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

Supporting Information for

Fabrication of Ru Nanoclusters on Co-doped NiSe Nanorods with Efficient Electrocatalytic Activity towards Alkaline Hydrogen Evolution via Hydrogen Spillover Effect

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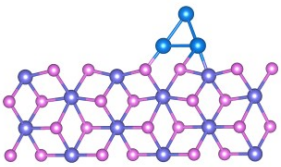
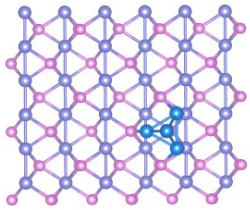
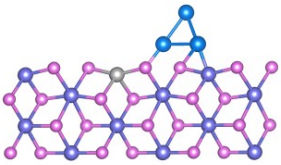
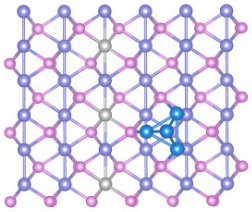
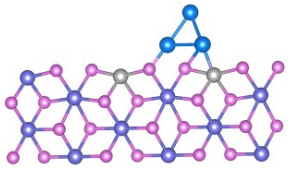
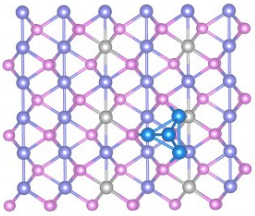
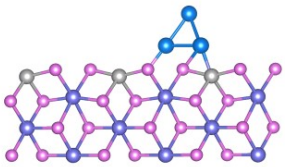
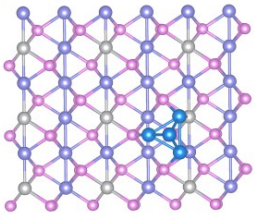
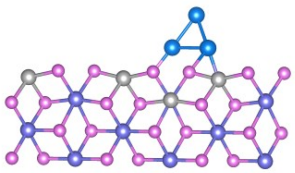
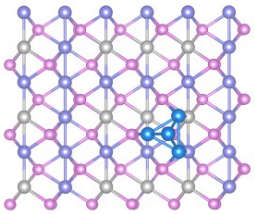
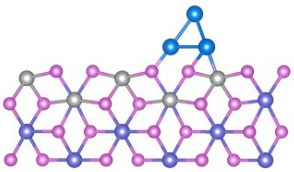
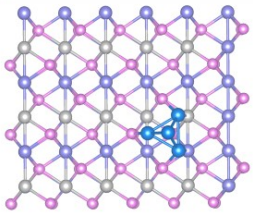
Samples	Atomic structure diagram	
	Side view	Top view
Ru-NiSe		
Ru-$Ni_{0.95}Co_{0.05}Se$		
Ru-$Ni_{0.90}Co_{0.10}Se$		
Ru-$Ni_{0.85}Co_{0.15}Se$		
Ru-$Ni_{0.80}Co_{0.20}Se$		
Ru-$Ni_{0.75}Co_{0.25}Se$		

Figure S1. Atomic Structure diagram of different samples.

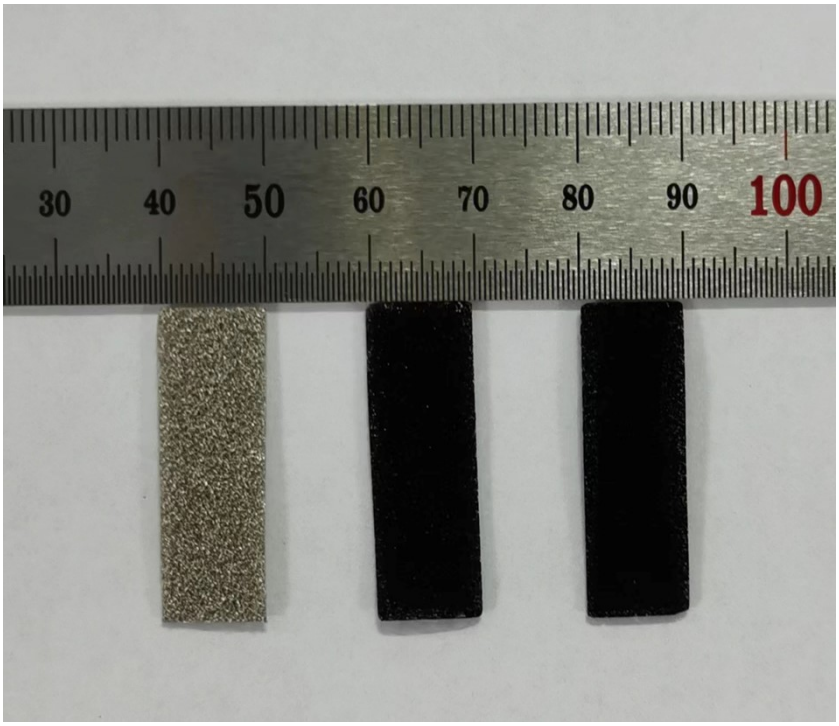


Figure S2. Photograph of blank Ni foam (left), NiSe NR/NF (mid) and Ru-$Ni_{0.85}Co_{0.15}Se$/NF (right).

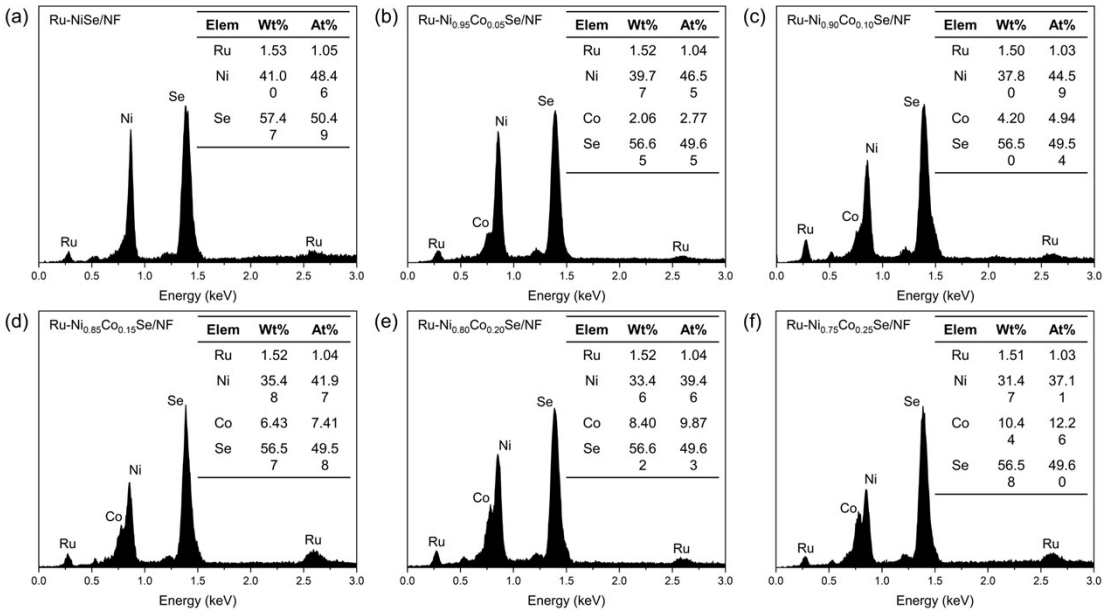


Figure S3. EDX spectra of (a) Ru-NiSe/NF, (b) Ru-$Ni_{0.95}Co_{0.05}Se$/NF, (c) Ru-$Ni_{0.90}Co_{0.10}Se$/NF, (d) Ru-$Ni_{0.85}Co_{0.15}Se$/NF, (e) Ru-$Ni_{0.80}Co_{0.20}Se$/NF and (f) Ru-$Ni_{0.75}Co_{0.25}Se$/NF.

