Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

-Electronic Supplementary Information-

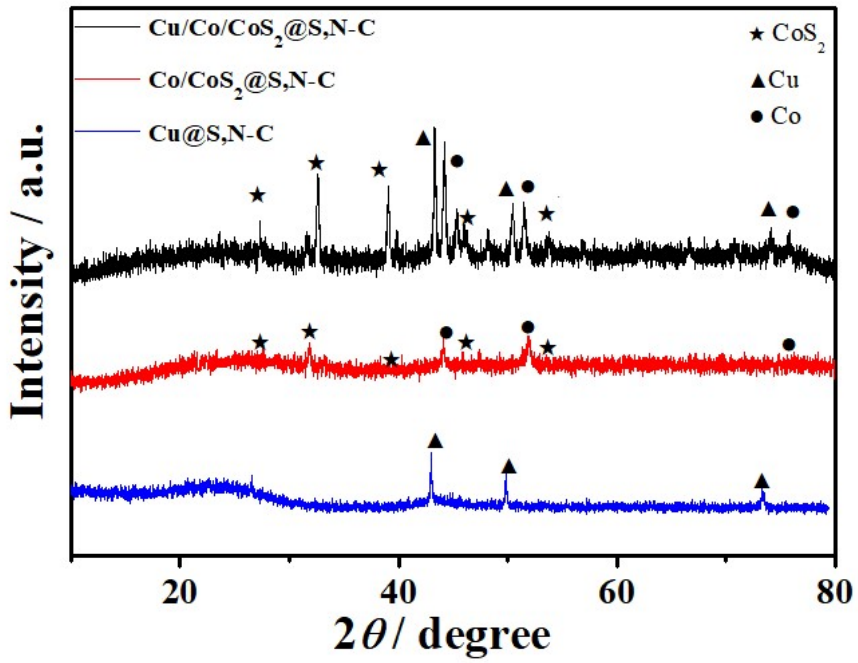

Figure S1. XRD pattern of as-prepared Cu/Co/CoS_2@S,N-C, Co/CoS_2@S,N-C, Cu@S,N-C.

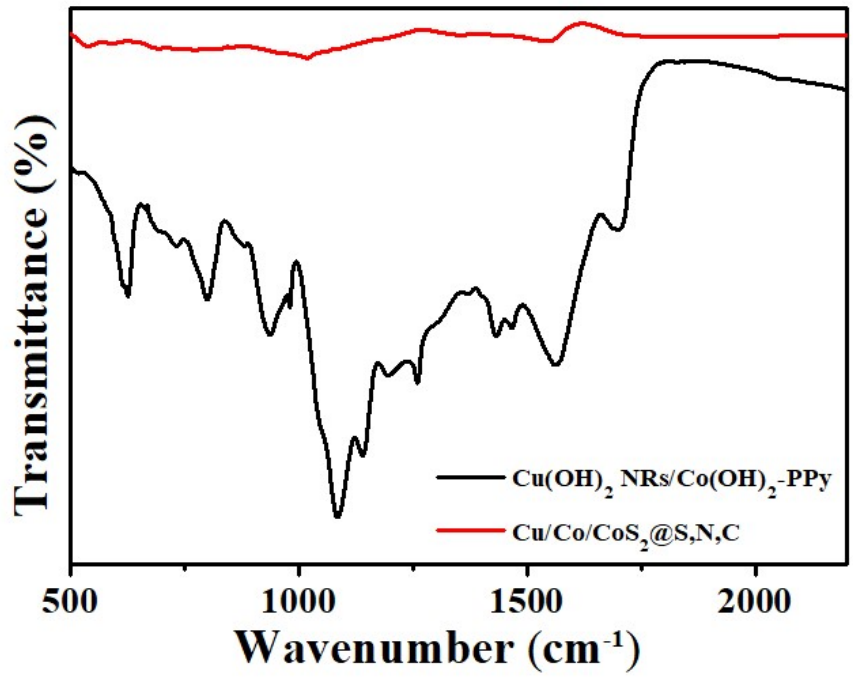

Figure S2. FTIR spectra of $Cu(OH)_2$ NRs/$Co(OH)_2$ NSs-PPy and Cu/Co/CoS_2@S,N-C.

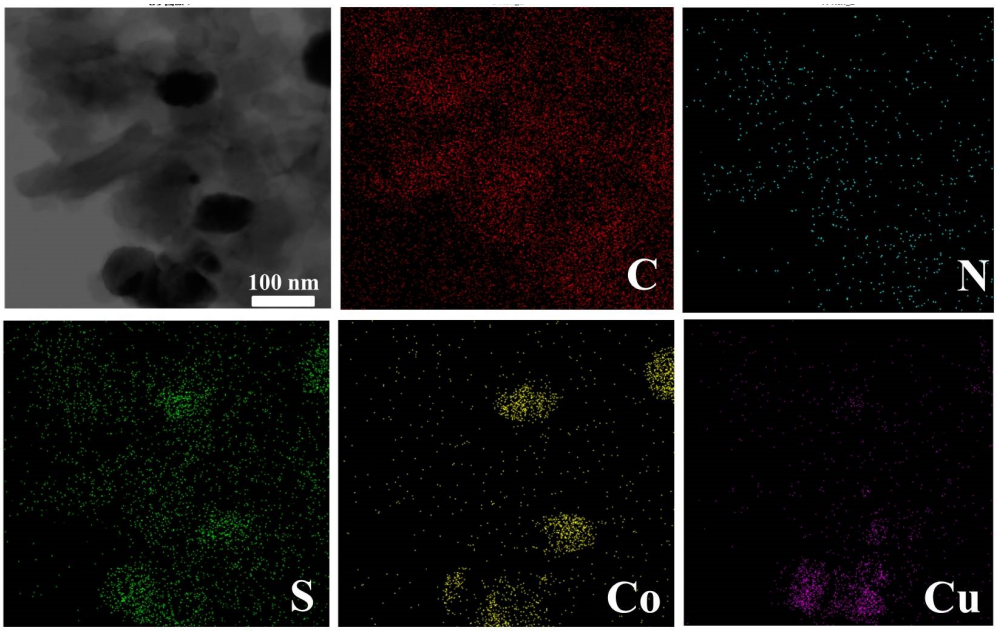

Figure S3. The corresponding elemental mapping images for C, N, S, Cu and Co of Cu/Co/CoS_2@S,N-C.

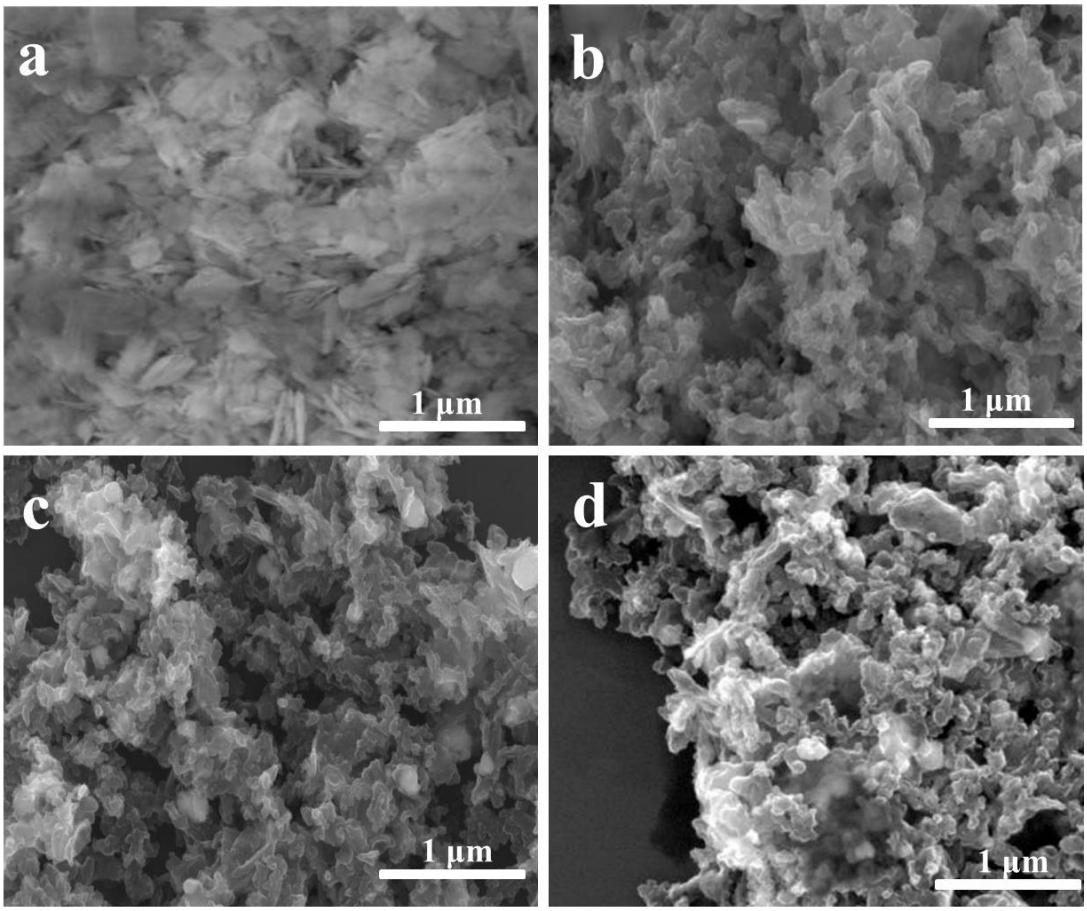

Figure S4. SEM images of (a) $Cu(OH)_2$ NRs/$Co(OH)_2$ NSs, (b) $Cu(OH)_2$ NRs/$Co(OH)_2$ NSs-PPy, (c) Cu/Co/CoS_2@S,N-C and (d) Cu/Co/CoS_2@S,N-C after 30000 s.

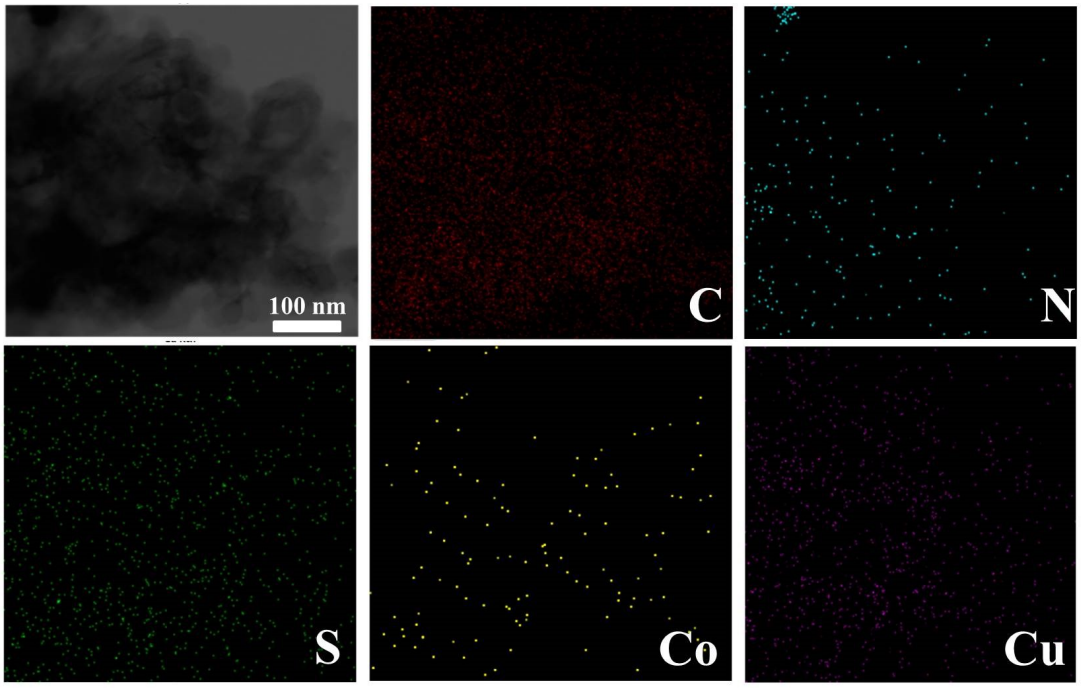

Figure S5. The corresponding elemental mapping images for C, N, S, Cu and Co of Cu/Co/CoS_2@S,N-C after 30000 s.

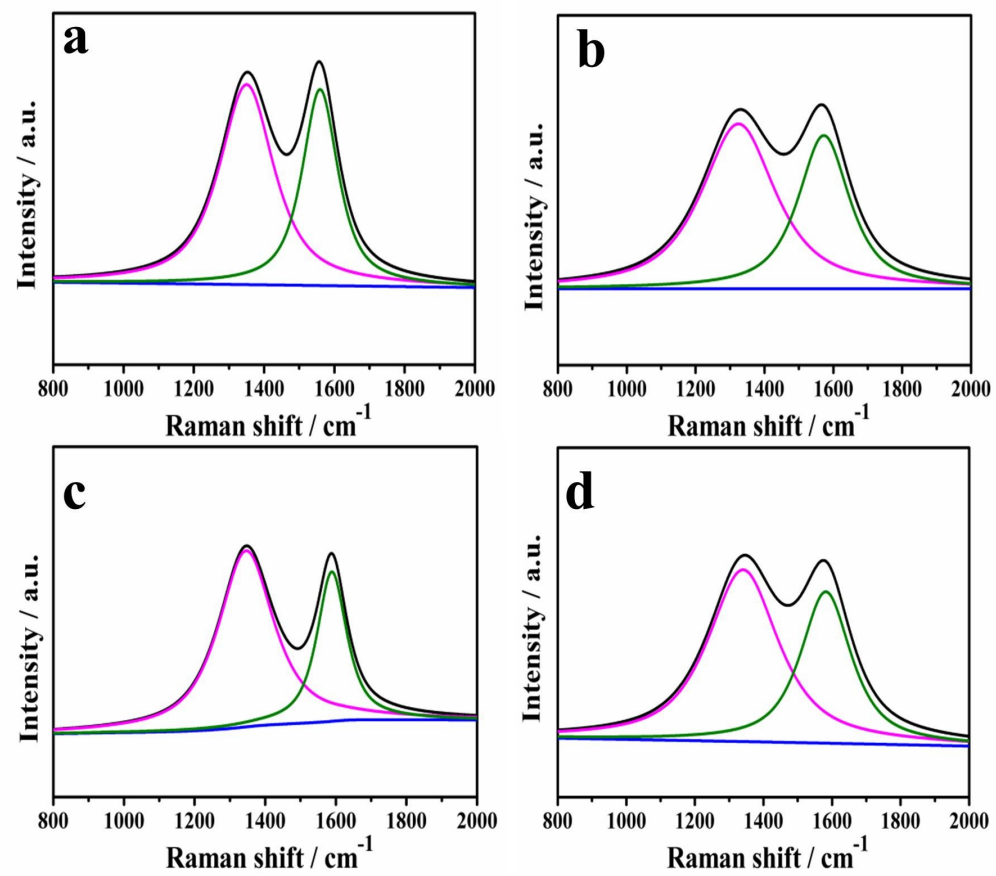

Figure S6. Raman spectra of Cu/Co/CoS_2@S,N-C-900 (a), Cu/Co/CoS_2@S,N-C-1100 (b), Cu/Co/CoS_2@S,N-C (1 mg), Cu/Co/CoS_2@S,N-C (20 mg).

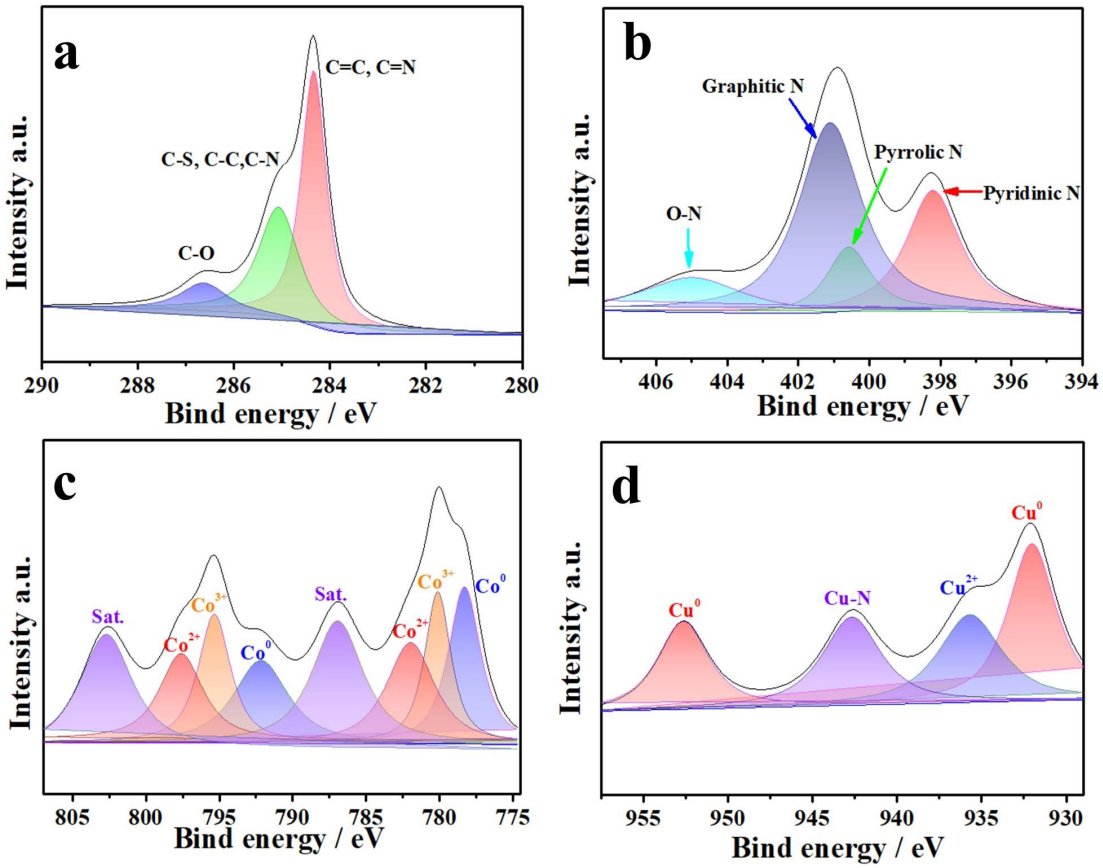

Figure S7. High-resolution C 1s (a), N 1s (b), Co 2p (c), Cu 2p (d), spectra of Cu/Co/@NC.

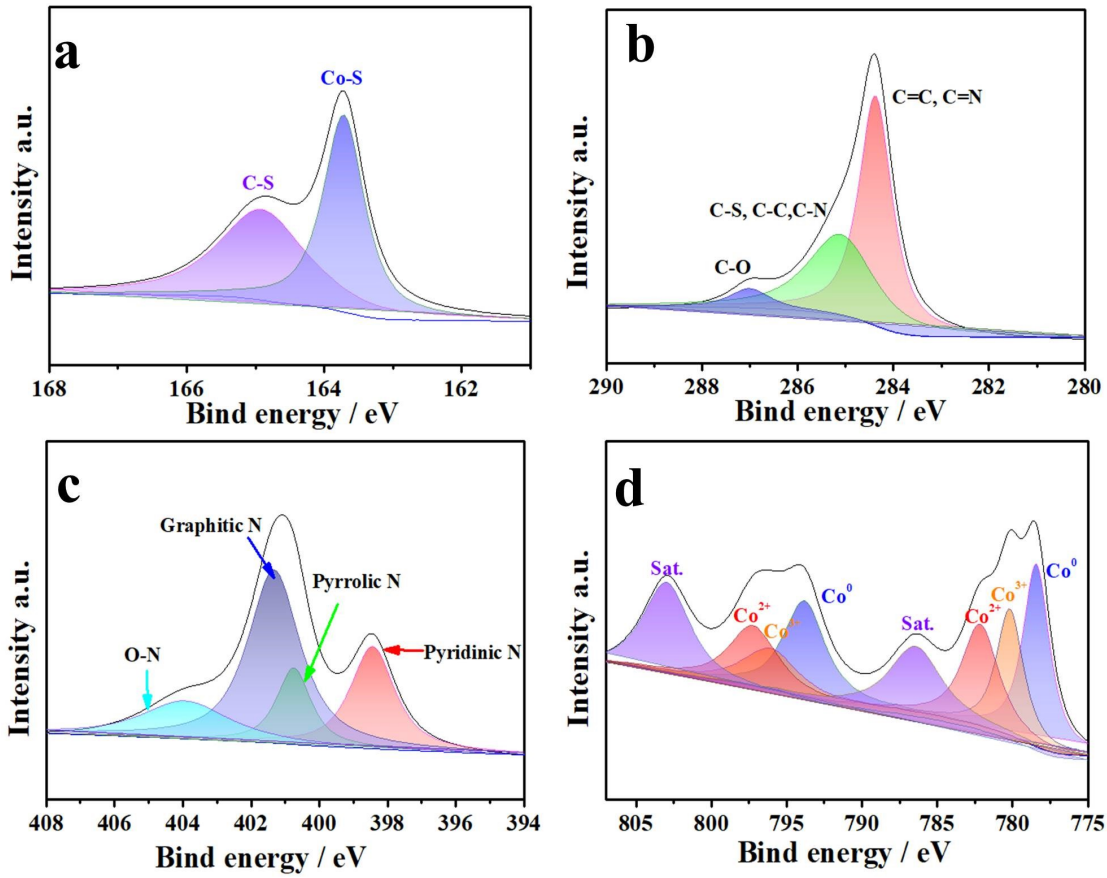

Figure S8. High-resolution S 1s (d), C 1s (a), N 1s (b), Co 2p (c), spectra of Co/CoS_2@S,N-C.

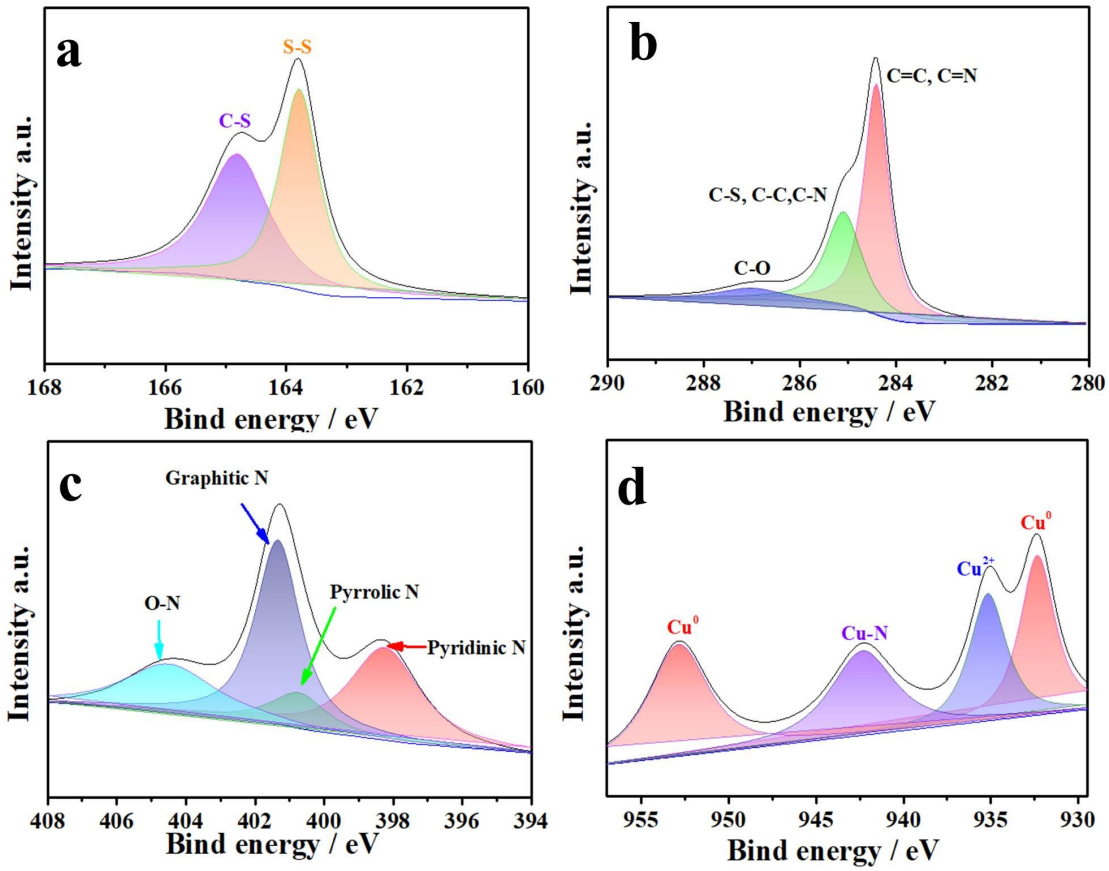

Figure S9. High-resolution S 1s (d), C 1s (a), N 1s (b), Co 2p (c), spectra of Cu@S,N-C.

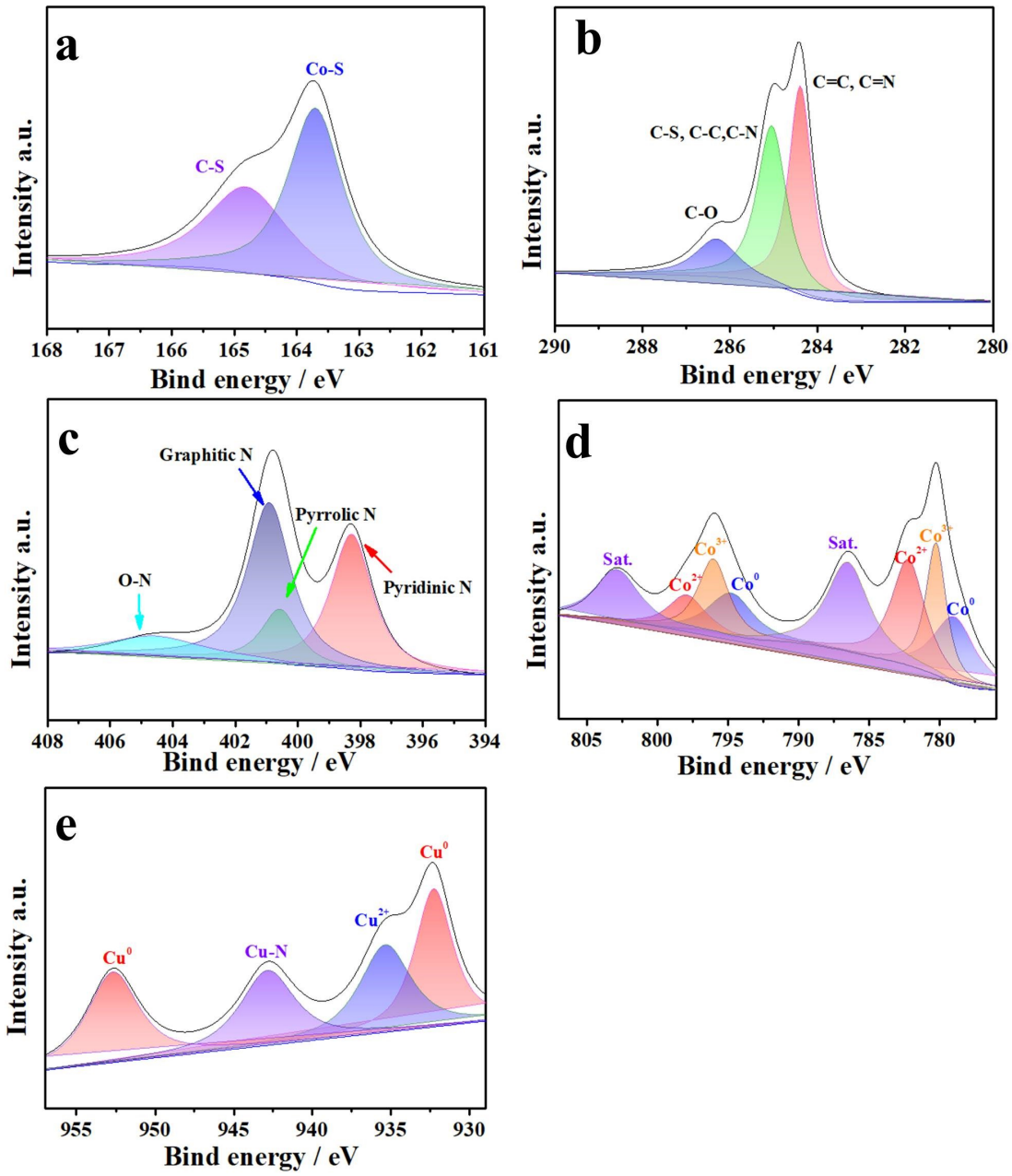

Figure S10. High-resolution S 1s (d), C 1s (a), N 1s (b), Co 2p (c), spectra of Cu/Co/CoS_2@S,N-C-900.

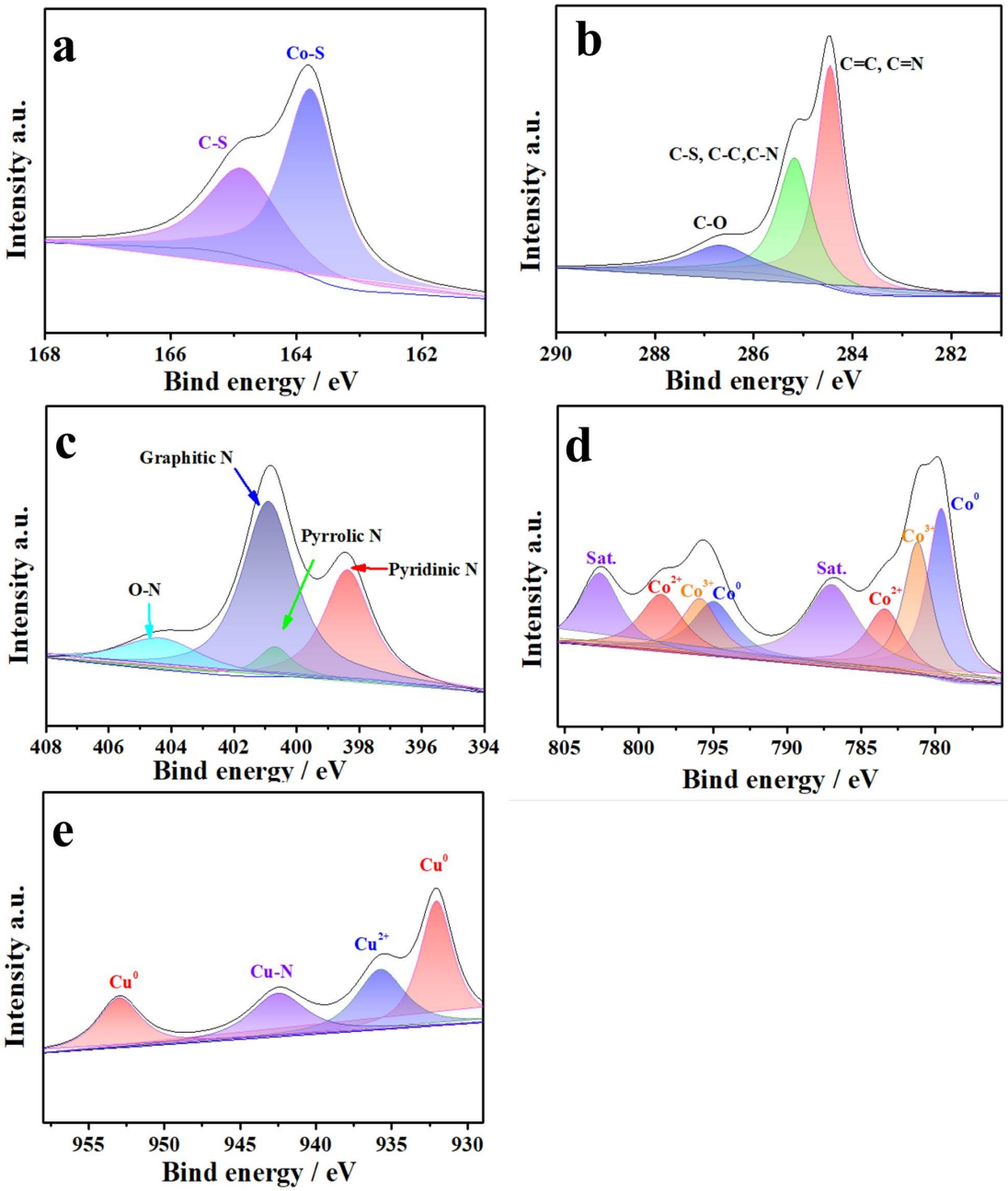

Figure S11. High-resolution S 1s (d), C 1s (a), N 1s (b), Co 2p (c), spectra of Cu/Co/CoS_2@S,N-C-1100.

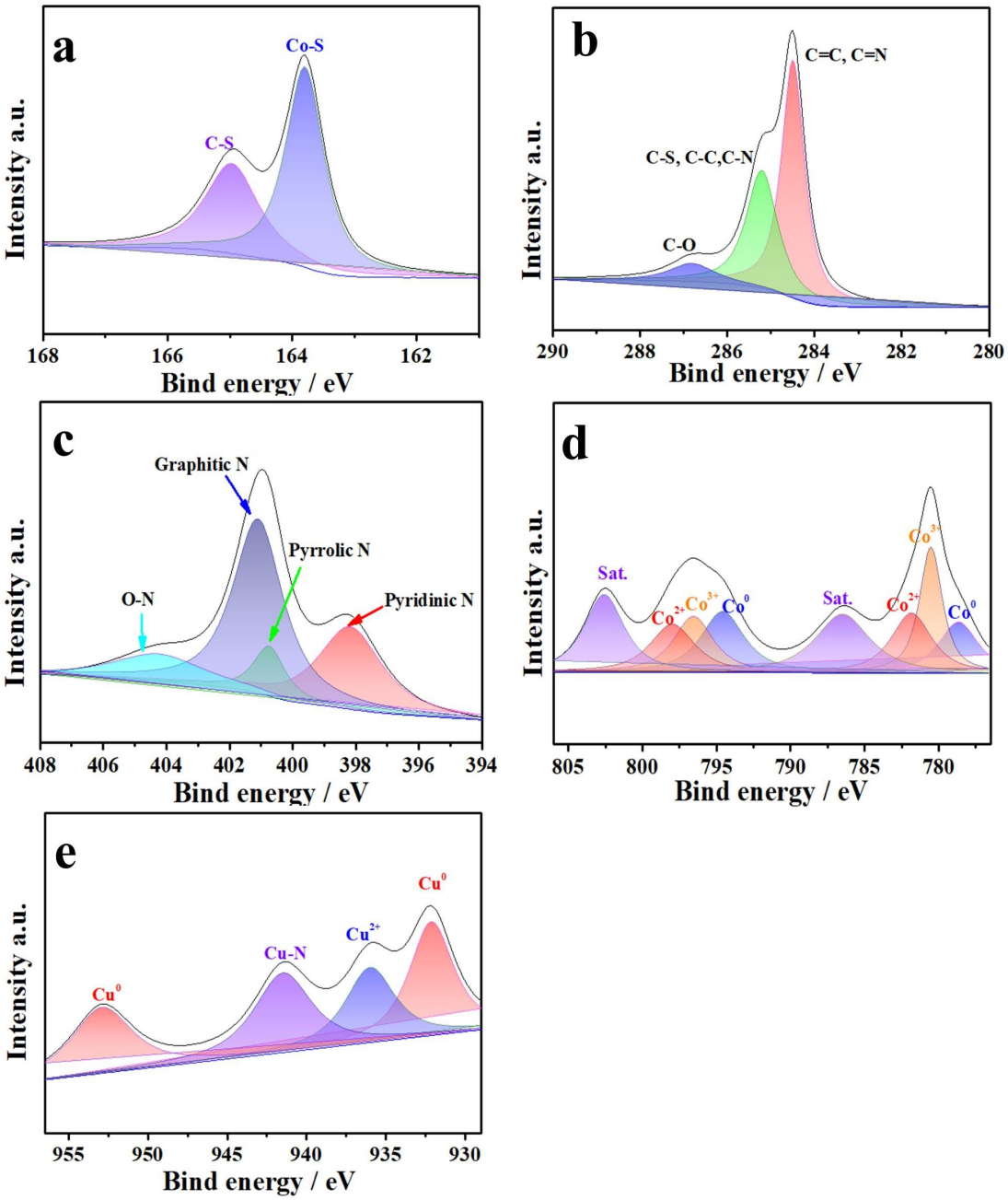

Figure S12. High-resolution S 1s (d), C 1s (a), N 1s (b), Co 2p (c), spectra of Cu/Co/CoS_2@S,N-C (5 mg).

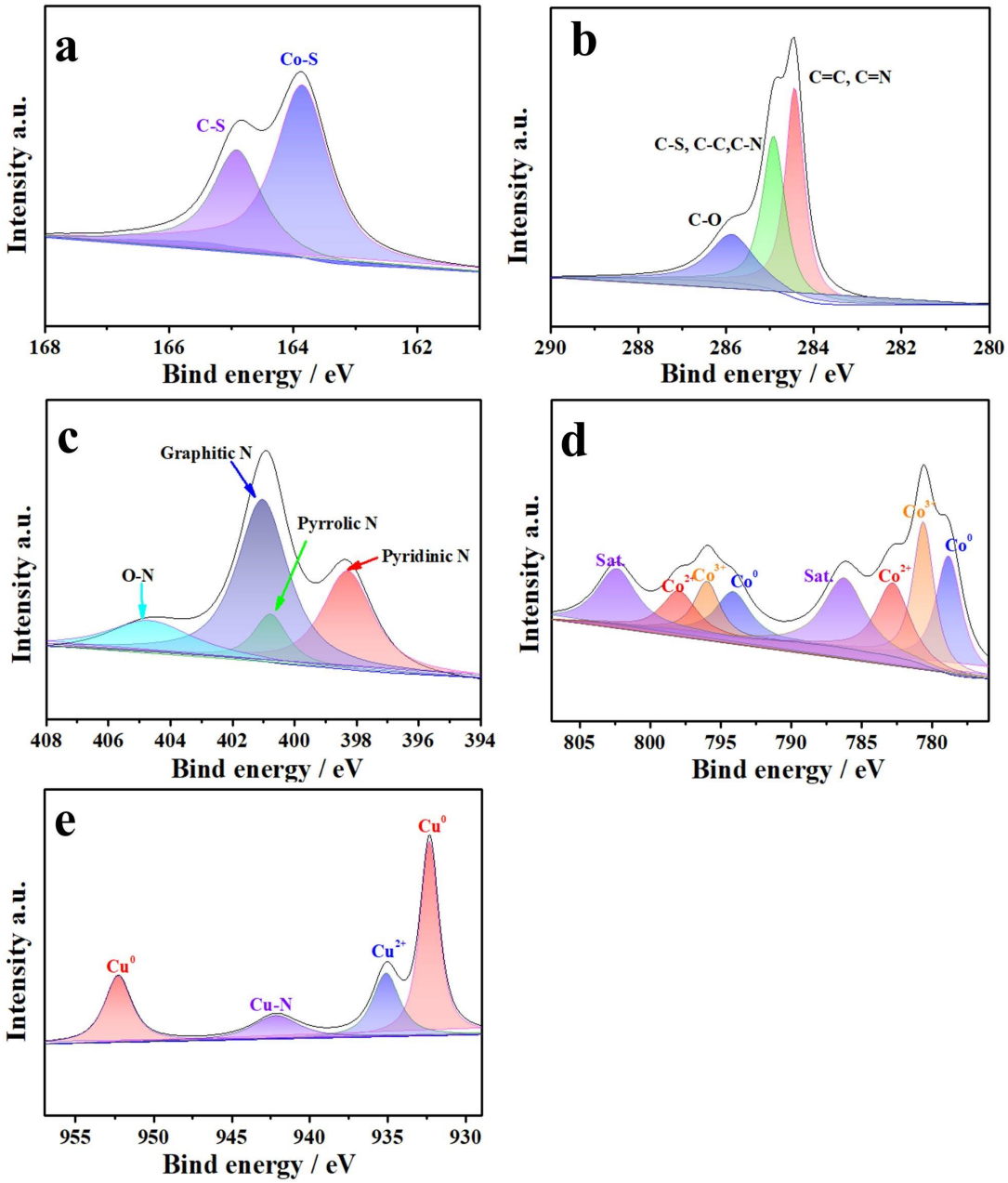

Figure S13. High-resolution S 1s (d), C 1s (a), N 1s (b), Co 2p (c), spectra of Cu/Co/CoS_2@S,N-C (100 mg).

Table S1 Pyridinic N & graphitic N dopant, sp^2C content and the I_D/I_G value of $Cu/Co/CoS_2$@S,N-C, $Cu/Co/CoS_2$@S,N-C-900, $Cu/Co/CoS_2$@S,N-C-1100, $Cu/Co/CoS_2$@S,N-C (5 mg) and $Cu/Co/CoS_2$@S,N-C (100 mg).

Sample	pyridinic N& graphitic N	sp^2 C	I_D/I_G
$Cu/Co/CoS_2$@S,N-C	80 %	61 %	1.88
$Cu/Co/CoS_2$@S,N-C-900	70 %	48 %	1.51
$Cu/Co/CoS_2$@S,N-C-1100	67 %	51%	1.43
$Cu/Co/CoS_2$@S,N-C (5 mg)	69 %	44%	1.41
$Cu/Co/CoS_2$@S,N-C (100 mg)	72 %	55%	1.55

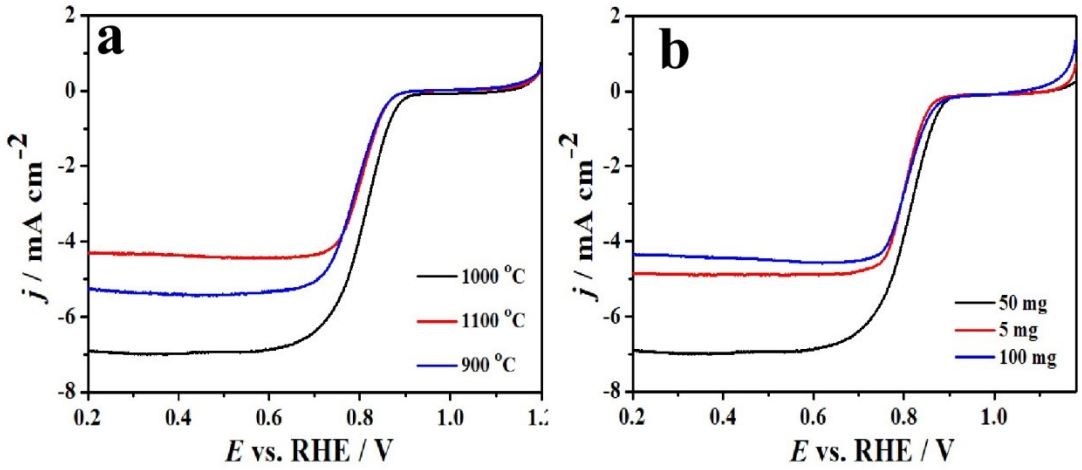

Figure S14. (a) LSV curves of the $Cu/Co/CoS_2$@S,N-C made from $Cu(OH)_2$ NRs/$Co(OH)_2$ NSs with variable contents in 0.1 M KOH; (b) LSVs of the $Cu(OH)_2$ NRs/$Co(OH)_2$ NSs calcined at various temperatures.

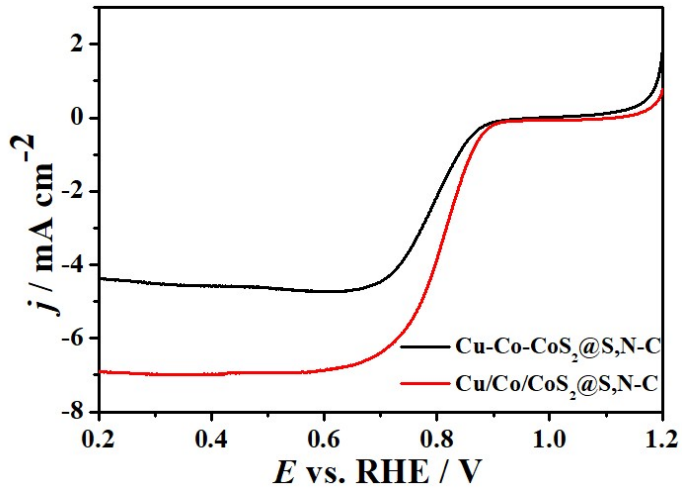

Figure S15. LSV curves of the Cu-Co-CoS_2@S,N-C and Cu/Co/CoS_2@S,N-C.

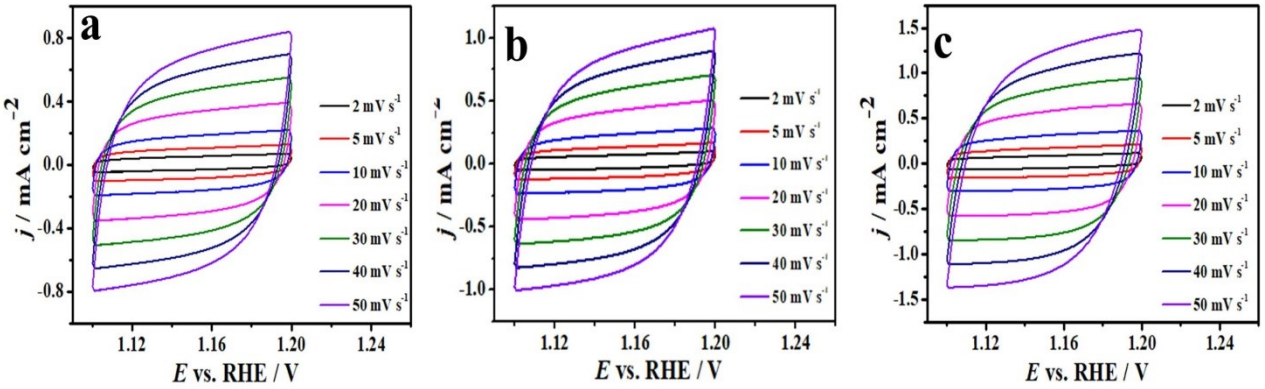

Figure S16. CV curves of the Co/CoS_2@S,N-C, Cu/Co@NC and Cu/Co/CoS_2@S,N-C.

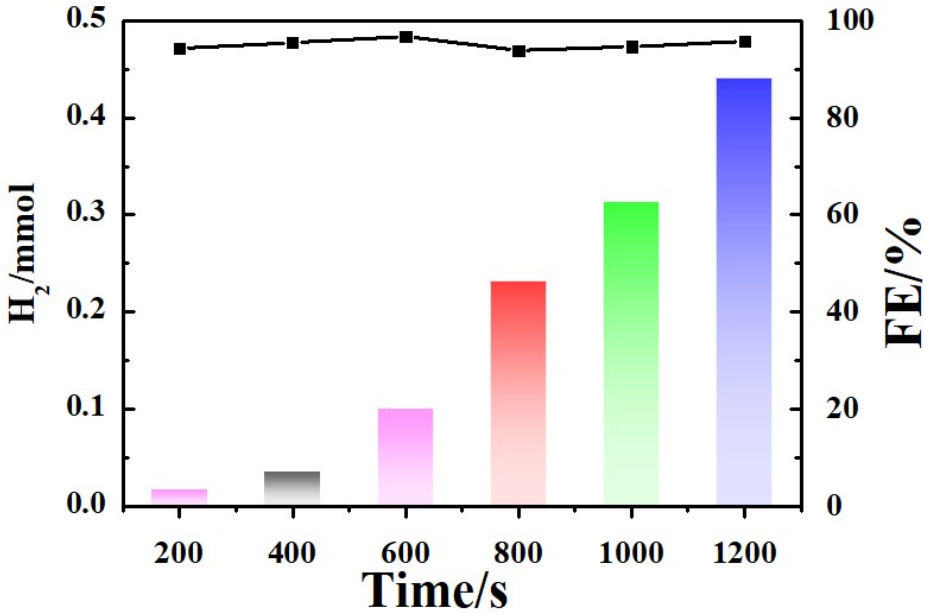

Figure S17. Gas volume versus time and corresponding Faradaic efficiency of Cu/Co/CoS_2@S,N-C.

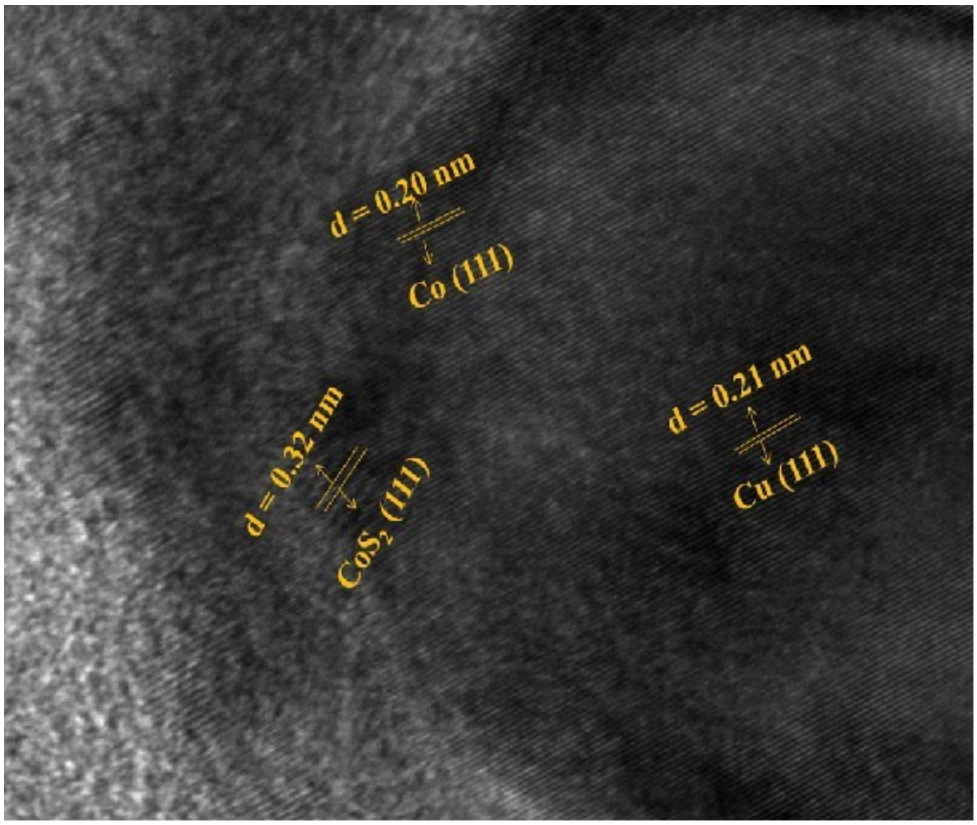

Figure S18. Magnified HRTEM image of Cu/Co/CoS_2@S,N-C.

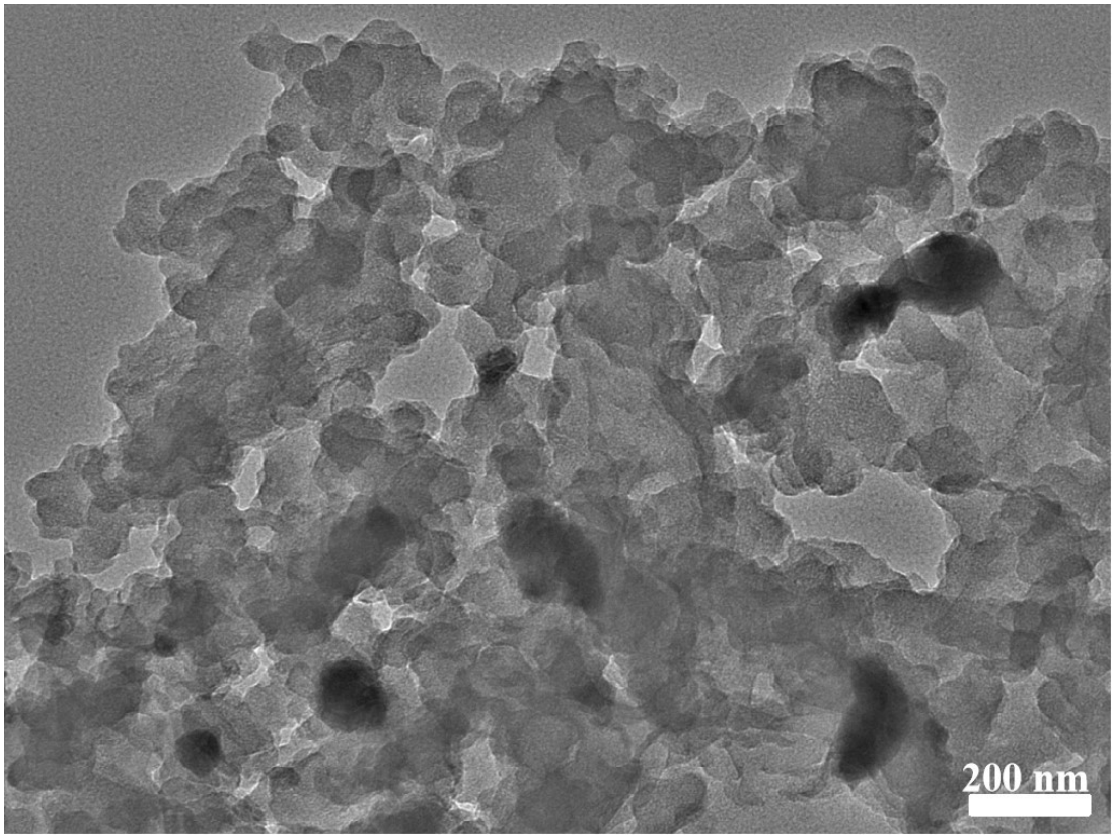

Figure S19. TEM image of Cu/Co/CoS_2@S,N-C after 30000 s.

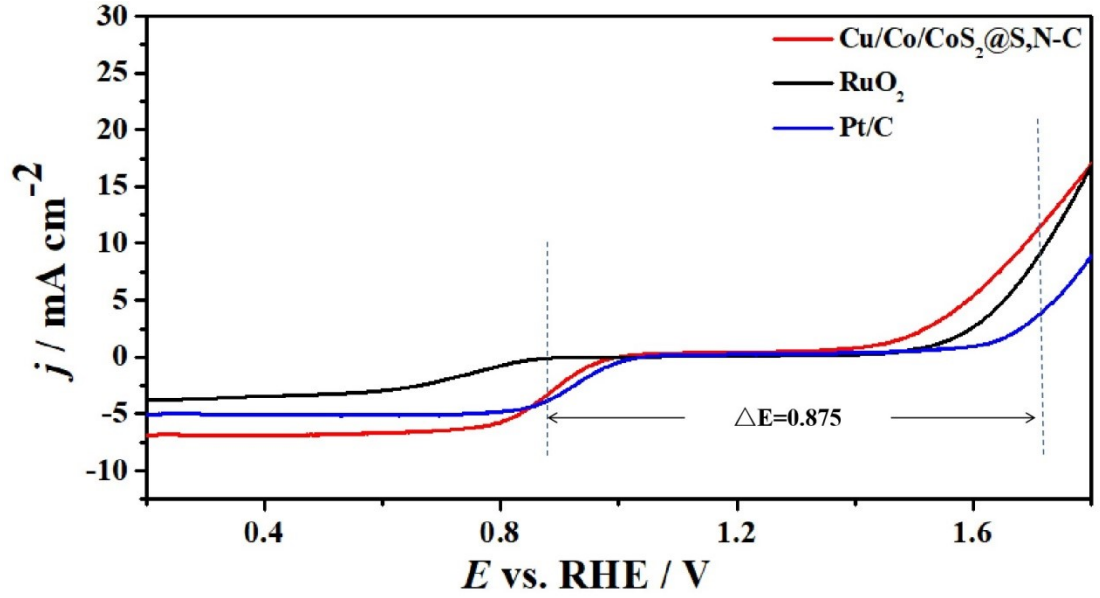

Figure S20. Bifunctional catalytic activity between the ORR and OER of Cu/Co/CoS_2@S,N-C, RuO_2 and Pt/C.

Table S2 Comparison of ORR/OER performances of reported Cu/Co/CoS_2@S,N-C -based electrocatalysts.

Catalysts	$E_{onset,ORR}$ (V)	$E_{1/2,ORR}$ (V)	Current density (mA cm^{-2})	Electrolyte	$E_{j=10,OER}$(V)	Electrolyte	Reference
Cu/Co/CoS_2@S,N-C	0.881	0.811	7.03	0.1 M	1.657	0.1 M	This work
M-NC-CoCu	0.85	0.75	-	0.1 M	1.54	1 M	[1]
CuCoS-4/N-rGO	0.97	0.86	5.2	0.1 M	1.52	1 M	[2]
CuCoS/CC	-	-	-	-	1.51	1 M	[3]
Cu-SAs@N-CNS	1.01	0.9	5.5	0.1 M	-	-	[4]
$CaMnO_3$-δ	0.84	0.80	4.27	0.1M	-	-	[5]
Co-S-C-700	0.8	0.79	-	0.1 M	1.58	0.1 M	[6]
CoNi/NHCS-TUC-3	0.91	0.88	5.13	0.1 M	-	-	[7]
$Co_{0.5}Fe_{0.5}S$@N-MC	0.913	0.808	5	0.1 M	1.57	1 M	[8]
Fe-Co-S/N	-	-	-	-	1.56	1 M	[9]
Zn-Co-S@NSC	0.955	-	5.92	0.1 M	-	-	[10]

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