Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

One-Pot Construction of CoSe Nanoparticles Anchored on Single-Atomic-Co Doped Carbon for pH-Universal Hydrogen Evolution

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Figure S1

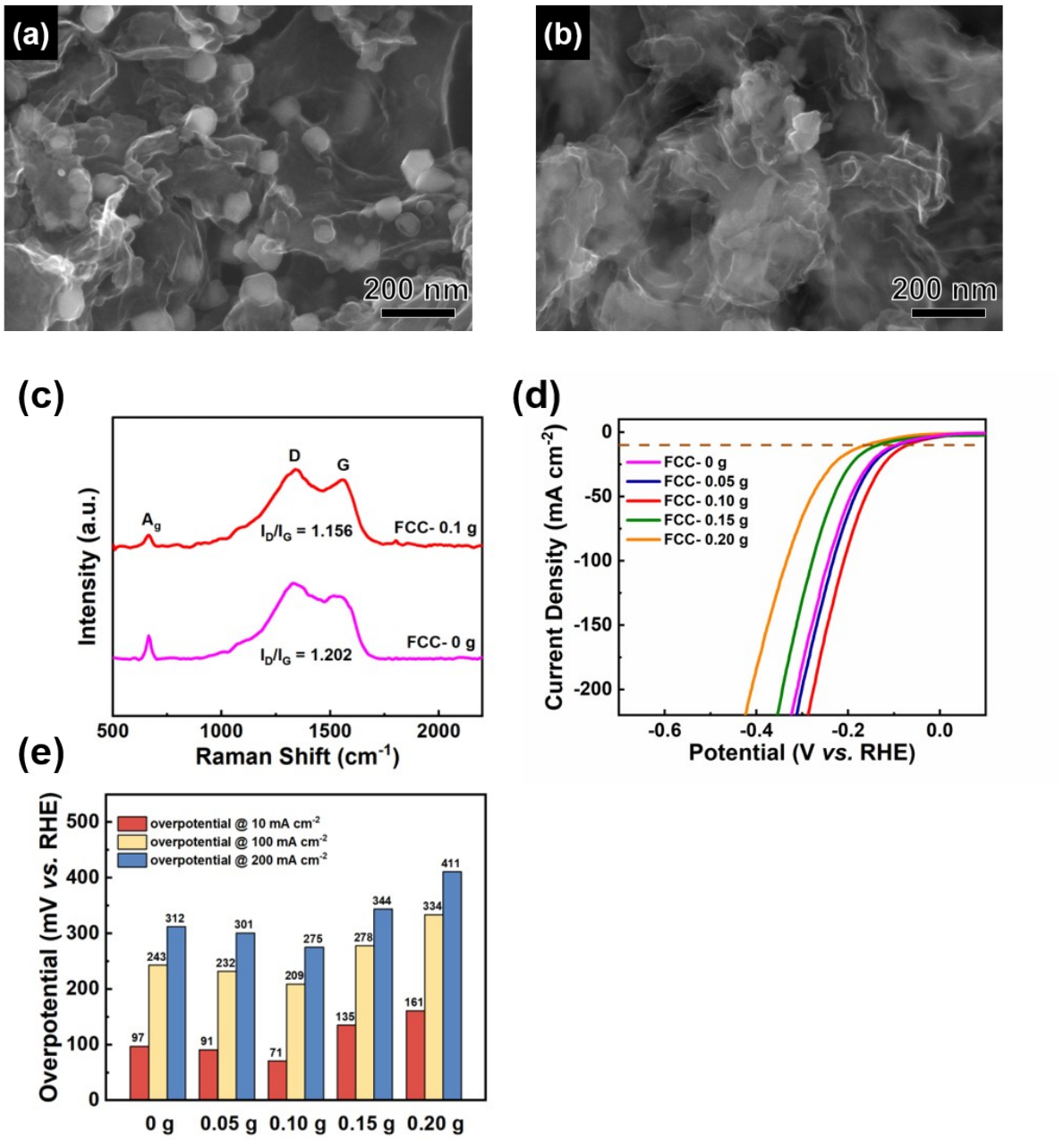

Figure S1. Synthetic optimization of CoSe/Co-N-C: amount of FCC slurry. SEM images of CoSe/Co-N-C with (a) 0.1 g slurry (optimized) and (b) 0 g slurry. (c) Raman spectra of CoSe/Co-N-C with 0 g and 0.1 g slurry. (d) HER LSV curves of CoSe/Co-N-C with 0 g-0.2 g slurry in 1.0 M KOH. (e) η_{10}, η_{100}, and η_{200} of CoSe/Co-N-C with 0 g-0.2 g slurry in 1.0 M KOH