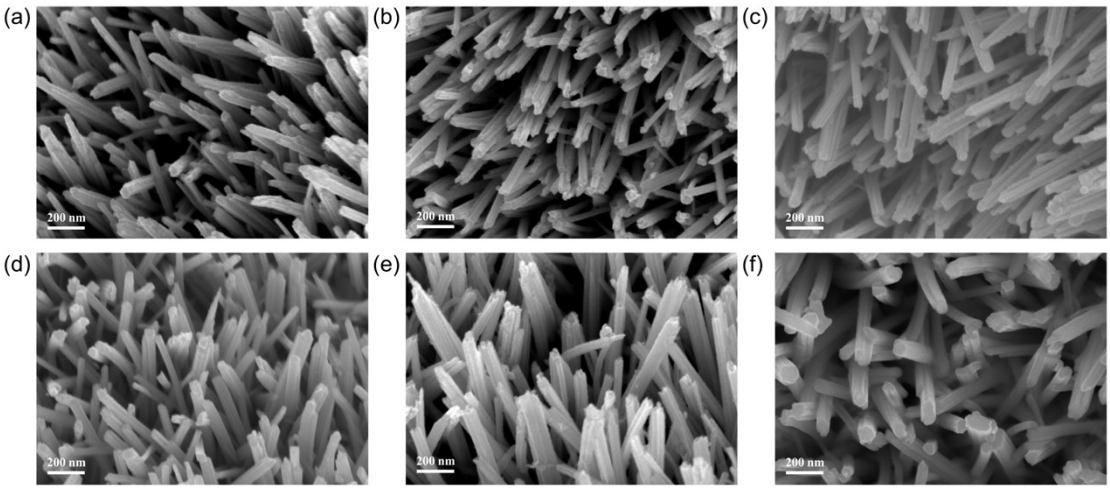


Figure S4. SEM images of (a) Ru-NiSe/NF, (b) Ru-$Ni_{0.95}Co_{0.05}Se$/NF, (c) Ru-$Ni_{0.90}Co_{0.10}Se$/NF, (d) Ru-$Ni_{0.85}Co_{0.15}Se$/NF, (e) Ru-$Ni_{0.80}Co_{0.20}Se$/NF and (f) Ru-$Ni_{0.75}Co_{0.25}Se$/NF.

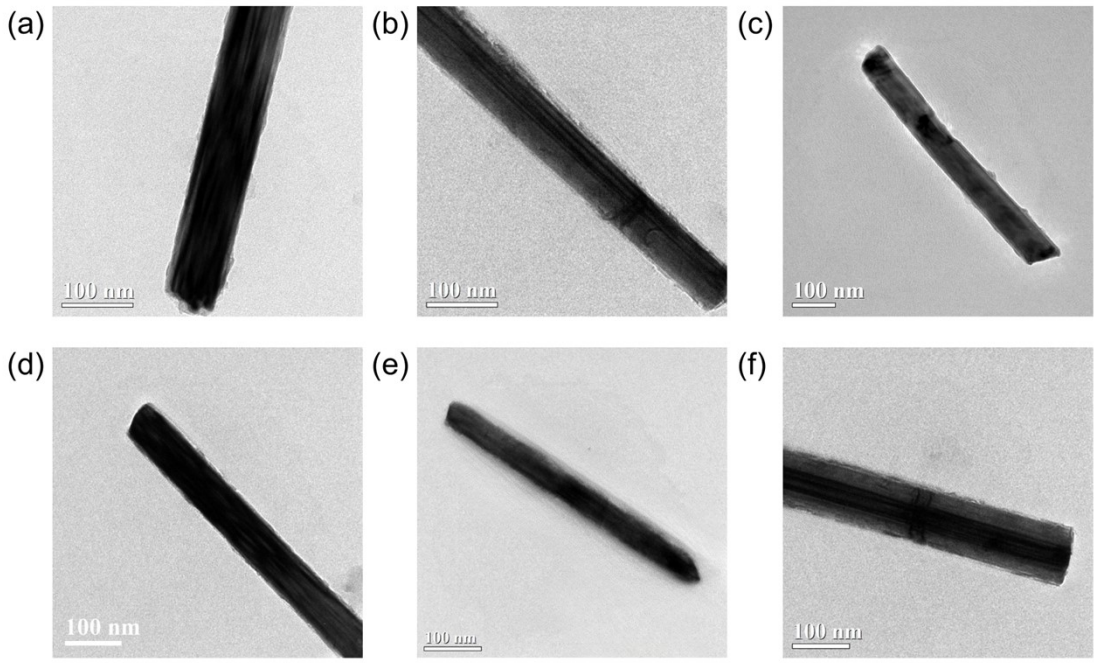


Figure S5. TEM images of (a) Ru-NiSe/NF, (b) Ru-$Ni_{0.95}Co_{0.05}Se$/NF, (c) Ru-$Ni_{0.90}Co_{0.10}Se$/NF, (d) Ru-$Ni_{0.85}Co_{0.15}Se$/NF, (e) Ru-$Ni_{0.80}Co_{0.20}Se$/NF and (f) Ru-$Ni_{0.75}Co_{0.25}Se$/NF.

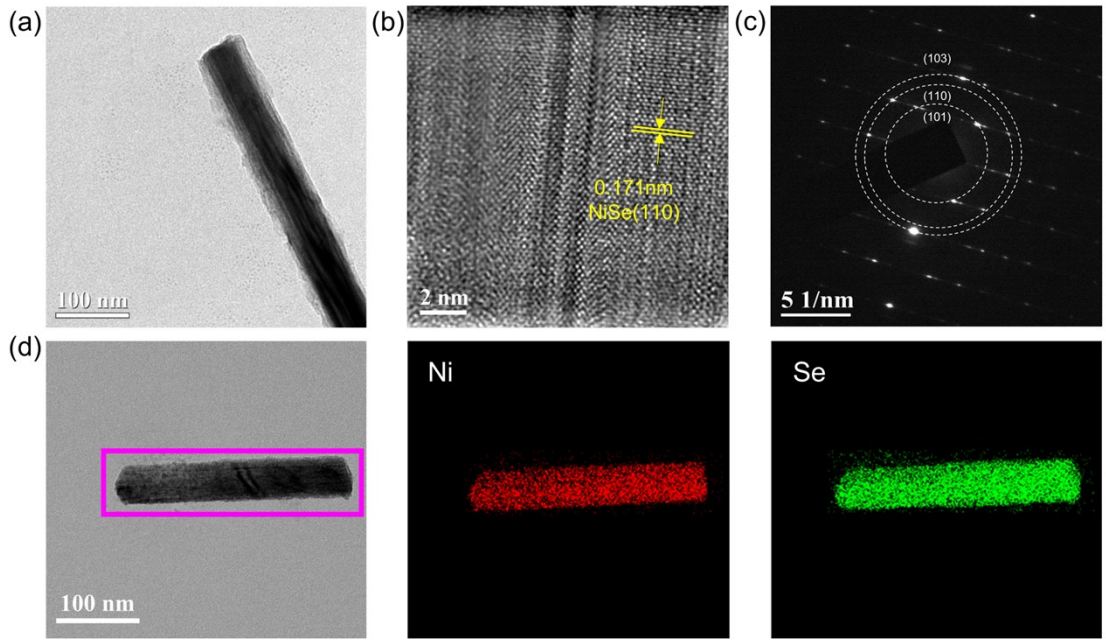


Figure S6. (a) TEM image, (b) HRTEM image, (c) SAED pattern, and (d) The high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) image and corresponding EDX elemental mapping images of an individual NiSe/NF.

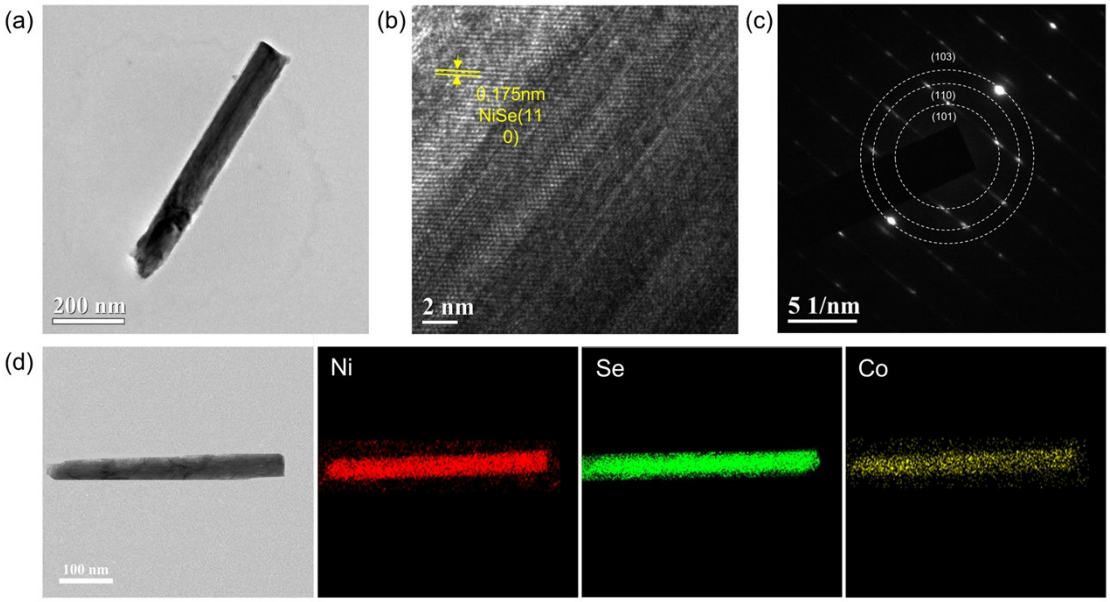


Figure S7. (a) TEM image, (b) HRTEM image, (c) SAED pattern, and (d) The high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) image and corresponding EDX elemental mapping images of an individual $Ni_{0.85}Co_{0.15}Se$/NF.

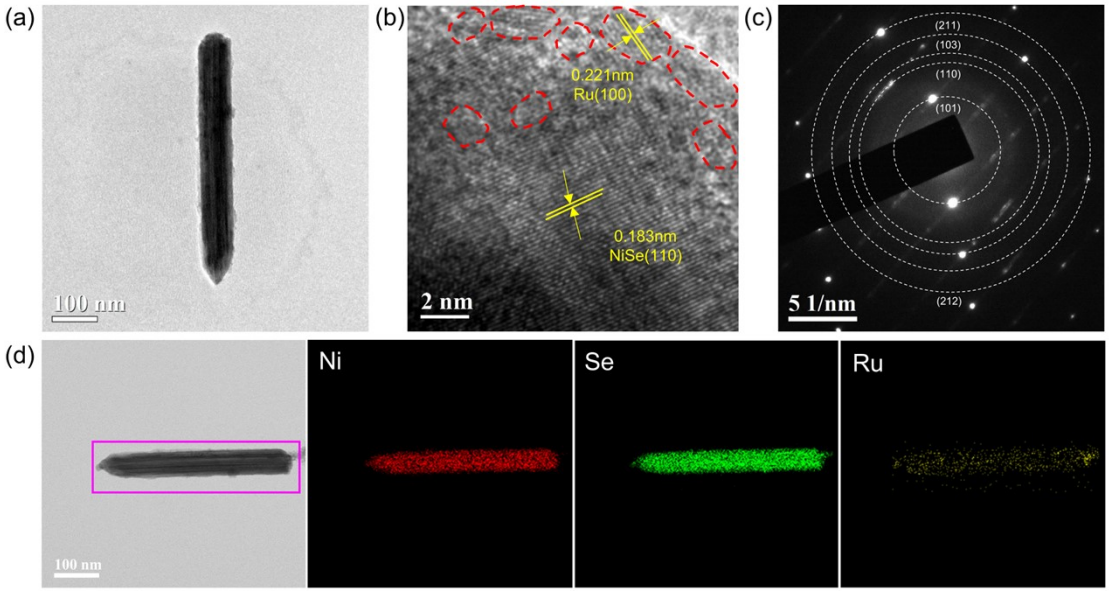


Figure S8. (a) TEM image, (b) HRTEM image, (c) SAED pattern, and (d) The high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) image and corresponding EDX elemental mapping images of an individual Ru-NiSe/NF.

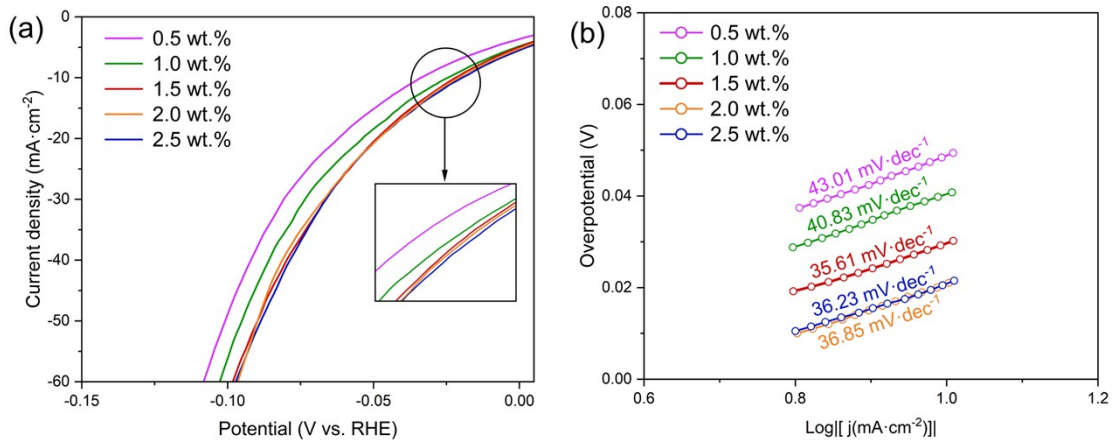


Figure S9. LSV curves and Tafel plots of the Ru-$Ni_{0.85}Co_{0.15}Se$/NF catalysts at different metal loading in 1.0 M KOH.

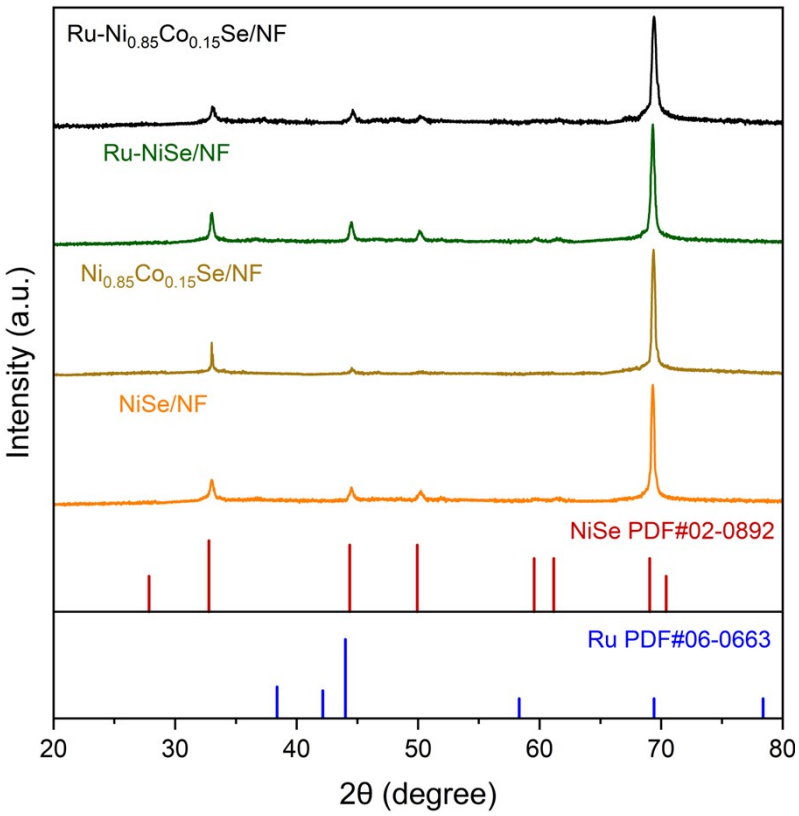


Figure S10. XRD patterns of NiSe/NF, Ru-NiSe/NF and Ru-$Ni_{0.85}Co_{0.15}Se$/NF.

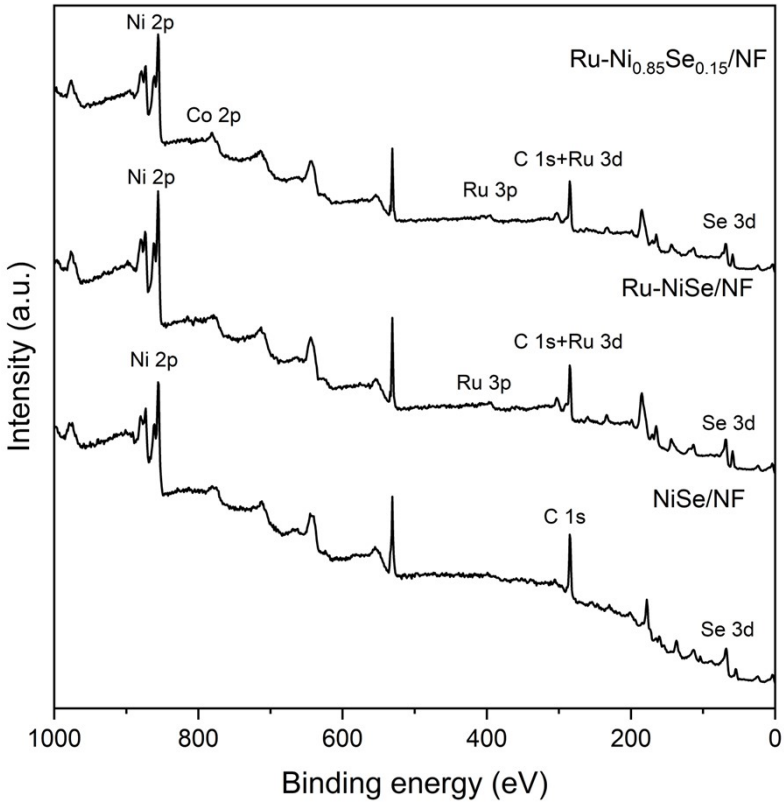


Figure S11. XPS spectra of NiSe/NF, Ru-NiSe/NF and Ru-$Ni_{0.85}Co_{0.15}Se$/NF.

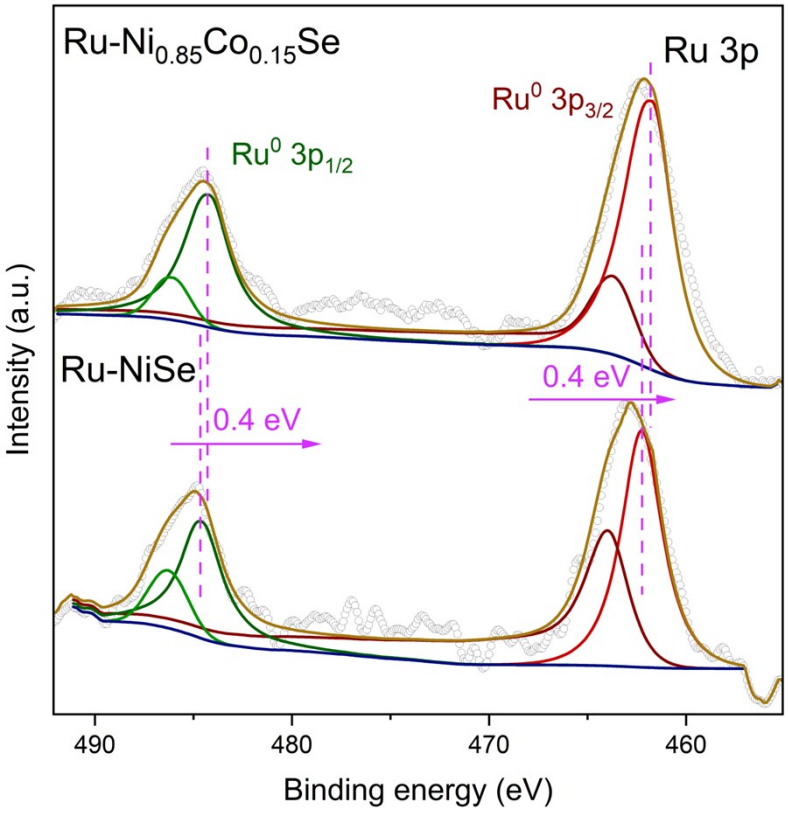


Figure S12. Ru 3*p* XPS spectra of Ru-NiSe/NF and Ru-$Ni_{0.85}Co_{0.15}Se$/NF.

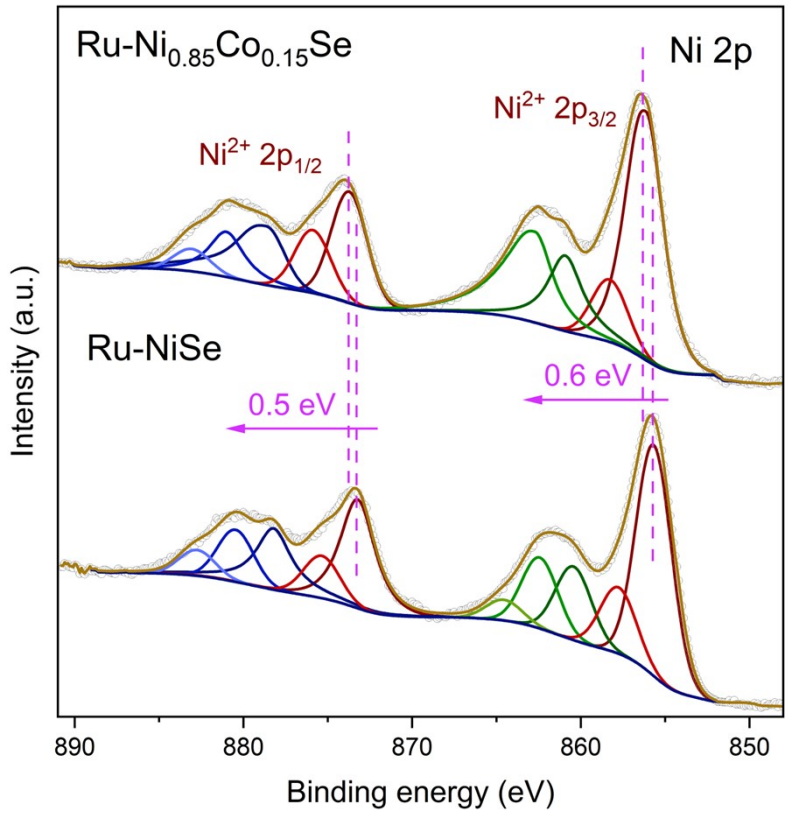


Figure S13. Ni 2*p* XPS spectra of Ru-NiSe/NF and Ru-$Ni_{0.85}Co_{0.15}Se$/NF.

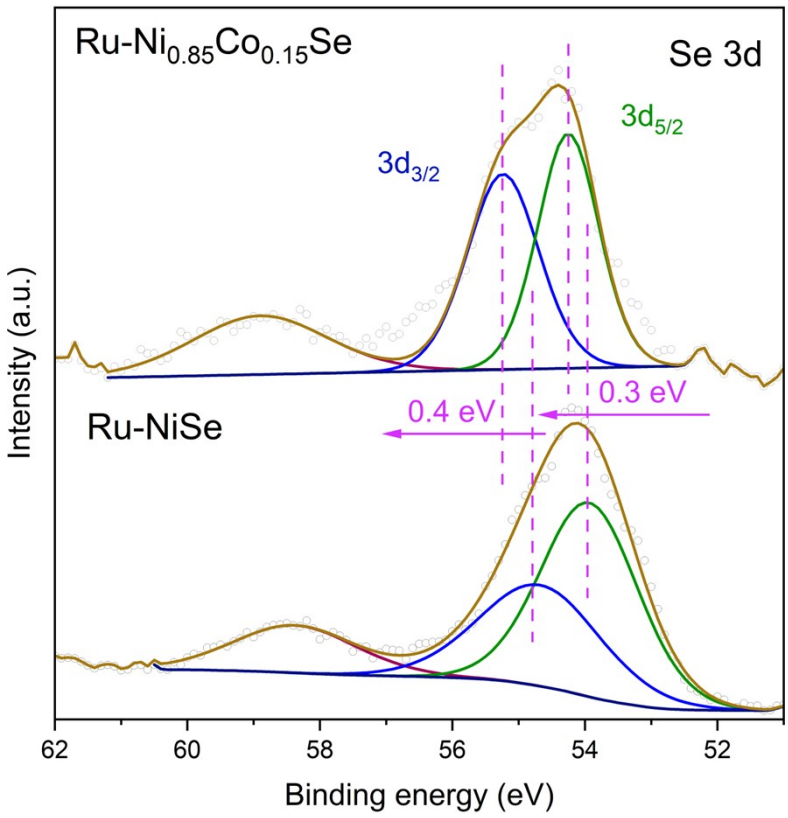


Figure S14. Se 3*d* XPS spectra of Ru-NiSe/NF and Ru-$Ni_{0.85}Co_{0.15}Se$/NF.

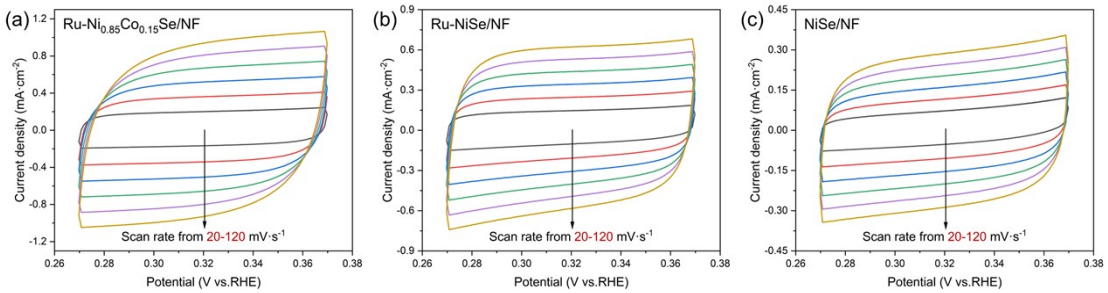


Figure S15. Cyclic voltammograms of (a)-(c) Ru-$Ni_{0.85}Co_{0.15}Se$/NF, Ru-NiSe/NF and NiSe/NF electrocatalysts in 1.0 M KOH at various scan rates.

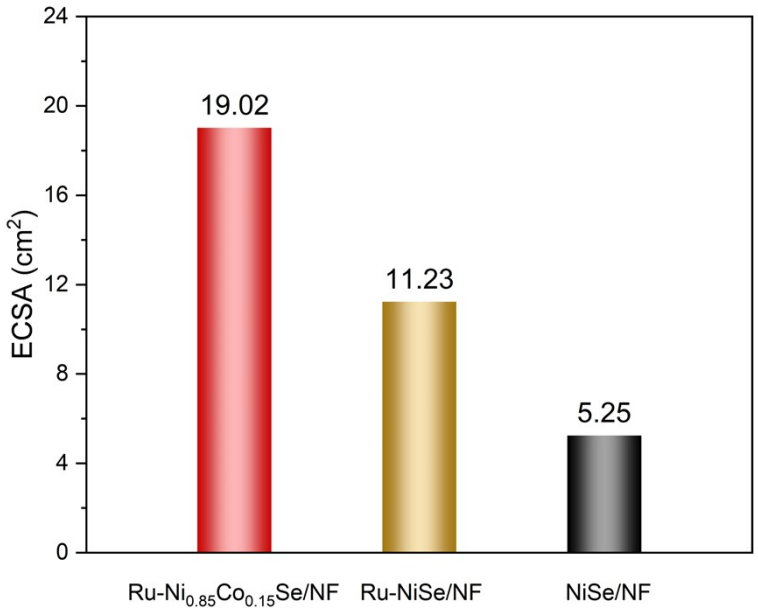


Figure S16. Electrochemcial active surface area of different catalysts for HER.

