Supplementary Information (SI) for Dalton Transactions.
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Supporting Information

Electronic structure regulation in medium-entropy CoNiFeSe enabling efficient and durable oxygen evolution electrocatalysis

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Calculation details:

All DFT calculations of the Geometry Optimization, and the partial density of states (PDOS) were performed based on density functional theory (DFT) using the CASTEP program in the Materials Studio (MS) package. The generalized gradient approximation with a Perdew–Burke–Ernzerhof (GGA-PBE) function was utilized to describe the electronic exchange with the core treatment of effective core potentials. Moreover, for all these studies, convergence tolerance energy is 1.0×10^{-4} eV/atom, max. force is 0.1 eV/Å, max. displacement is 5.0×10^{-3} Å, SCF density convergence is 1.0×10^{-5}, and SCF charge mixing is 0.5, the max SCF iterations and cycle numbers were set as 300, respectively.

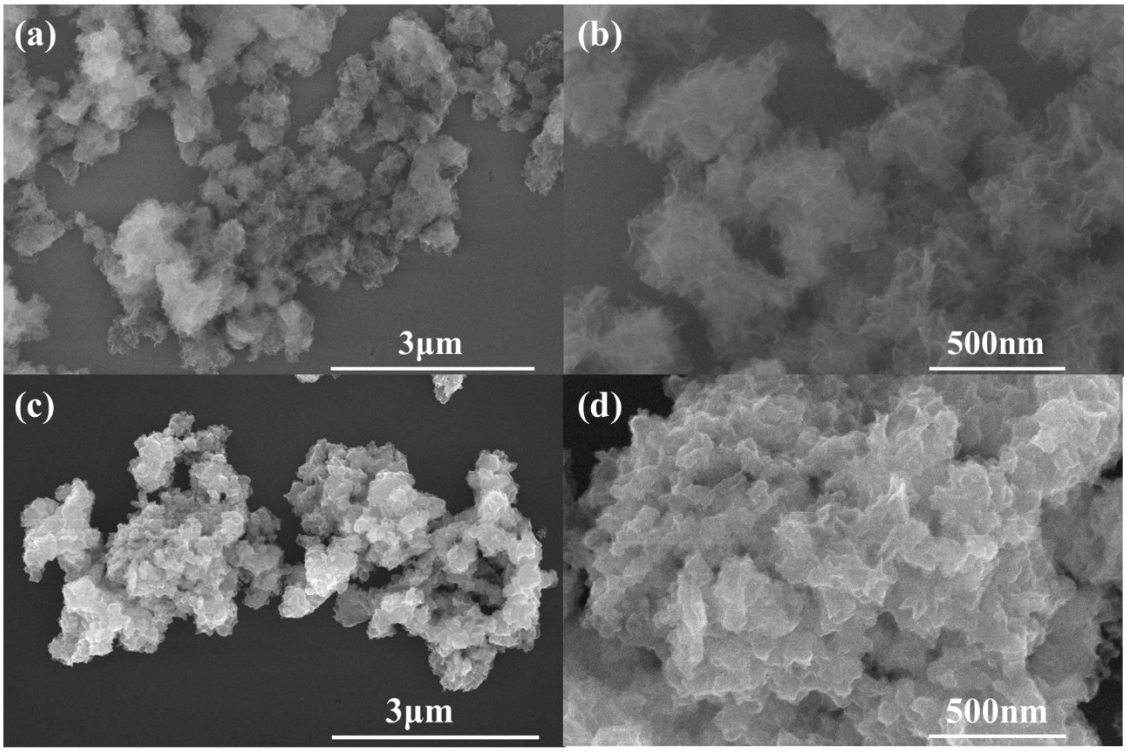

Fig. S1 (a,b) SEM images of CoNi-LDH, and (c,d) SEM images of CoNiSe.