Figure S2

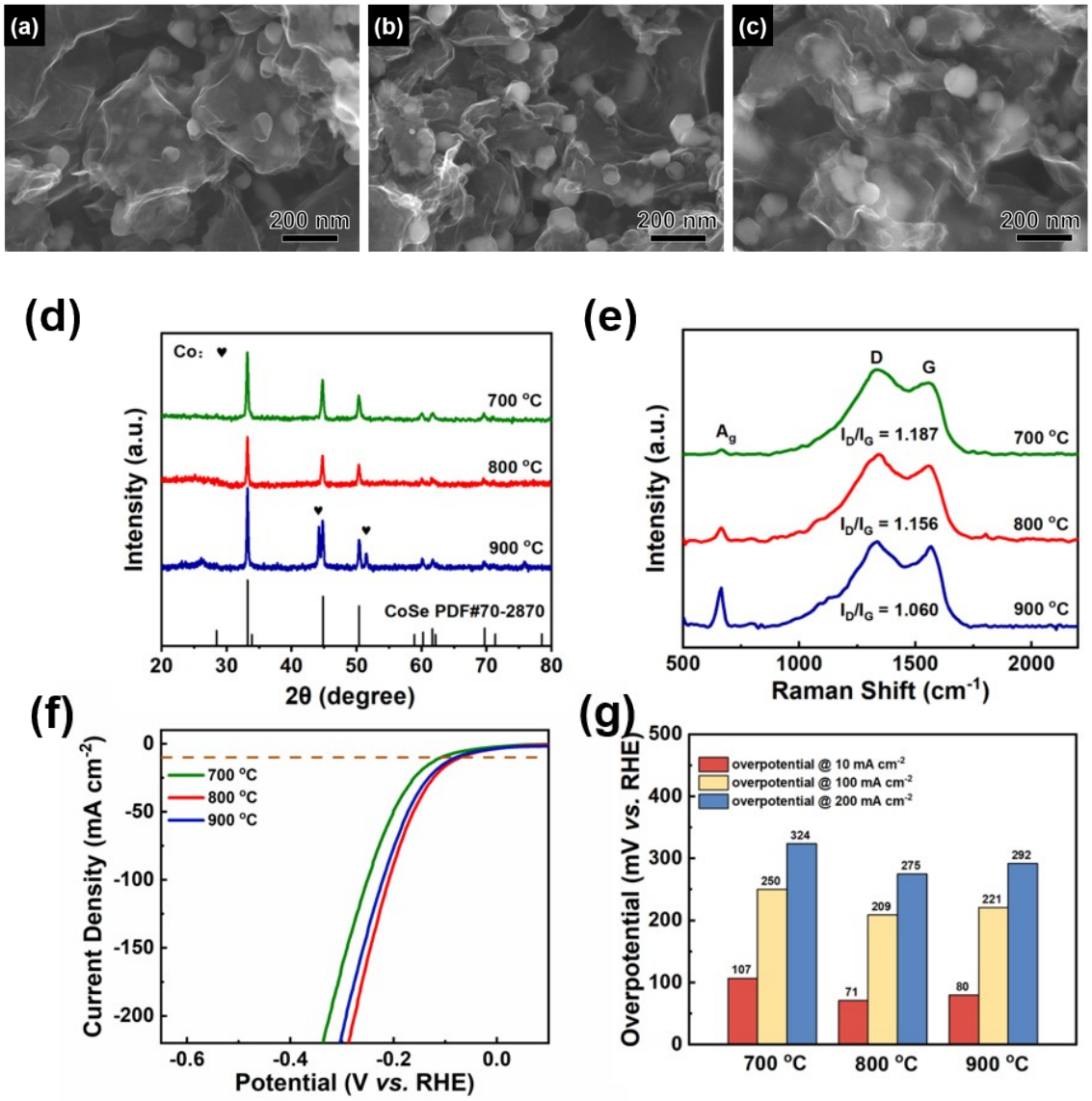

Figure S2. Synthetic optimization of CoSe/Co-N-C: pyrolysis temperature. SEM images of CoSe/Co-N-C pyrolyzed at (a) 800 °C, (b) 700 °C, and (c) 900 °C. (d) XRD spectra of CoSe/Co-N-C pyrolyzed at 700 °C, 800 °C, and 900 °C. (e) Raman spectra of CoSe/Co-N-C pyrolyzed at 700 °C, 800 °C, and 900 °C. (f) HER LSV curves of CoSe/Co-N-C pyrolyzed at 700 °C, 800 °C, and 900 °C in 1.0 M KOH. (g) η_{10}, η_{100}, and η_{200} of CoSe/Co-N-C pyrolyzed at 700 °C, 800 °C, and 900 °C in 1.0 M KOH

Figure S3

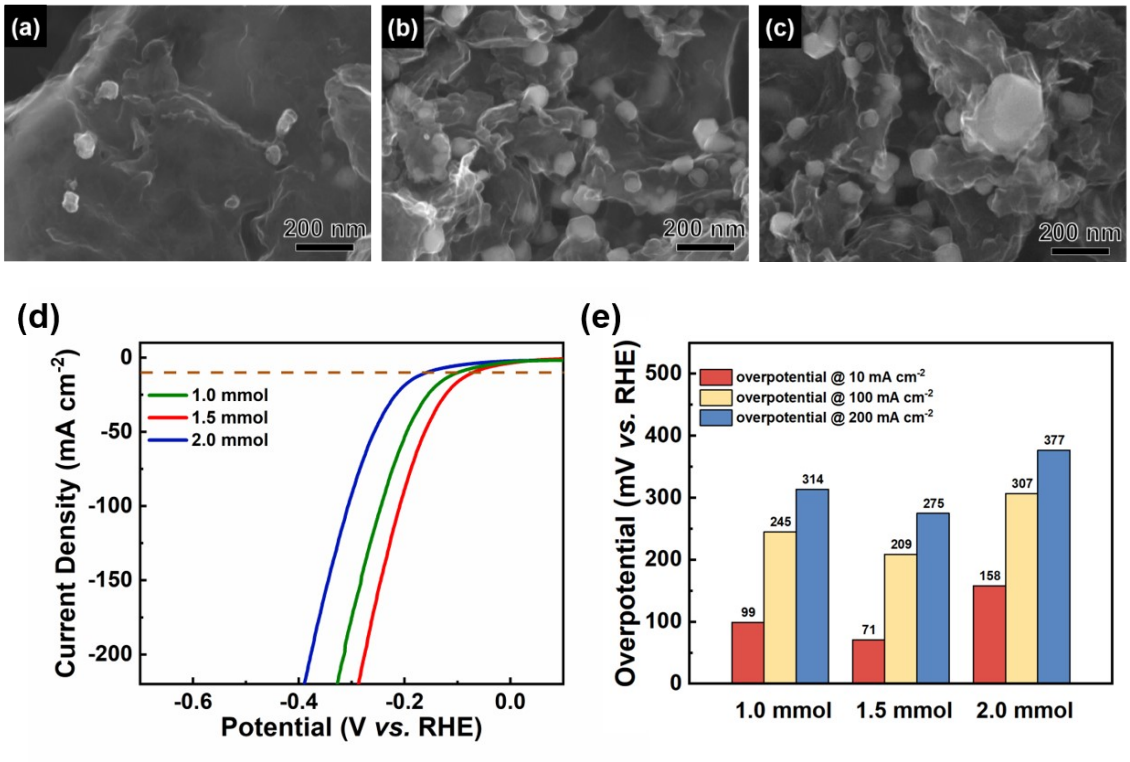

Figure S3. Synthetic optimization of CoSe/Co-N-C: total amount of $CoCl_2$. SEM images of CoSe/Co-N-C with (a) 1.0 mmol $CoCl_2$, (b) 1.5 mmol $CoCl_2$ (optimized), and (c) 2.0 mmol $CoCl_2$. (d) HER LSV curves of CoSe/Co-N-C with 1.0 mmol, 1.5 mmol, and 2.0 mmol $CoCl_2$ in 1.0 M KOH. (g) η_{10}, η_{100}, and η_{200} of CoSe/Co-N-C with 1.0 mmol, 1.5 mmol, and 2.0 mmol $CoCl_2$ in 1.0 M KOH

Figure S4

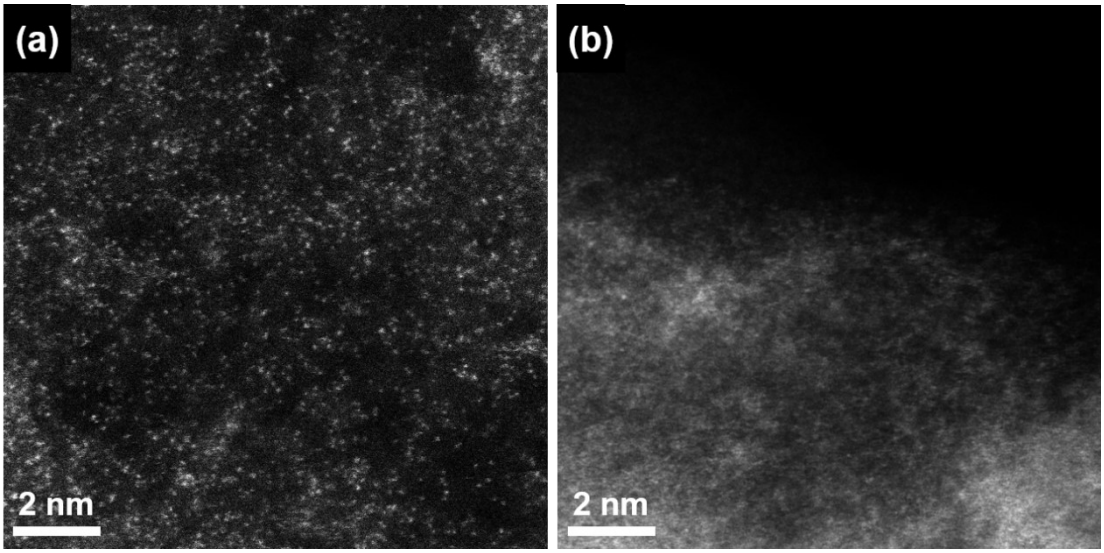

Figure S4. Aberration-corrected high-angle annular darkfield scanning transmission electron microscopy (AC HAADF-STEM) images of (a) Co-N-C and (b) CoSe/N-C.

Table S1. Porosity analysis of the representative catalysts

Catalysts	BET suface area (m^2 g^{-1})	Pore size (nm)	Pore volume (cm^3 g^{-1})
CoSe/Co-N-C	177	15.14	0.67
CoSe/N-C	109	16.00	0.44
Co-N-C	308	6.32	0.49
CoSe	17	25.72	0.11

Figure S5

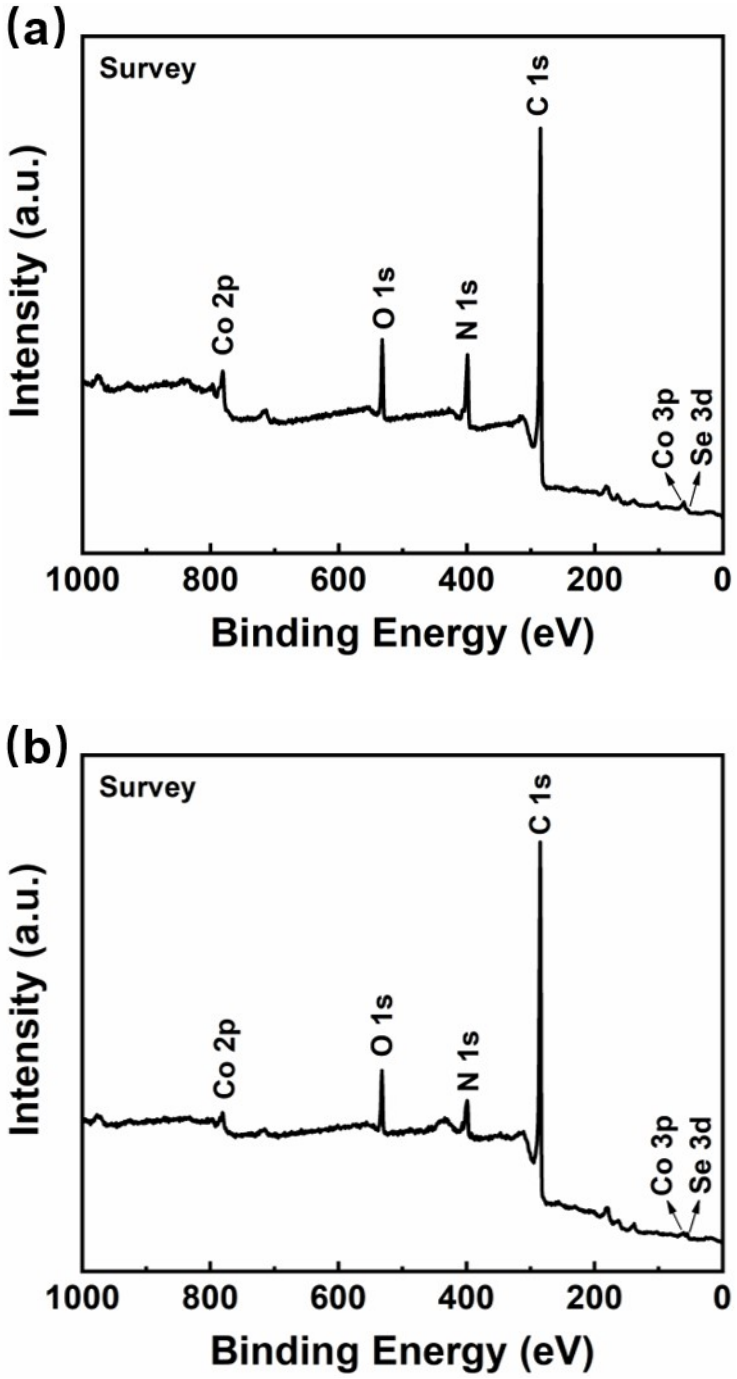
(a)
Survey
C 1s
O 1s
N 1s
Co 2p
Co 3p
Se 3d
Intensity (a.u.)
1000
800
600
400
200
0
Binding Energy (eV)
(b)
Survey
C 1s
O 1s
N 1s
Co 2p
Co 3p
Se 3d
Intensity (a.u.)
1000
800
600
400
200
0
Binding Energy (eV)

Figure S5. XPS survey spectra of (a) CoSe/Co-N-C, (b) CoSe/N-C, and (c) Co-N-C

Table S2. Binding energies of Co and Se in CoSe/Co-N-C and CoSe/N-C

XPS signal		CoSe/Co-N-C Binding Energy (Ev)	CoSe/N-C Binding Energy (eV)
Co	Co^{2+} $2p_{1/2}$	798.0	797.6
	Co^{3+} $2p_{1/2}$	796.0	795.7
	Co^{2+} $2p_{3/2}$	783.0	781.5
	Co^{3+} $2p_{3/2}$	780.6	780.1
Se	$3d_{3/2}$	55.6	55.9
	$3d_{5/2}$	54.3	54.6

Table S3. XPS elemental analysis of CoSe/Co-N-C

Name	Atomic (%)	Weight (%)
C	75.06	63.38
N	13.85	13.64
O	7.99	9.00
Co	2.31	9.59
Se	0.79	4.39

Figure S6

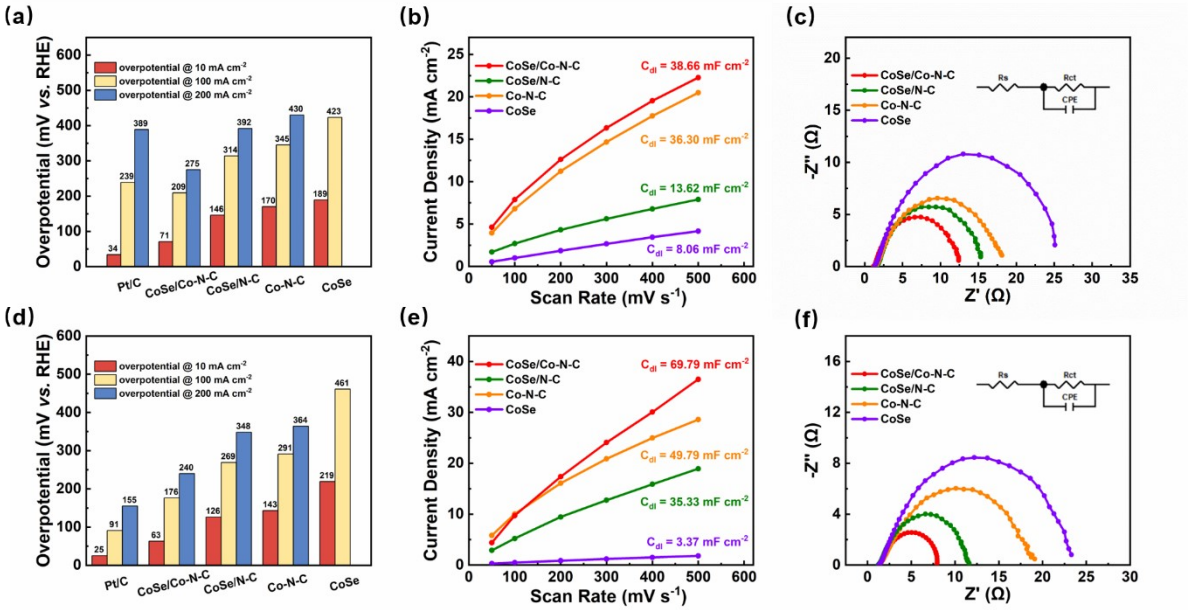

Figure S6. HER performances of CoSe/Co-N-C, CoSe/N-C, Co-N-C, CoSe, and 10% Pt/C. (a) summary of η_{10}, η_{100}, and η_{200}, (b) capacitive current density as a function of scan rates, and (c) Nyquist plots of CoSe/Co-N-C and other references in 1.0 M KOH. (d) summary of η_{10}, η_{100}, and η_{200}, (e) capacitive current density as a function of scan rates, and (f) Nyquist plots of CoSe/Co-N-C and other references in 0.5 M H_2SO_4.

Figure S7

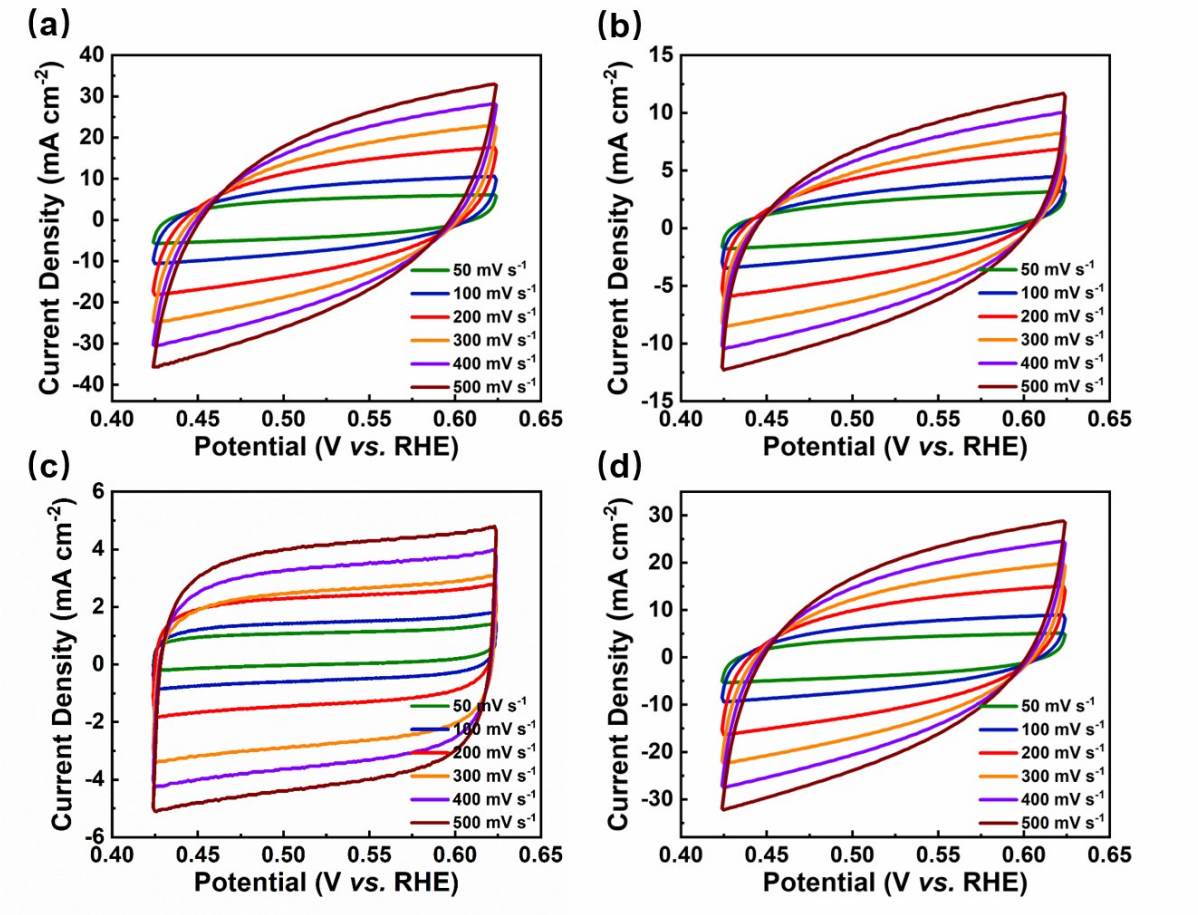

Figure S7. CV spectra of (a) CoSe/Co-N-C, (b) CoSe/N-C, (c) CoSe, and (d) Co-N-C with various scan rates (50-500 mV s^{-1}) in 1.0 M KOH.

Figure S8

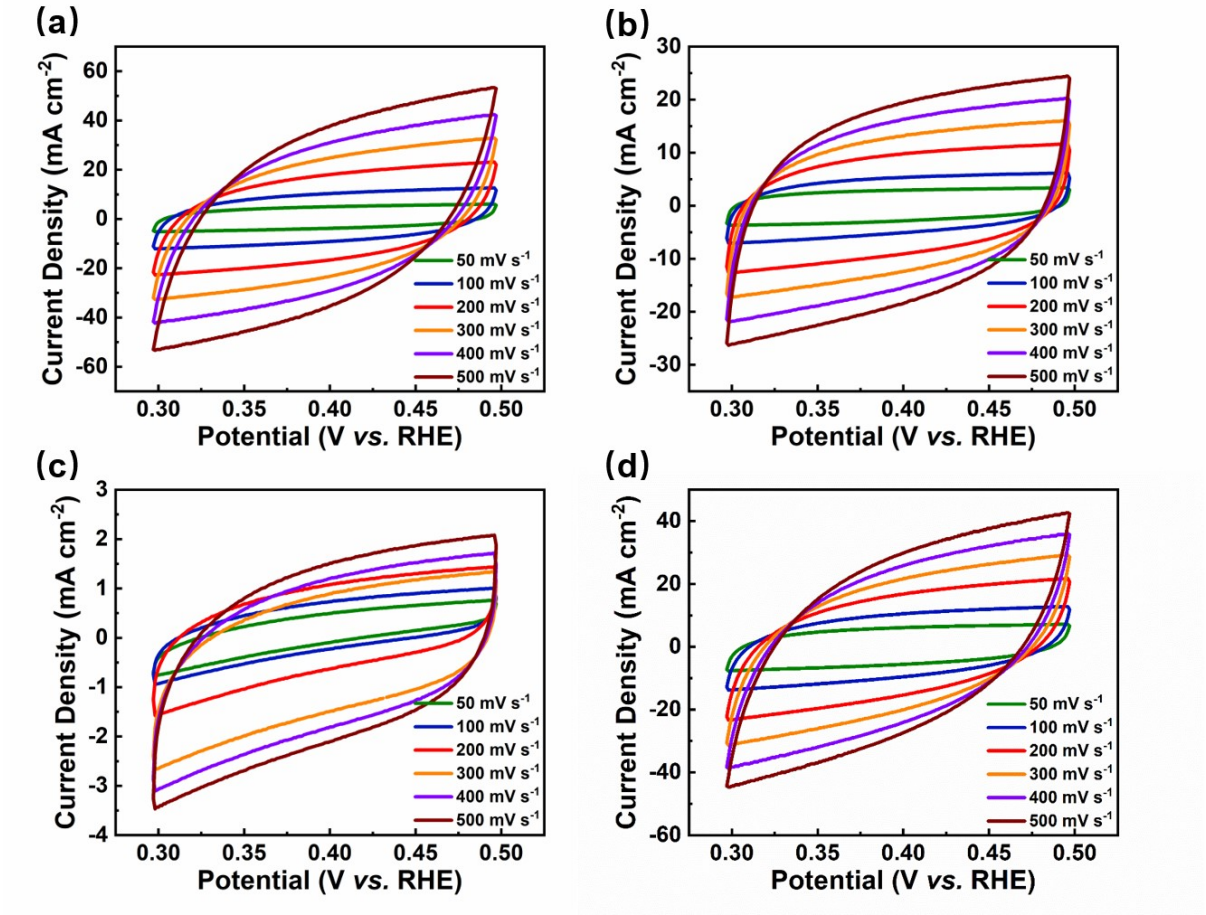

Figure S8. CV spectra of (a) CoSe/Co-N-C, (b) CoSe/N-C, (c) CoSe, and (d) Co-N-C with various scan rates (50-500 mV s^{-1}) in 0.5 M H_2SO_4.

Figure S9

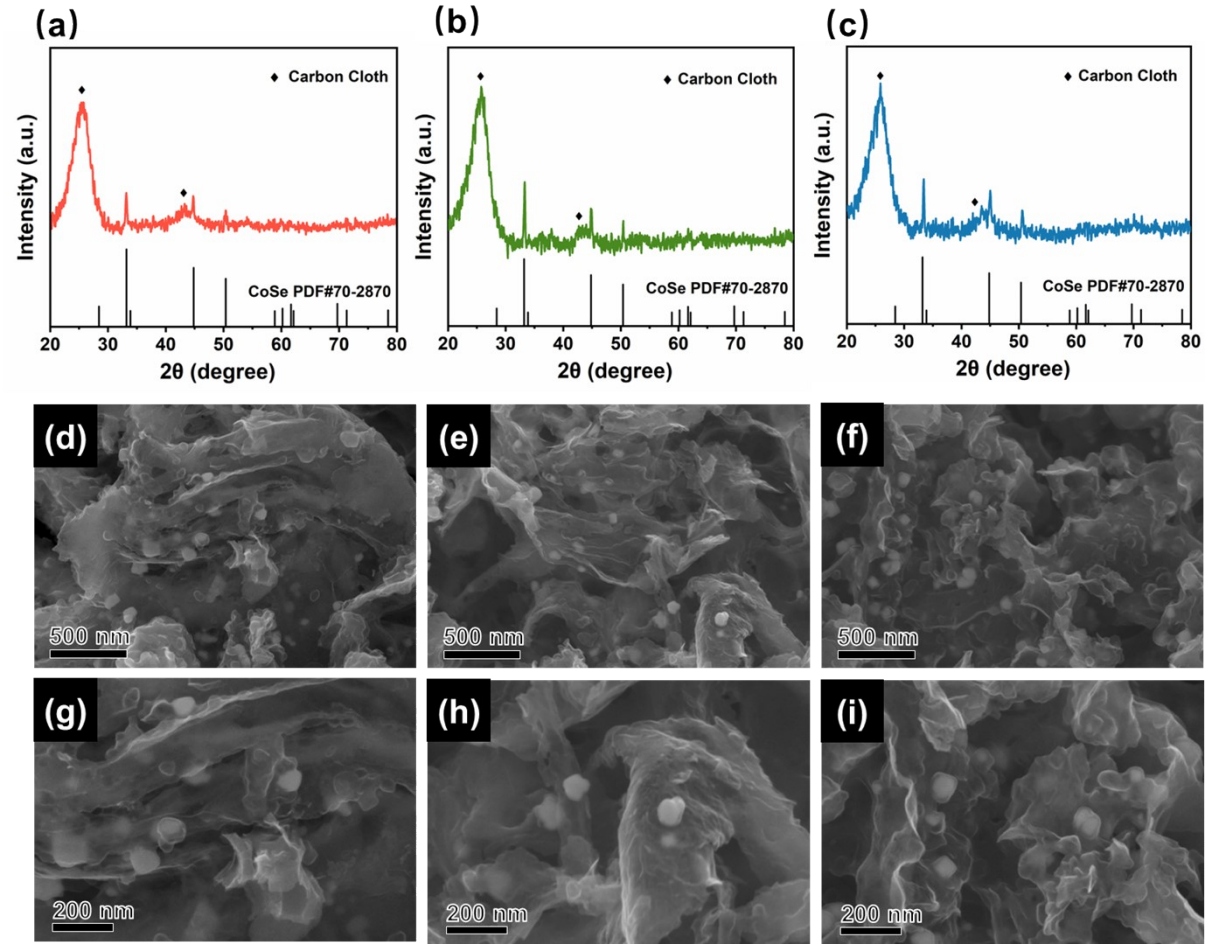

Figure S9. (a) XRD spectrum and (d, g) SEM images of CoSe/Co-N-C after 2000 CV electrocatalytic cycles in 1.0 M KOH; (b) XRD spectrum and (e, h) SEM images of CoSe/Co-N-C after 2000 CV electrocatalytic cycles in 0.5 M H_2SO_4; (c) XRD spectrum and (f, i) SEM images of CoSe/Co-N-C after 2000 CV electrocatalytic cycles in 1.0 M PBS.

Table S4. HER activity summary of CoSe/Co-N-C, CoSe/N-C, Co-N-C, and CoSe in various electrolytes.

Electrolytes		η_{10} (mV)	η_{100} (mV)	η_{200} (mV)	Tafel Slope (mV dec^{-1})
1.0 M KOH	CoSe/Co-N-C	71	209	275	79
	CoSe/N-C	146	314	392	139
	Co-N-C	170	345	430	147
	CoSe	189	423	N/A	180
0.5 M H_2SO_4	CoSe/Co-N-C	63	176	240	65
	CoSe/N-C	126	269	348	108
	Co-N-C	143	291	364	125
	CoSe	219	461	N/A	153
1.0 M PBS	CoSe/Co-N-C	128	293	360	110

Table S5. Summary of HER performances of CoSe/Co-N-C and other TMSes electrocatalysts in the literatures.

Catalysts	Tafel slope (mV/dec)	Overpotential (mV)@10mA/cm^2	Electrolyte	Stability (h)	References
CoSe/Co-N-C	**79**	**71**	**1.0 M KOH**	**36**	**This work**
	65	**63**	**0.5 M H_2SO_4**		
$CoSe_2$-NC	95	234	1.0 M KOH	14	[1]
	62	156	0.5 M H_2SO_4		
$NiSe_2$@NG	37.8	248	1.0 M KOH	18	[2]
	79.8	201	0.5 M H_2SO_4		
$Ni_{0.85}Se$@NC	97	135	1.0 M KOH	10	[3]
	85	131	0.5 M H_2SO_4		
$NiSe_2$@NC	88	162	1.0 M KOH	40	[4]
	37	183	0.5 M H_2SO_4		
$MoSe_2$-NiSe@carbon	80.6	180	1.0 M KOH	10	[5]
	76.3	154	0.5 M H_2SO_4		
NiSe@NC	55.3	250	1.0 M KOH	12	[6]
	53.3	123	0.5 M H_2SO_4		
$Co_{0.9}Ni_{0.1}Se$	58	185.7	0.5 M H_2SO_4	-	[7]
$CoS_{0.46}Se_{0.54}$@C	105.43	251	1.0 M KOH	-	[8]
$Co_{0.85}Se$@NC	125	230	1.0 M KOH	10	[9]
CoNiSe/NC	66.5	100	1.0 M KOH	3.33	[10]
$Co_{0.8}Mo_{0.2}Se$	58.7	86.7	0.5 M H_2SO_4	10	[11]
CoSe@NCNT/NCN	43	197	0.5 M H_2SO_4	18	[12]

Table S6. The interaction energies (E_{int}) of CoSe/N-C and CoSe/Co-N-C, and the Bader Charge on NC and Co-N-C backbones.

Samples	E_{int} (eV)	$C_{NC}/C_{Co\text{-}N\text{-}C}$ (|e|)
CoSe/N-C	-3.20	0.15
CoSe/Co-N-C	-3.48	0.34

Figure S8

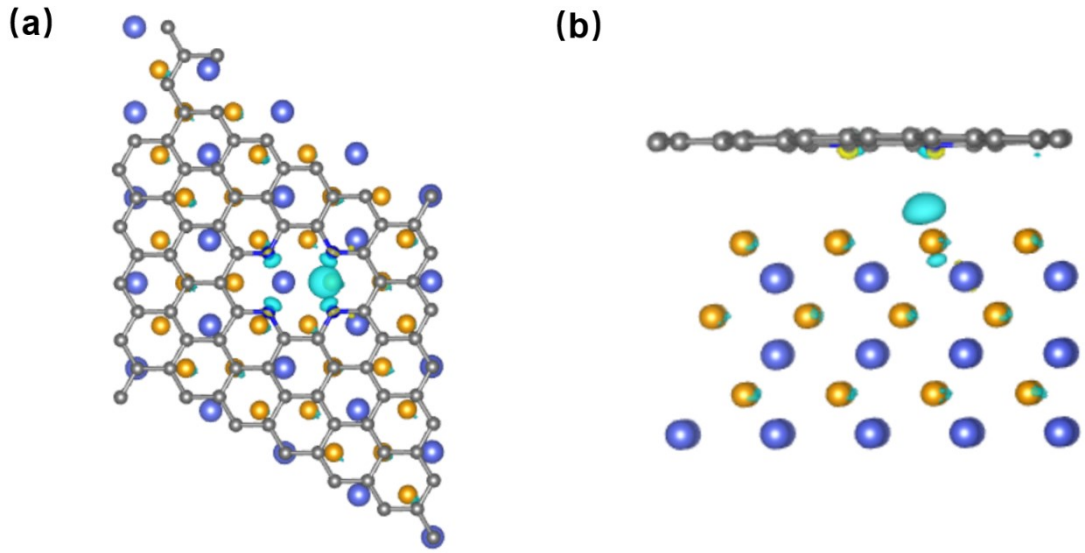

Figure S8. (a) Top view and (b) side view of the charge density in the heterostructure interface of CoSe/N-C. The charge accumulation and depletion were colored in cyan and yellow, respectively. Gray balls: C atoms; blue balls: Co atoms; yellow balls: Se atoms.

Reference

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