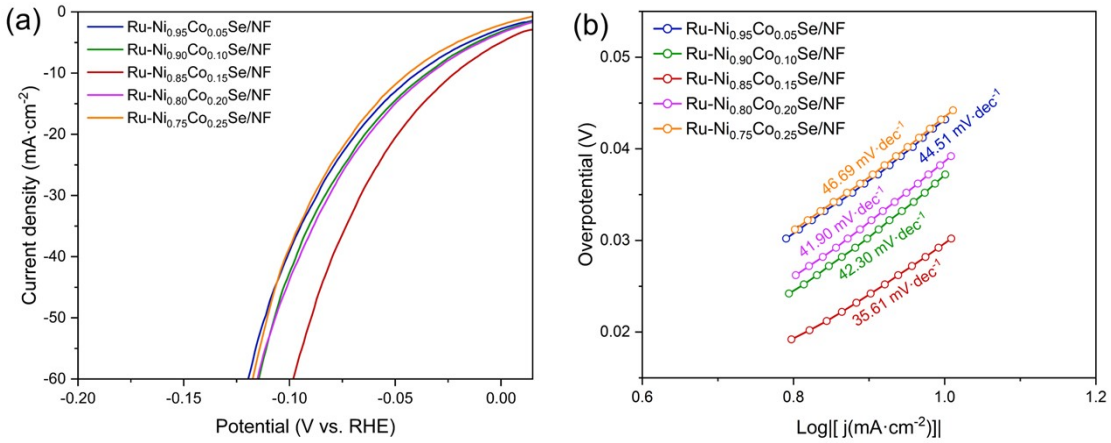


Figure S17. LSV curves and Tafel plots of different electrocatalysts in 1.0 M KOH.

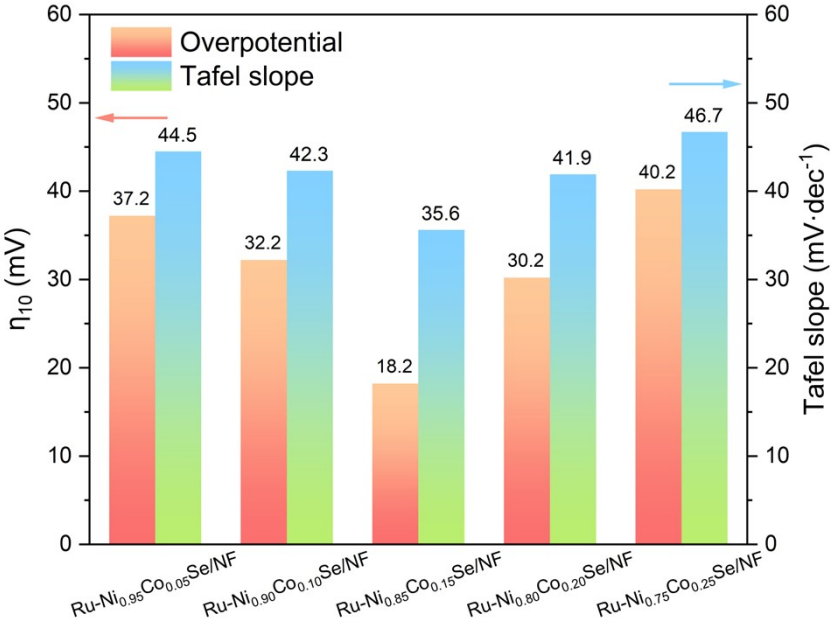


Figure S18. η changes at 10 mA·cm^{-2} and Tafel slope.

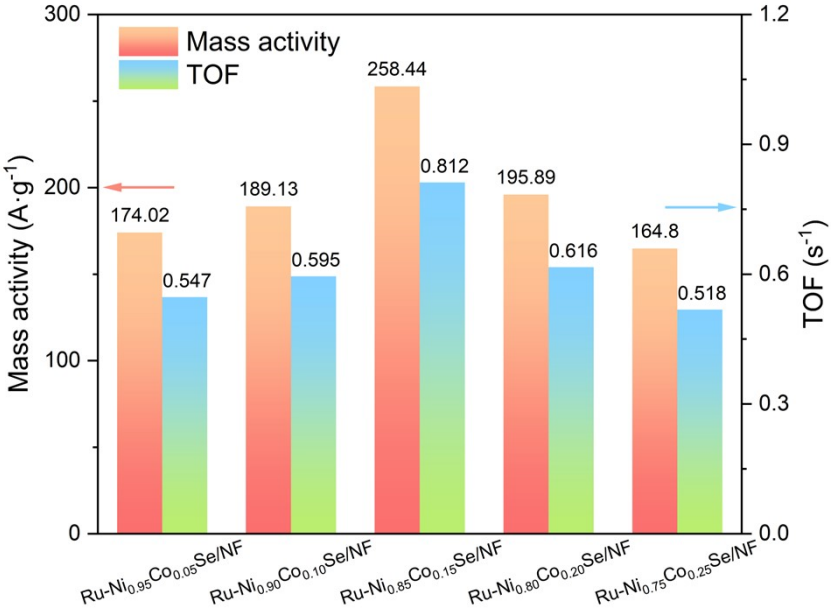


Figure S19. Mass activity and TOF of different catalysts in 1.0 M KOH.

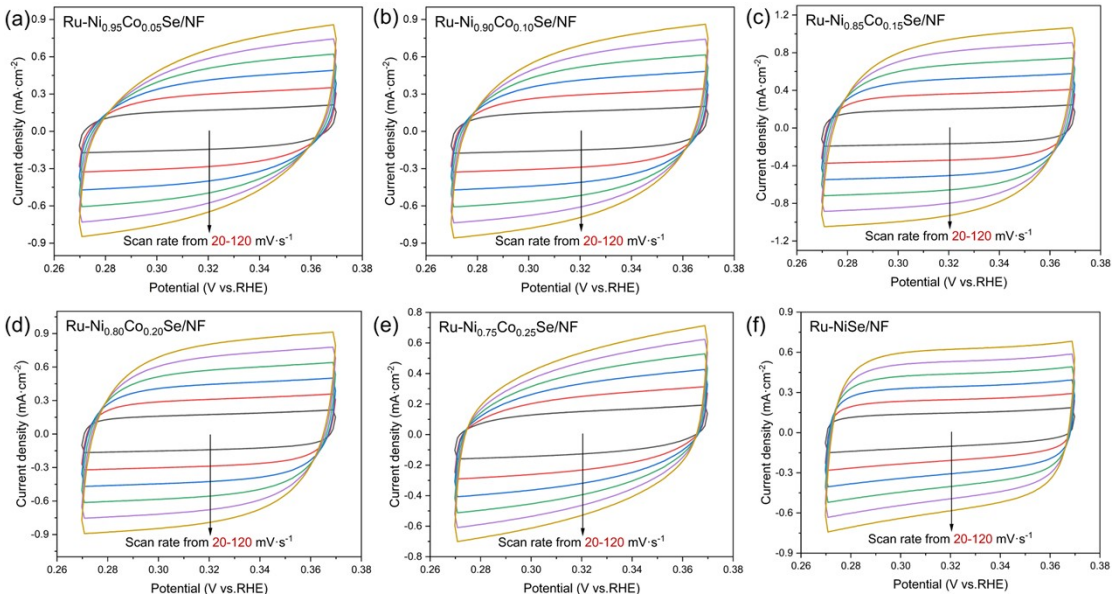


Figure S20. Cyclic voltammograms of (a)-(f) Ru-$Ni_{0.95}Co_{0.05}$Se/NF, Ru-$Ni_{0.90}Co_{0.10}$Se/NF, Ru-$Ni_{0.85}Co_{0.15}$Se/NF, Ru-$Ni_{0.80}Co_{0.20}$Se/NF, Ru-$Ni_{0.75}Co_{0.25}$Se/NF and Ru-NiSe/NF electrocatalysts in 1.0 M KOH at various scan rates.