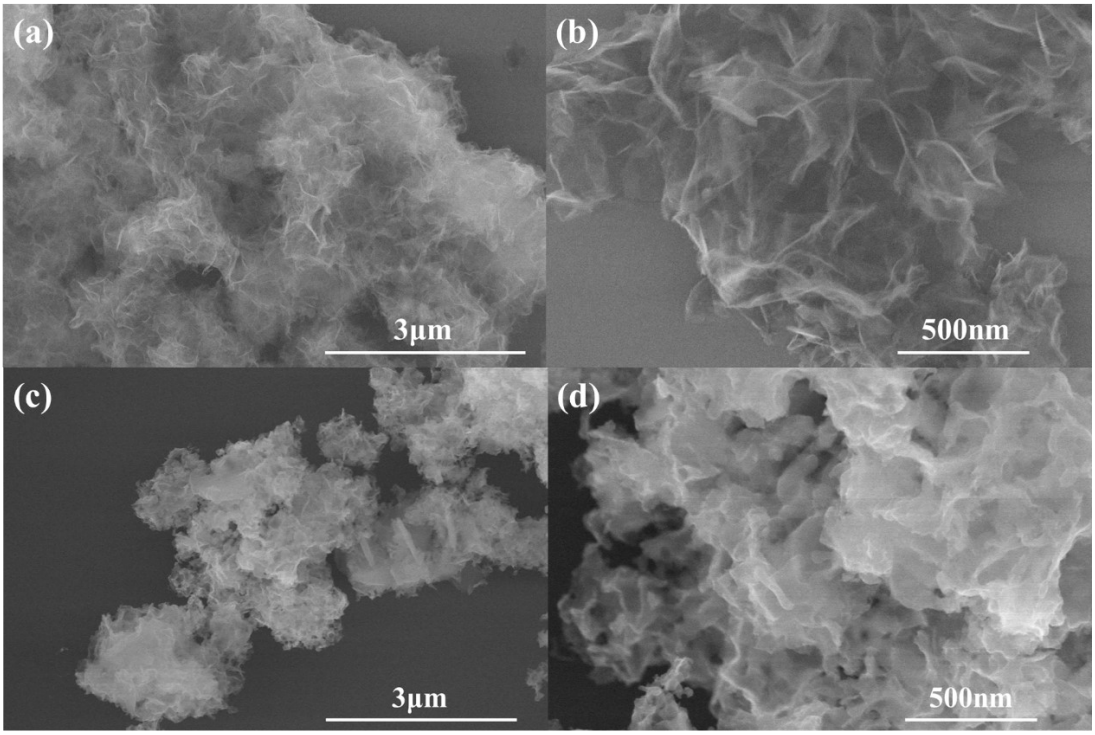

Fig. S2 (a,b) SEM images of Co-LDH, and (c,d) SEM images of CoSe.

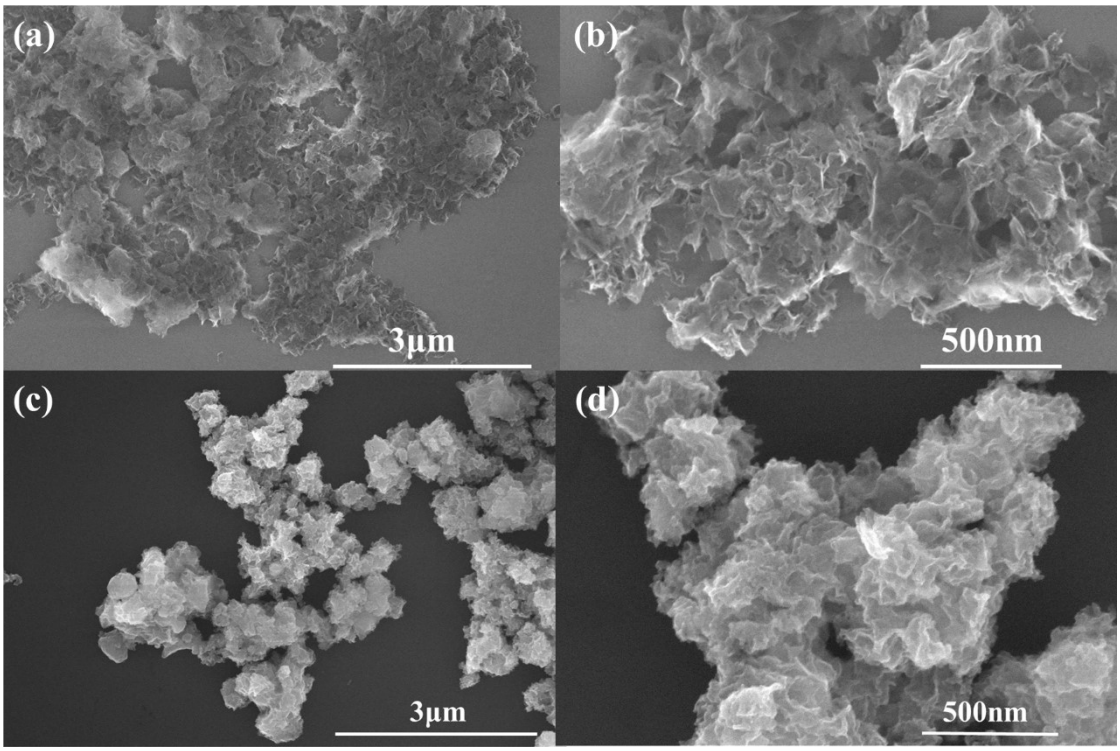

Fig. S3 (a,b) SEM images of CoFe-LDH, and (c,d) SEM images of CoFeSe.

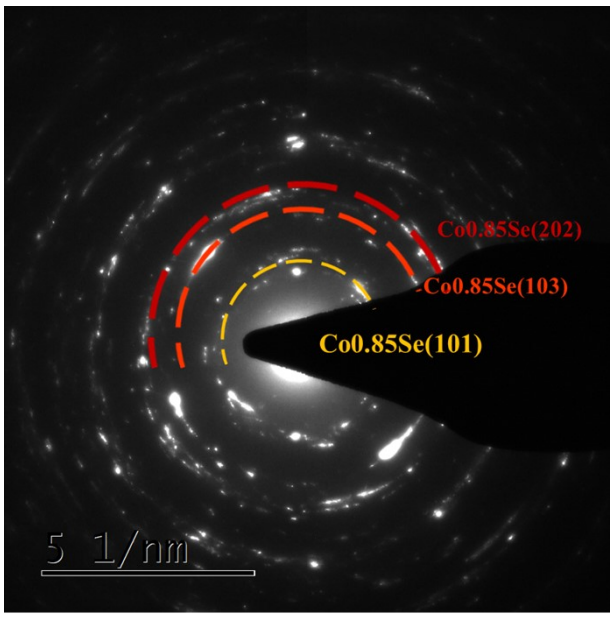

Fig. S4 SAED pattern of CoNiFeSe.

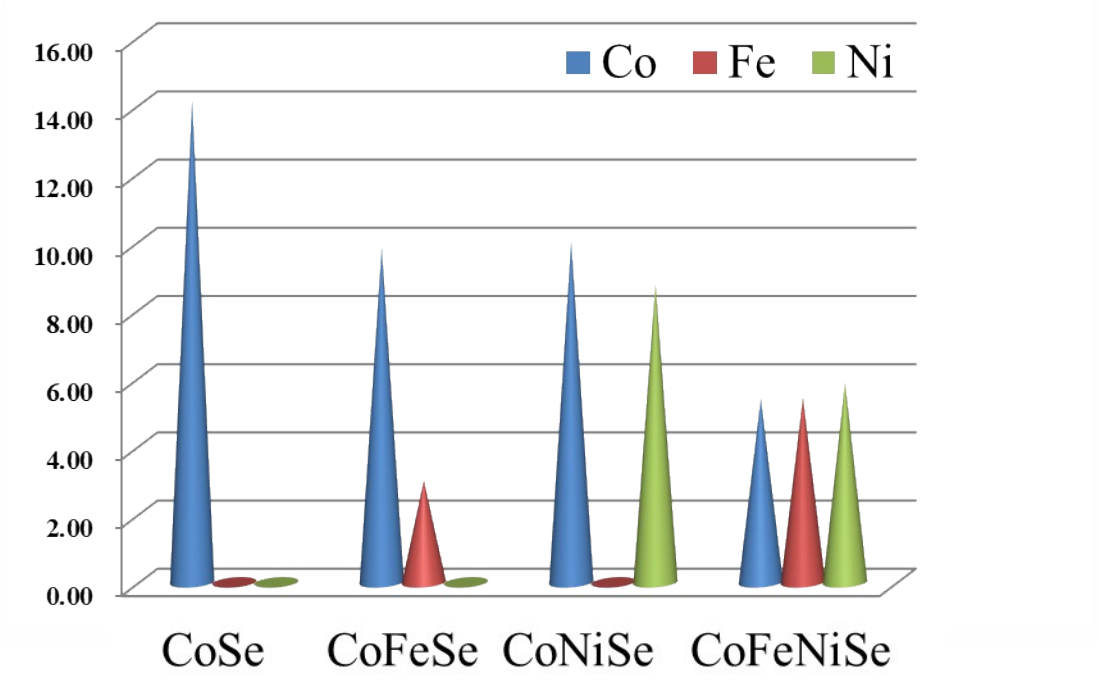

Fig. S5 Atomic ratio of CoSe, CoNiSe, CoFeSe and CoNiFeSe.

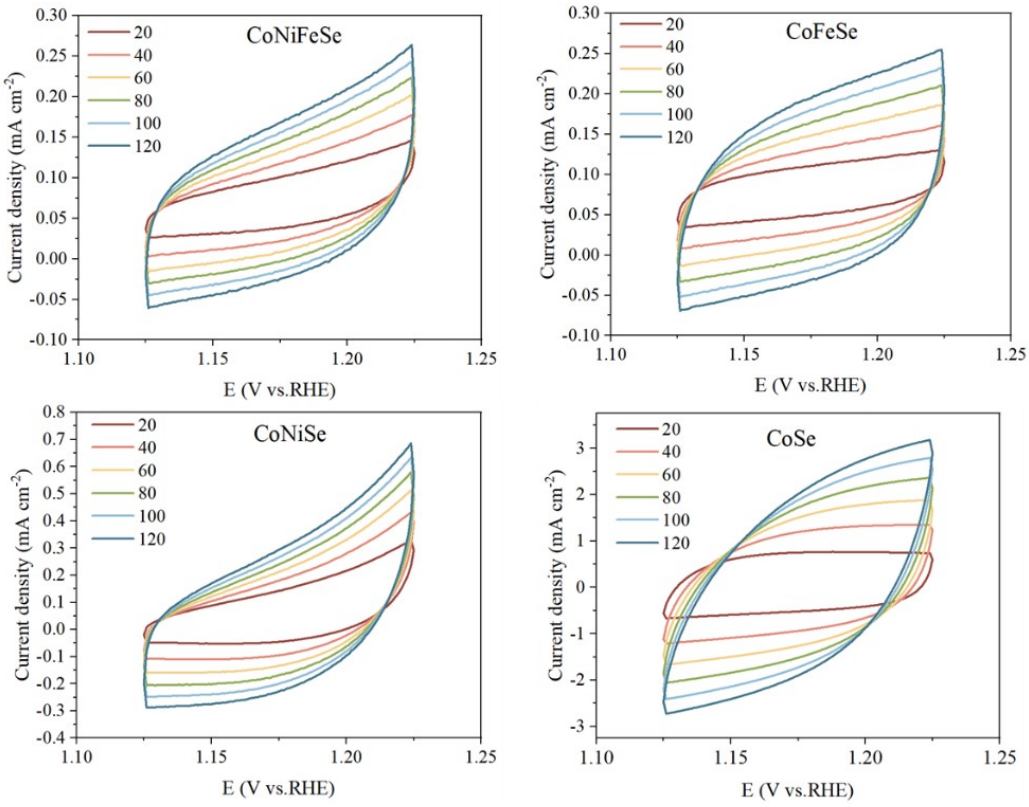

Fig. S6. CV curves of (a) CoNiFeSe, (b)CoFeSe, (c) CoNiSe and (d) CoSe.

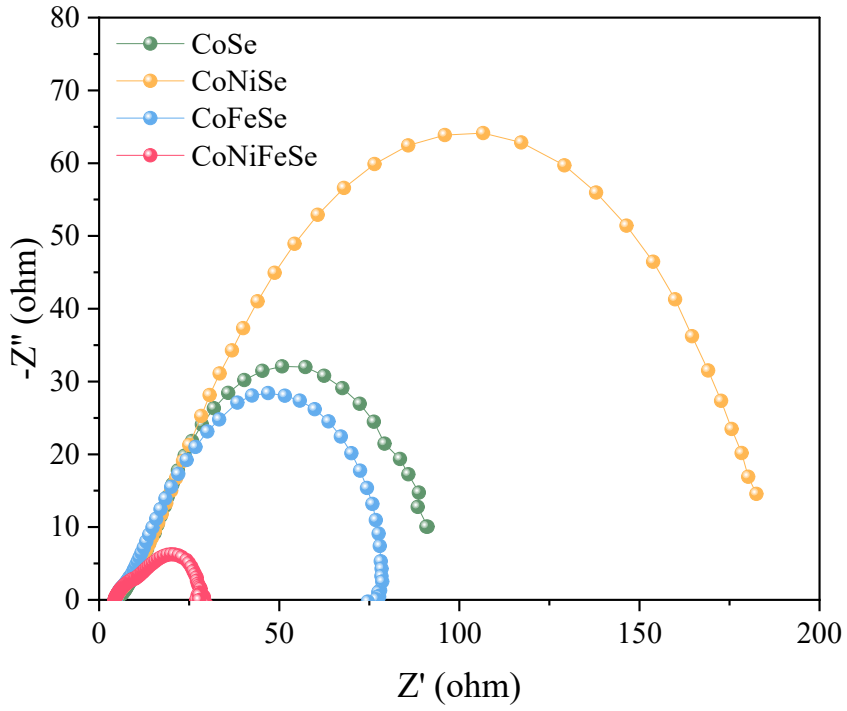

Fig. S7. The original EIS curves of CoNiFeSe, CoFeSe, CoNiSe and CoSe for fitting.

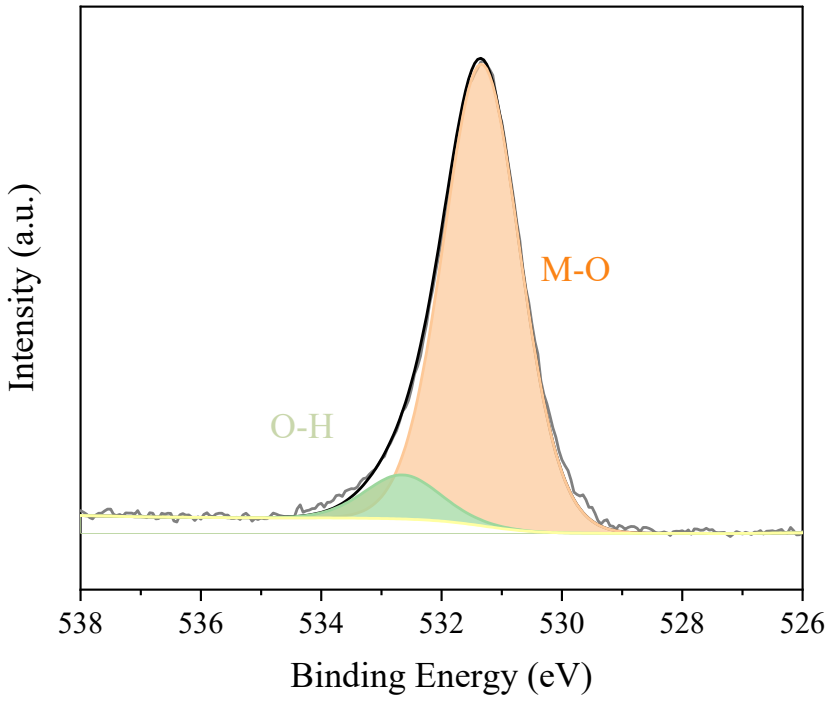

Fig. S8. O 1s XPS spectrum of CoNiFeSe.
The O 1s spectrum in Fig. S8 will resolve surface hydroxyls as O–H bond and metal-oxygen bonds as M–O.

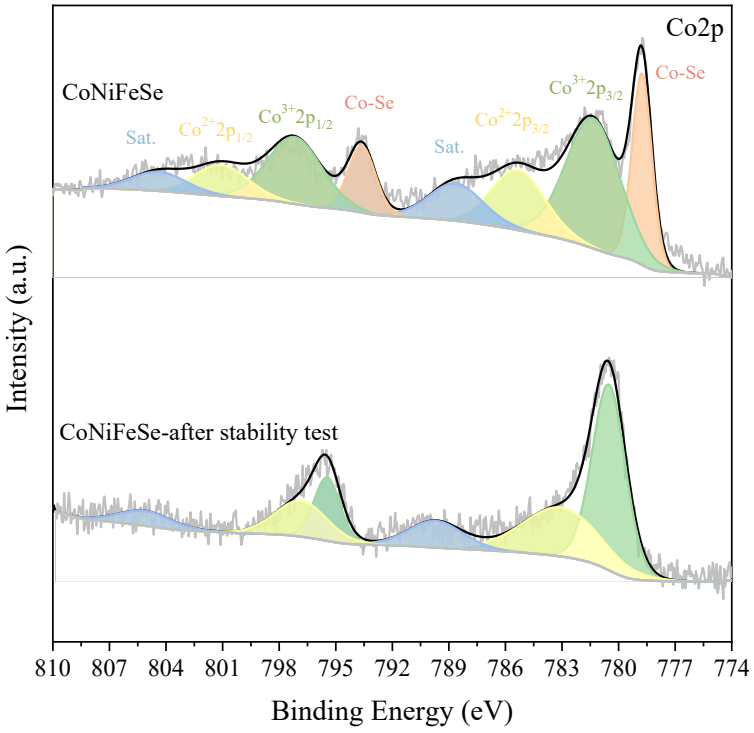

Fig. S9. Co 2p spectrum of CoNiFeSe before and after stability test.

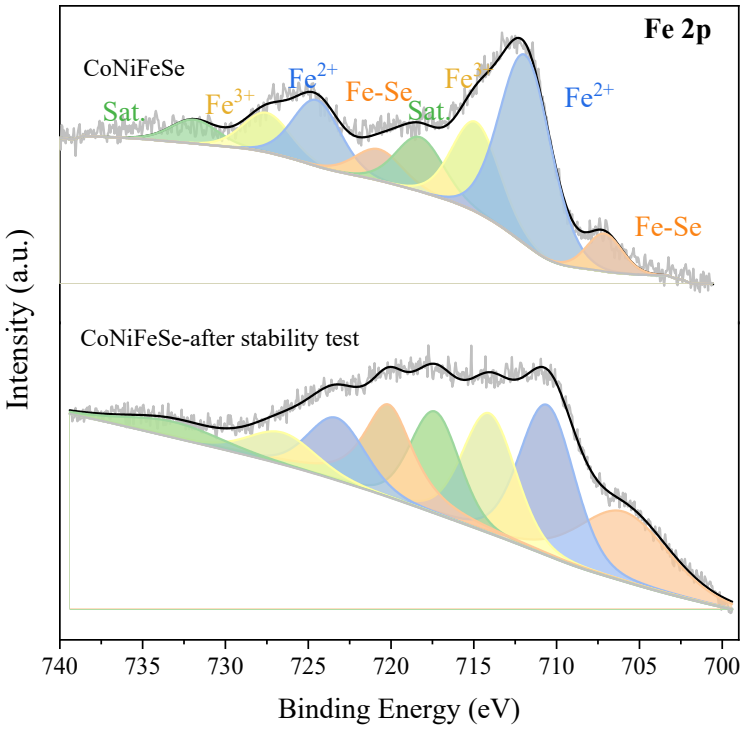

Fig. S10. Fe 2p spectrum of CoNiFeSe before and after stability test.

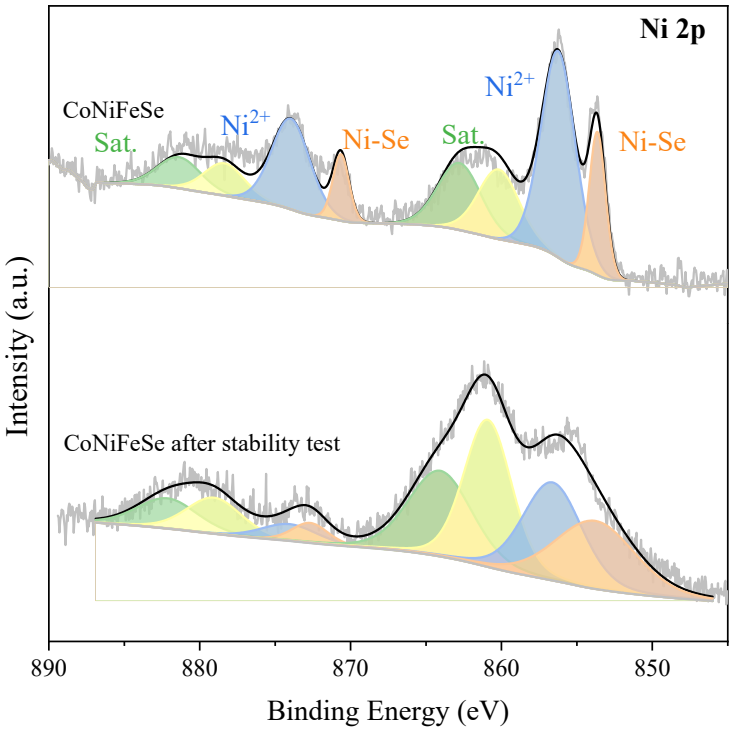

Fig. S11. Ni 2p spectrum of CoNiFeSe before and after stability test.

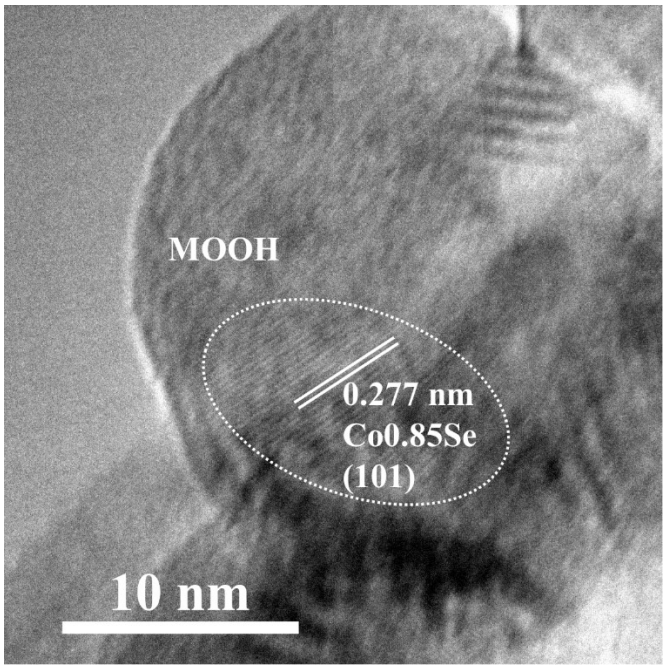

Fig. S12 HRTEM image of CoNiFeSe after stability test.

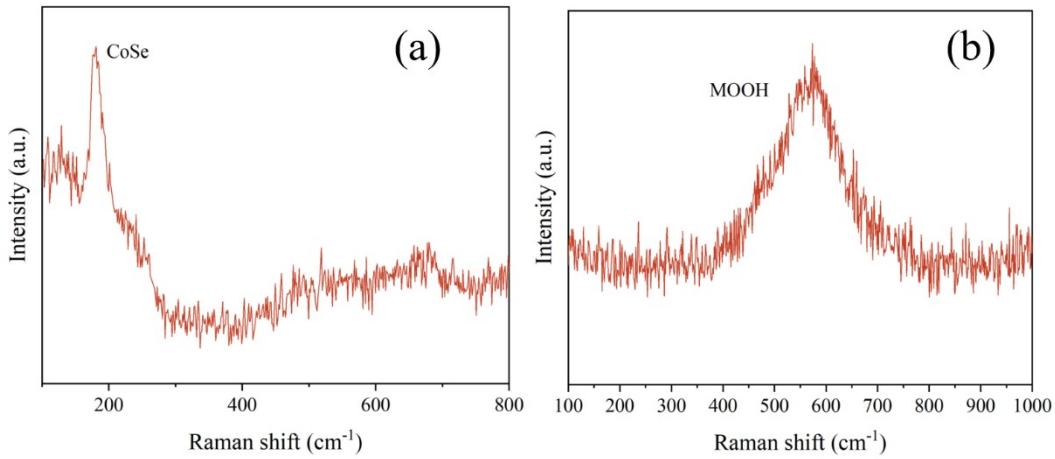

Fig. S13 Raman spectrum of CoNiFeSe before (a) and after (b) stability test.

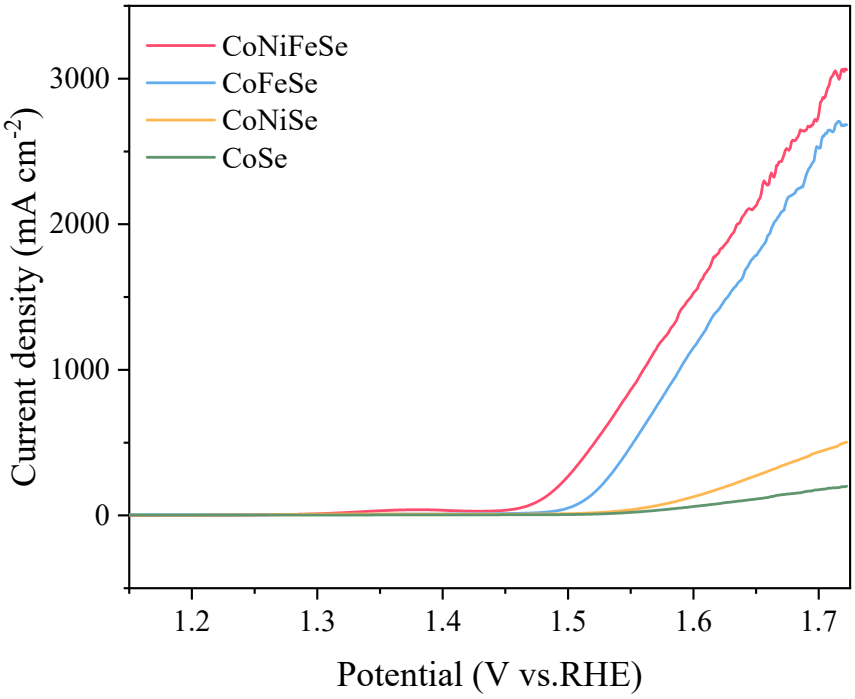

Fig. S14 The ECSA-normalized current curves of CoNiFeSe, CoFeSe, CoNiSe and CoSe.

ECSA-normalized current curves are determined through CV scans conducted at different scan rates within a non-Faradaic potential range, using the formula ECSA=C_{dl}/C_s. Here, C_s denotes the specific capacitance of a flat and smooth electrode material, which is typically 0.04 mF cm^{-2}. The ECSA-normalized current curves

presented in Fig. S14 clearly demonstrate that CoNiFeSe remains the most efficient catalyst and superior catalytic performance.[1]

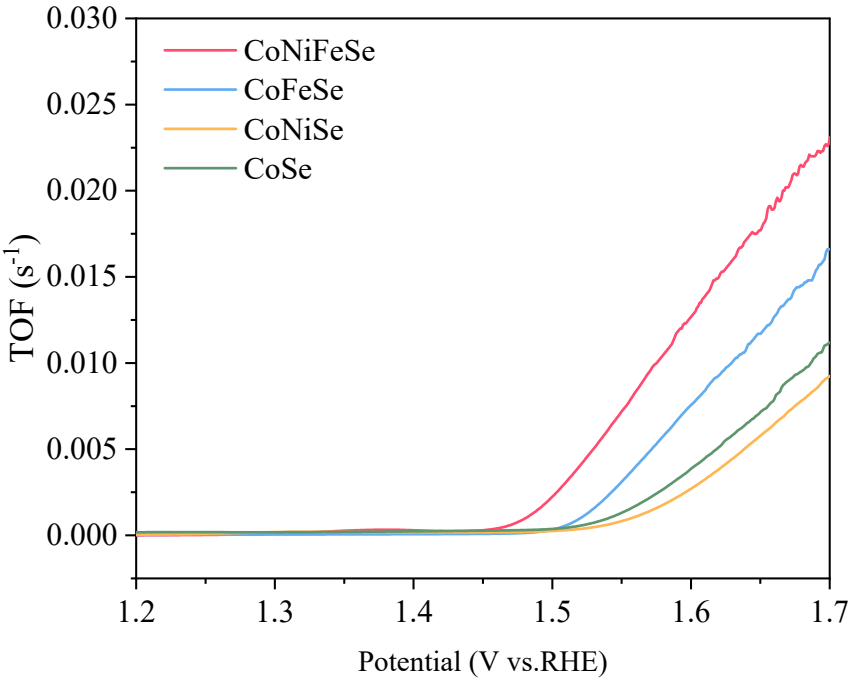

Fig. S15 The TOF curves of CoNiFeSe, CoFeSe, CoNiSe and CoSe.

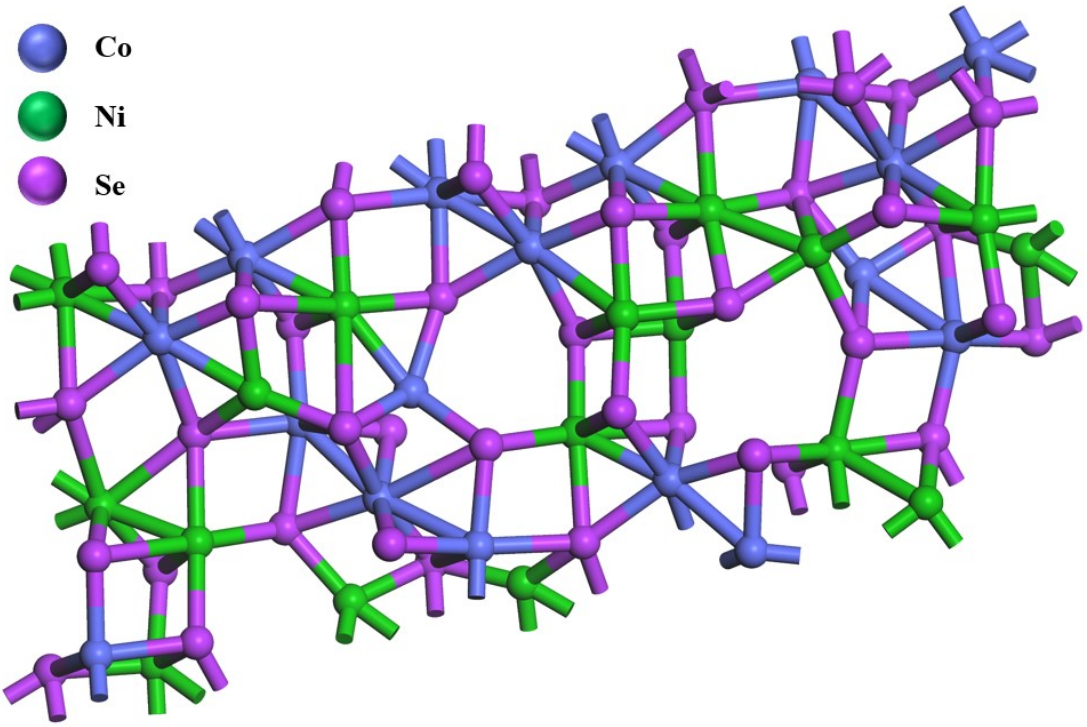

Fig. S16 The model of CoNiSe.

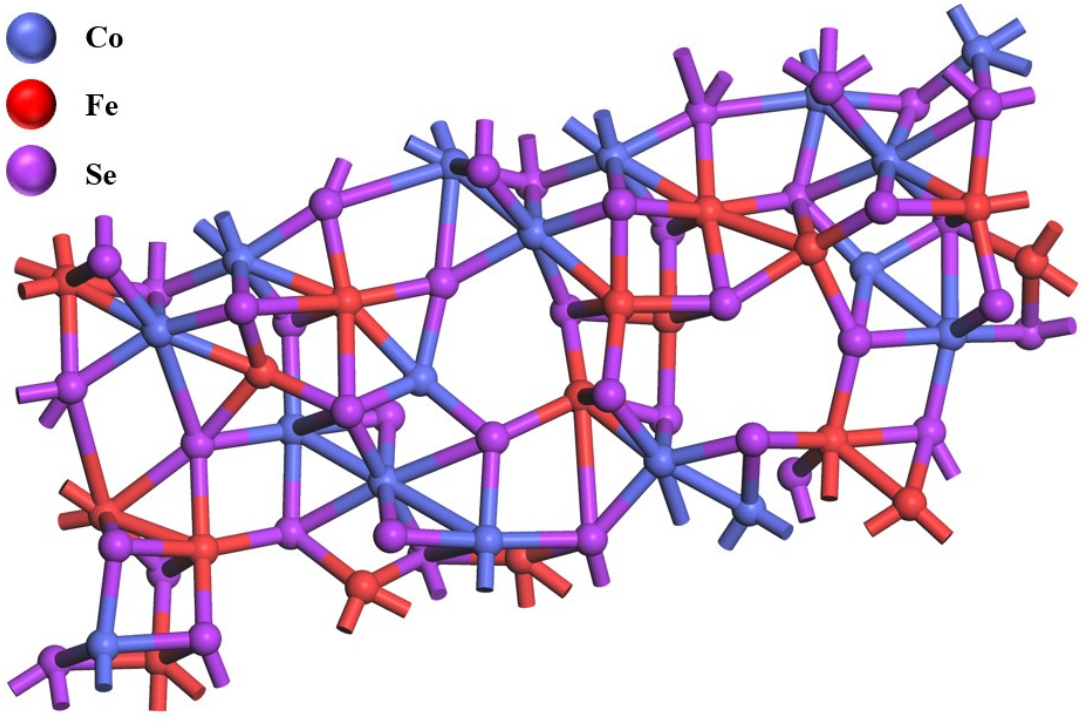

Fig. S17 The model of CoFeSe.

Table S1. Comparison of the electrocatalytic OER performance of medium-entropy CoNiFeSe and other reported materials.

Catalyst	Structure	Electrolyte	Overpotential at 10 mA cm^{-2}(mV)(vs.RHE) Anode (OER)	Tafelslope	Ref.
CoNiFeSe	**Nano-sakura**	**1.0 M KOH**	**268 mV**	**53.33mV dec^{-1}**	**This work**
CoFeNi@N-PCF	nanoparticles	1.0 M KOH	320 mV	60mV dec^{-1}	2
(FeCoNi)-S250 ℃	nanospheres	1.0 M KOH	298 mV	29mV dec^{-1}	3
FeCoNi/V3O5	nanoparticles	1.0 M KOH	265 mV	40.69mV dec^{-1}	4
FeCo0.5Ni2.5-NBs	nano-bundles	1.0 M KOH	273 mV	51.10mV dec^{-1}	5
N–CoNiFe	Nanoflake-like	1.0 M KOH	318 mV	72.20mV dec^{-1}	6
CoNiFe (2:2:1)/M		1.0 M KOH	291 mV	32.00mV dec^{-1}	7
(FeCoNiCuZn)O		1.0 M KOH	323 mV	64.5 mV dec^{-1}	8
(MgFeCoNiZn)O	rock salt type	1.0 M KOH	300 mV	44.9 mV dec^{-1}	9
$(FeCoNiCrMn)_3O_4$	sphere	1.0 M KOH	263 mV	41.24 mV dec^{-1}	10
$Cu_{0.5}Fe_{0.5}NNi_2Co_{0.5}Fe_{0.5}$	thin film	1.0 M KOH	370 mV	55 mV dec^{-1}	11
$Ni_{0.5}$ $Fe_{0.5}$ -THQ	granular structure	1.0 M KOH	272 mV	47.9 mV dec^{-1}	12
rGO/Ni_3Se_2/NF	nanoforest	1.0 M KOH	251.0 mV	143.00 mV dec^{-1}	13
SrSe@CuS		1.0 M KOH	290 mV	67 mV dec^{-1}	14

Table S2. EDS analysis attached in SEM equipment of the obtained samples.

Samples	Co (atom%)	Fe (atom%)	Ni (atom%)	Se (atom%)	O (atom%)
CoSe	14.16	0.00	0.00	33.50	52.35
CoFeSe	9.84	3.00	0.00	36.75	50.41
CoNiSe	10.02	0.00	8.78	35.43	45.77
CoNiFeSe	5.41	5.44	5.88	27.21	56.06

Table S3. CoNiFeSe, CoFeSe, CoNiSe and CoSe samples calculated TOF data

	CoNiFeSe	CoFeSe	CoNiSe	CoSe
Weight%(Co) from EDS	7.94	13.01	12.74	19.33
n(Co)/mol	$8.61*10^{-8}$	$1.41*10^{-7}$	$1.38*10^{-7}$	$2.10*10^{-7}$

Table S4. The R_{ct} value after equivalent circuit fittings.

	CoNiFeSe	CoFeSe	CoNiSe	CoSe
R_{ct} value (Ω)	30.52	92.23	202.50	110.70

References

1. J. Zhou, F. Qiao, Z. Ren, X. Hou, Z. Chen, S. Dai, G. Su, Z. Cao, H. Jiang and M. Huang, *Adv. Funct. Mater.*, 2024, **34**, 2304380.
2. M. Li, L. Zong, J. Zhao, K. Fan, F. Song, Q. Zhang, Z. Wang and L. Wang, *J. Alloys Compd.*, 2024, **976**, 173183.
3. Z. Yousefi, A. A. Asgharinezhad, A. Larimi and C. Ghotbi, *J. Alloys Compd.*, 2024, **1002**, 175214.
4. Q. Wan, Y. Zhang, Q. Qi, H. Feng, Y. Feng, F. Bai, C. Zhang and J. Hu, *Mater. Lett.*, 2024, **365**, 136485.
5. T. Liu, Y. Zhang, J. Yu, M. Hu, Z. Wu, X. Wei, S. Yu and Y. