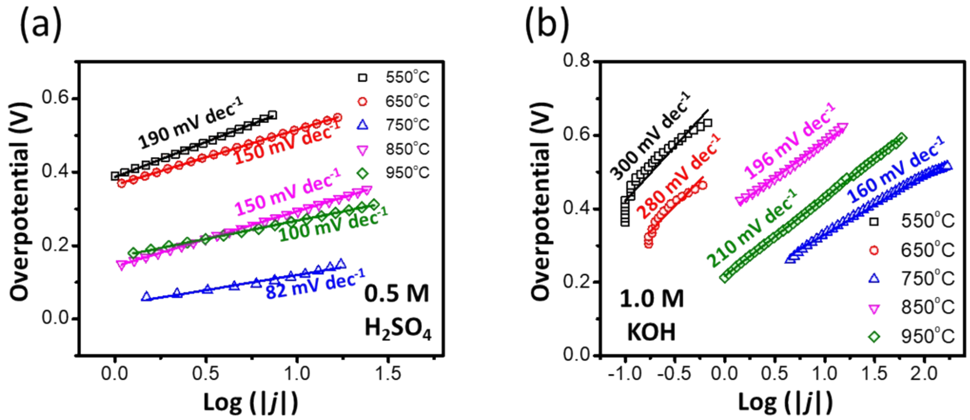

Figure S11. Tafel slope of the electrocatalysts in 0.5 M H_2SO_4 and 1.0 M KOH.

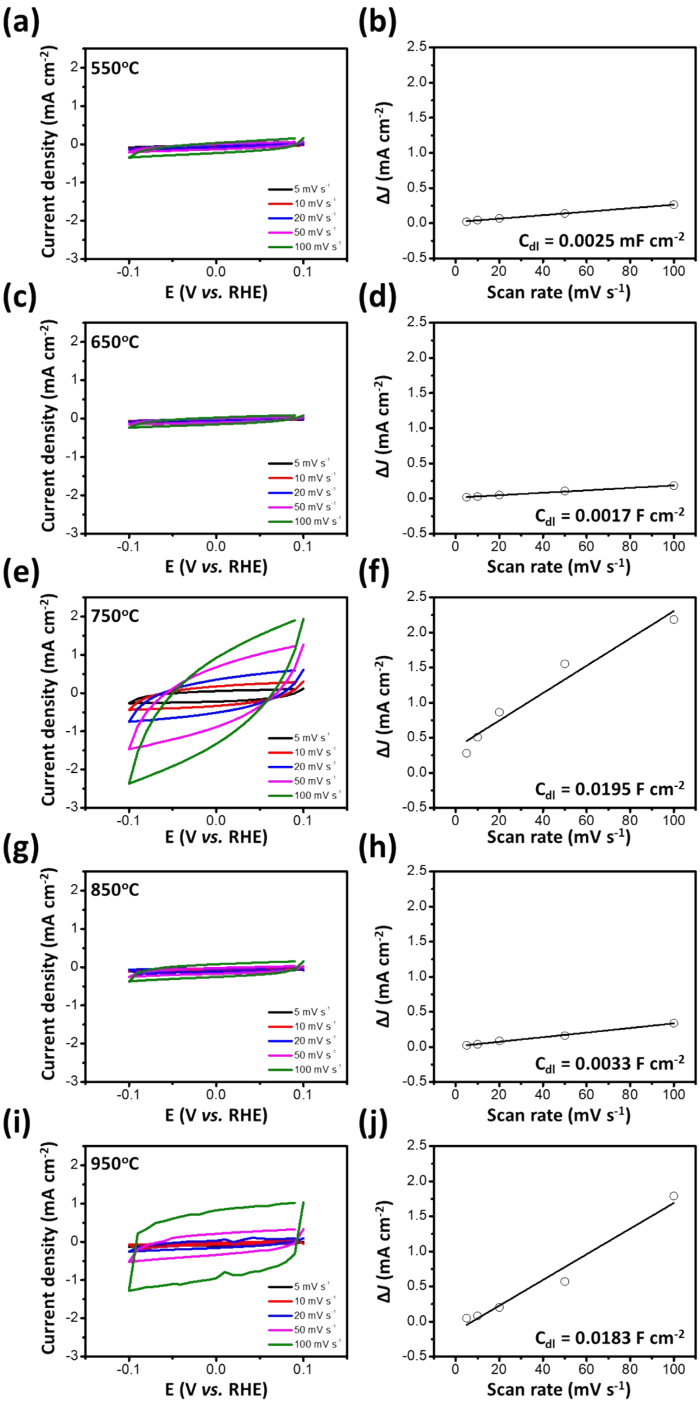

Figure S12. (a, c, e, g, i) Cyclic voltammetry and (b, d, f, h, j) Fitting plots of Δ*J* versus scan rates for *S*-*T* samples obtained at different temperatures.

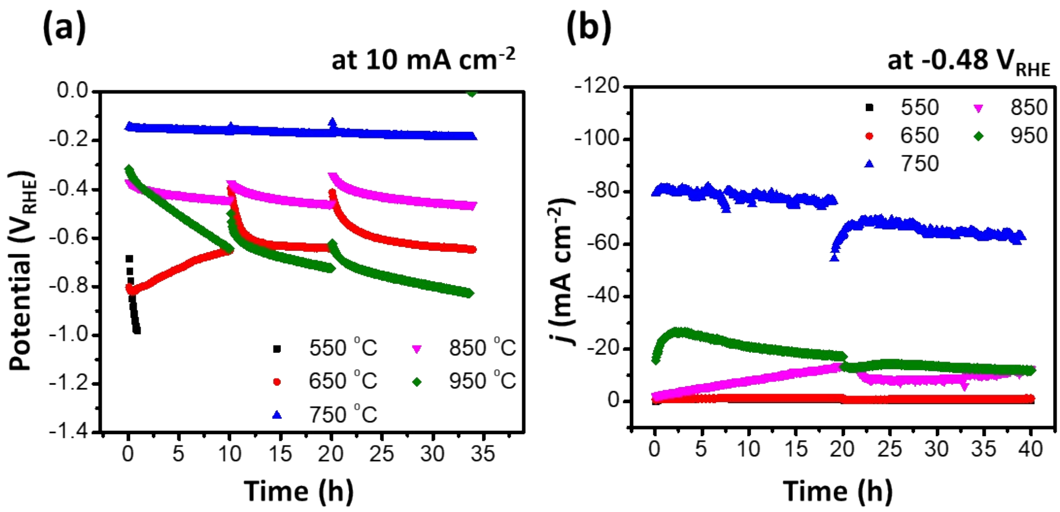

Figure S13. Stability of the sample obtained at different temperatures: 550 to 950 °C in (a) 0.5 M H_2SO_4 and (b) 1.0 M KOH. Noted that: S-750 and Co/Co_xS_y@NC-750 refer to the similar sample.

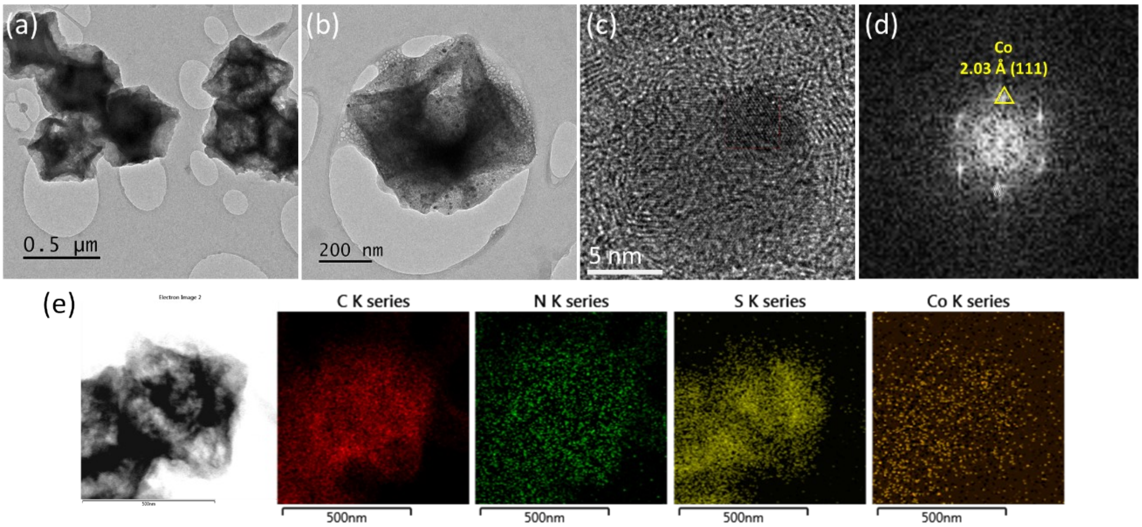

Figure S14. (a, b, c) TEM, (d) FFT, and (e) EDX mapping of Co/Co_xS_y@NC-750 after long-term stability test in 0.5 M H_2SO_4.

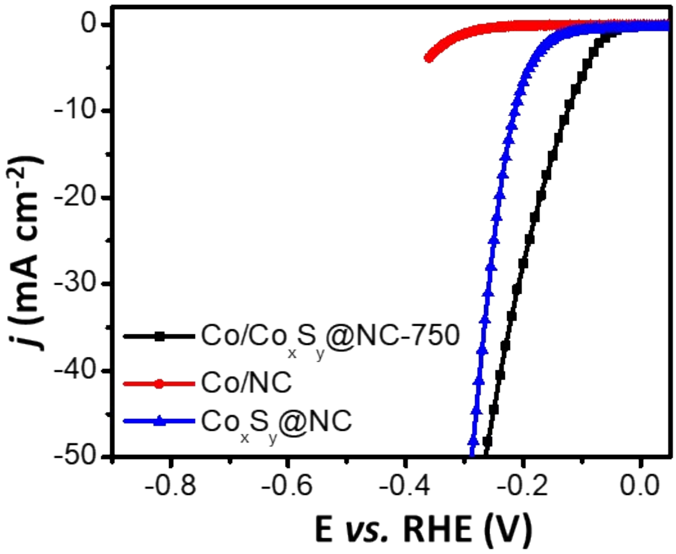

Figure S15. Comparison of HER performance of Co/Co_xS_y@NC-750 versus Co/NC and Co_xS_y/NC in 0.5 M H_2SO_4.

Table S1. Composition of Co^0, Co^{II}, and Co^{III} species in *S-T* samples determined from XPS.

Samples	**Co^0**	**Co^{II}**	**Co^{III}**
S-*550*	12.9	26.4	60.7
S-*650*	26.7	20.9	52.4
S-*750* (Co/Co_xS_y@NC-750)	28.3	26.1	45.7
S-*850*	23.8	19.0	57.2
S-*950*	0	16.5	83.5

Table S2. Performance of earth-abundant MOF-derived HER catalysts.

Sample	Overpotential	Tafel slope	electrolyte	Ref.
Co/Co_xS_y@NC-750	**η_{10} = 130 mV**	**82 mV/dec**	**0.5M H_2SO_4**	**This work**
Co/Co_xS_y@NC-750	**η_{10} = 330 mV**	**160 mV/dec**	**1.0M KOH**	**This work**
Ir-COF@ZIF_{800}	η_{10} = 48 mV	44 mV/dec	0.5M H_2SO_4	[1]
CoS_2@NSC	η_{10} = 95 mV	69 mV/dec	0.5M H_2SO_4	[2]
CPCS8	η_{10} = 156 mV	74 mV/dec	0.5M H_2SO_4	[3]
ZnCo-11-NC	η_{10} = 213 mV	77 mV/dec	0.5M H_2SO_4	[4]
$Fe_{0.39}Co_{0.61}S_2$/rGO	η_{10} = 198 mV	94 mV/dec	0.5M H_2SO_4	[5]
Sn-CoS_2/CC	η_{10} = 161 mV	94 mV/dec	0.5M H_2SO_4	[6]
Co@NC/B-NCNTS	η_{10} = 182 mV	105 mV/dec	0.5M H_2SO_4	[7]
Co-NC@Mo_2C	η_{10} = 143 mV	60 mV/dec	0.5M H_2SO_4	[8]
CoP@NC/GR	η_{10} = 105 mV	47.5 mV/dec	0.5M H_2SO_4	[9]
Ni_2P/Ni@C	η_{10} = 149 mV	61.2 mV/dec	0.5M H_2SO_4	[10]
Co_3O_4/C	η_{10} = 194.8 mV	71.6 mV/dec	0.5M H_2SO_4	[11]
Pd-CoS_2MoS_2/C-600	η_{10} = 144 mV	59.9 mV/dec	0.5M H_2SO_4	[12]
MoS_2/CoS_2 NTs	η_{10} = 90 mV	30 mV/dec	0.5M H_2SO_4	[13]
$NiRu_2$@NC-600	η_{10} = 85 mV	45.54 mV/dec	0.5M H_2SO_4	[14]
rePCN-222(Hf)-700	η_{10} = 31.6 mV	22 mV/dec	0.5M H_2SO_4	[15]

CoSP/NC	η_{10} = 183 mV	64.25 mV/dec	1.0M KOH	[16]
Co-M-Fe/Ni	η_{10} = 149 mV	65 mV/dec	1.0M KOH	[17]
Co@N-SC/N-HCP@CC	η_{10} = 66 mV	65 mV/dec	1.0M KOH	[18]
CoS_2QDs@rGO	η_{10} = 287 mV	78 mV/dec	1.0M KOH	[19]
CoP/CNTHPs	η_{10} = 147 mV	78.1 mV/dec	1.0M KOH	[20]
Co-S-P/CC	η_{10} = 167 mV	86mV/dec	1.0M KOH	[21]
CoNiP/CoNi/N-rGO	η_{10} = 150 mV	47.51 mV/dec	1.0M KOH	[22]
HNi/NiO/C	η_{10} = 87 mV	91.7 mV/dec	1.0M KOH	[23]
Ru-MoO_2@PC/rGO	η_{10} = 126 mV	43.5 mV/dec	1.0M KOH	[24]
Ni@NC-600	η_{10} = 180 mV	120 mV/dec	1.0M KOH	[25]
Fe-Ni@NC-CNTs	η_{10} = 202 mV	113.7 mV/dec	1.0M KOH	[26]
ZnSP/NC	η_{10} = 171 mV	54.78 mV/dec	1.0M KOH	[27]
Co/Ni@GC/NCNTs/CN	η_{10} = 150 mV	86 mV/dec	1.0M KOH	[28]
Co/Ni-MOFs@P	η_{10} = 194 mV	58.3 mV/dec	1.0M KOH	[29]
Co/Ni-MOFs@Se	η_{10} = 247 mV	88.9 mV/dec	1.0M KOH	[29]

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