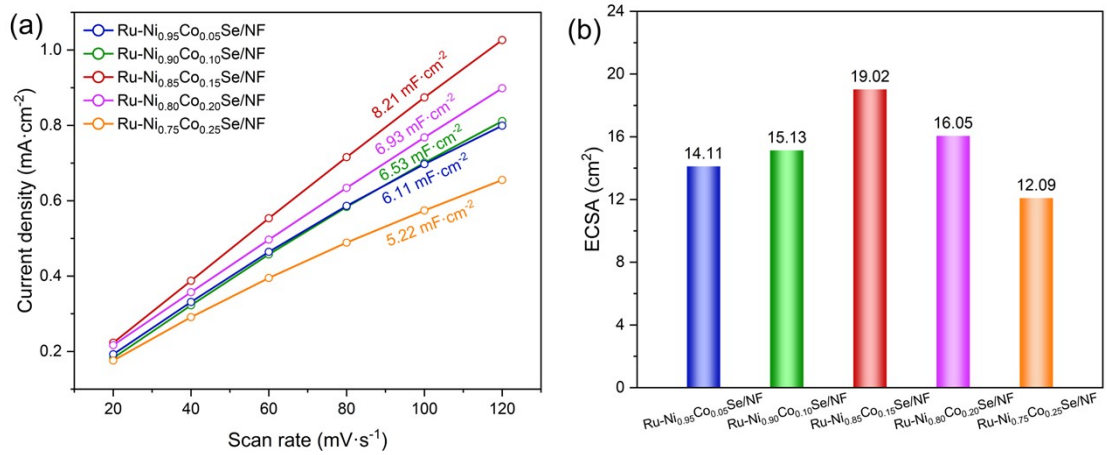


Figure S21. (a) The double-layer capacitance (C_{dl}) of different electrocatalysts. (b) Electrochemcial active surface area of different catalysts for HER.

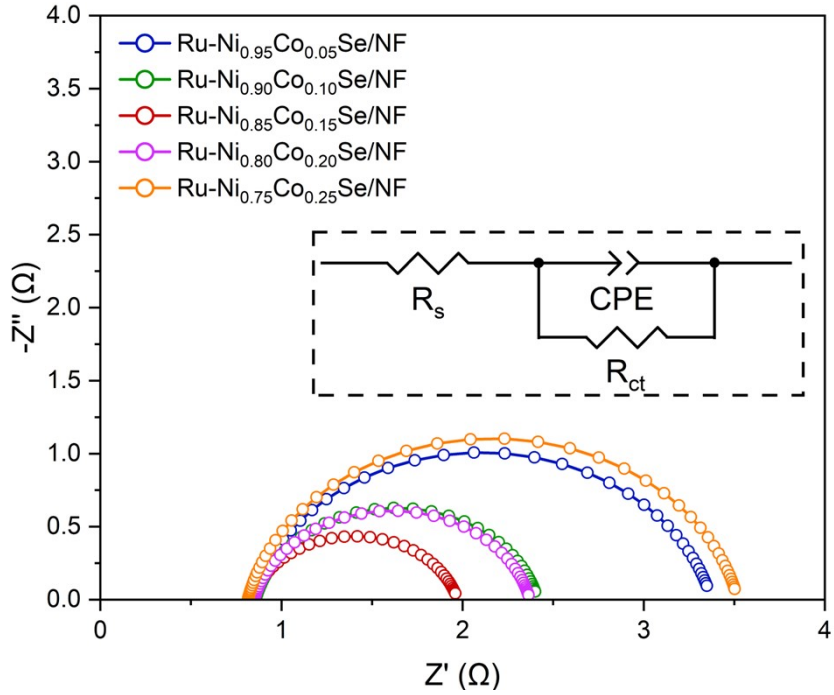


Figure S22. Nyquist plots of Ru-$Ni_{0.95}Co_{0.05}Se$/NF, Ru-$Ni_{0.90}Co_{0.10}Se$/NF, Ru-$Ni_{0.85}Co_{0.15}Se$/NF, Ru-$Ni_{0.80}Co_{0.20}Se$/NF and Ru-$Ni_{0.75}Co_{0.25}Se$/NF for HER.

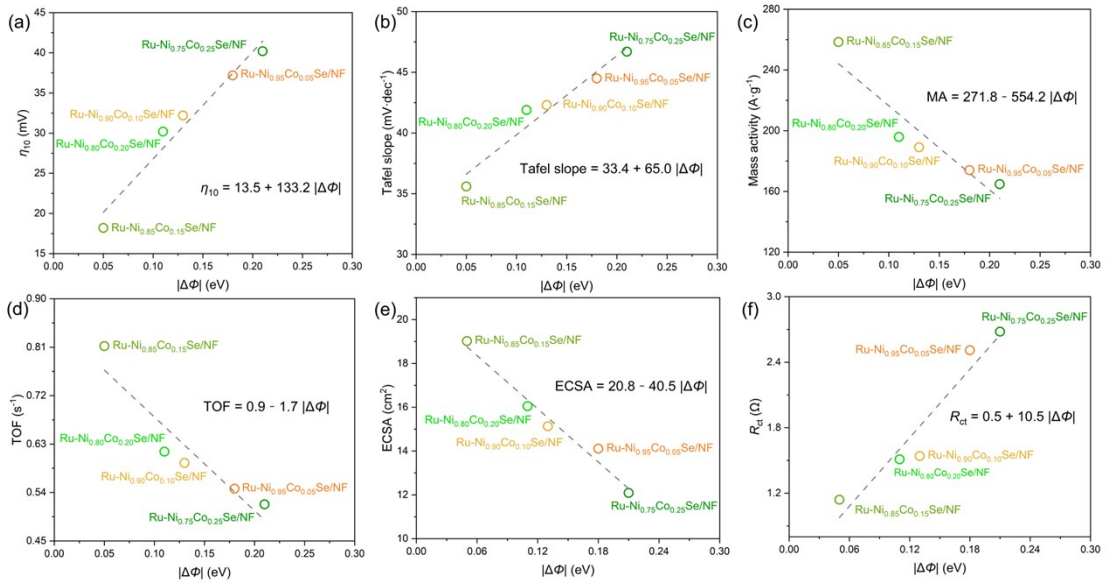


Figure S23. Plots of (a) η_{10}, (b) Tafel slope, (c) Mass activity, (d) TOF, (e) ECSA and (f) R_{ct} values as a function of the $|\Delta\Phi|$.

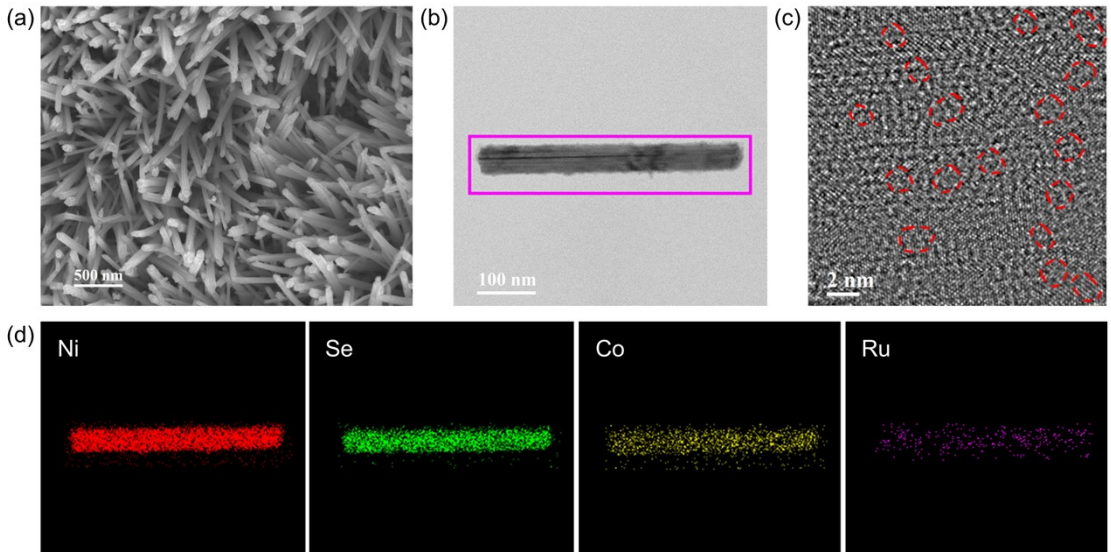


Figure S24. TEM images of Ru-$Ni_{0.85}Co_{0.15}Se$/NF after the stability test.

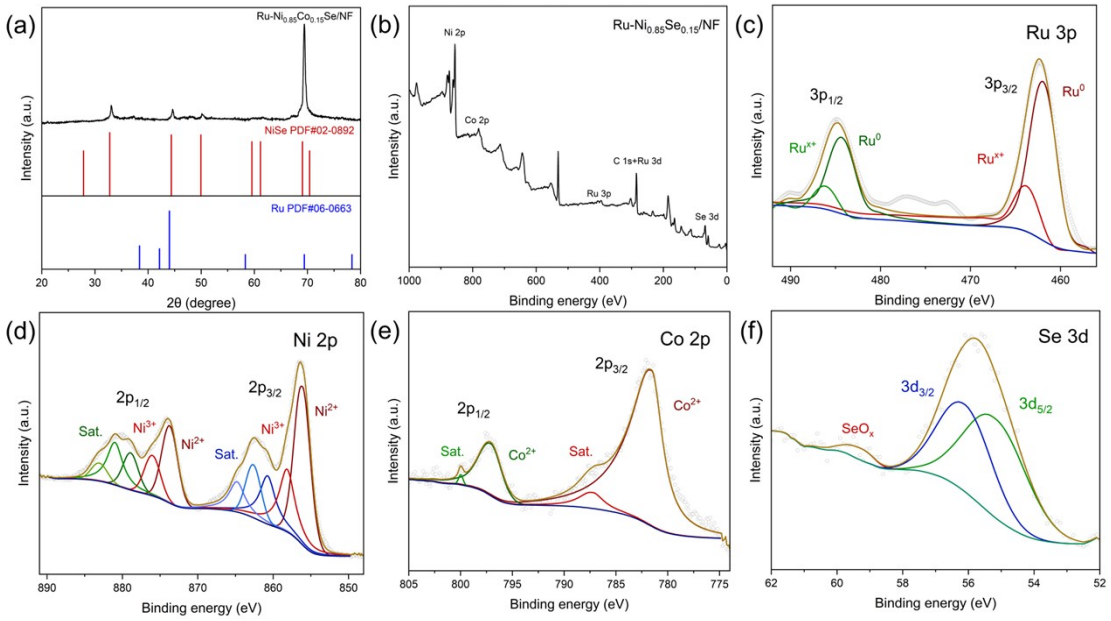


Figure S25. (a) XRD patterns of the Ru-$Ni_{0.85}Co_{0.15}Se$/NF after long-term stability test. XPS spectra of (b) survey spectra, (c) Ru 3*p* spectra and fitting curves, (d) Ni 2*p* spectra and fitting curves, (e) Co 2*p* spectra and fitting curves and (f) Se 3*d* spectra and fitting curves for Ru-$Ni_{0.85}Co_{0.15}Se$/NF after long-term stability test.

Table S1. HER performance of Ru-$Ni_{0.85}Co_{0.15}Se$/NF and other comparative samples in 1.0 M KOH media solution.

Electrocatalysts	η_{10} (mV)	Tafel slope ($mV \cdot dec^{-1}$)	C_{dl} ($mF \cdot cm^{-2}$)	ECSA (cm^2)	R_{ct} (Ω)
NiSe/NF	93.2	107.83	2.27	5.26	5.182
Ru-NiSe/NF	54.2	70.58	4.85	11.23	3.209
Ru-$Ni_{0.95}Co_{0.05}Se$/NF	37.2	44.51	6.53	15.13	2.542
Ru-$Ni_{0.90}Co_{0.10}Se$/NF	24.0	41.90	6.11	14.11	1.561
Ru-$Ni_{0.85}Co_{0.15}Se$/NF	18.2	35.61	8.21	19.02	1.142
Ru-$Ni_{0.80}Co_{0.20}Se$/NF	30.2	42.30	6.93	16.05	1.516
Ru-$Ni_{0.75}Co_{0.25}Se$/NF	40.2	46.69	5.22	12.09	2.707

Table S2. HER performance of different catalysts in 1.0 M KOH media solution.

Electrocatalysts	η_{10} (mV)	Tafel slope ($mV \cdot dec^{-1}$)	Reference
Ru-$Ni_{0.85}Co_{0.15}Se$/NF	**18.20**	**35.61**	**This work**
Ru@Ni-MOF	22.00	40.00	Angew. Chem. Int. Ed. 60 (2021) 22276–22282.
Ru MNSs	24.00	33.80	Angew. Chem. Int. Ed. 61 (2022) e202116867.
Ru/np-MoS_2	30.00	31.00	Nat. Commun. 12 (2021) 1687.
Ru/Co_3O_4 NWs	30.98	69.75	Nano Energy. 85 (2021) 105940.
Ru-$NiCo_2S_4$	32.00	41.30	Adv. Funct. Mater. 2022, 32, 2109731.
$NiRu_{0.13}$-BDC	34.00	32.00	Nat. Commun. 12 (2021) 1369.
Ru-MnFeP/NF	35.00	36.00	Adv. Energy Mater. 2020, 10, 2000814.
V_O-Ru/HfO_2-OP	39.00	29.00	Nat. Commun. 13 (2022) 1270.
Ru SAs/N-Mo_2C NSs	43.00	38.67	Applied Catalysis B: Environmental. 277 (2020) 119236.
Ru_1CoP/CDs	51.00	73.40	Angew. Chem. Int. Ed. 60 (2021) 7234–7244.
$Ru_{0.10}$@2H-MoS_2	51.00	64.90	Applied Catalysis B: Environmental. 298 (2021) 120490.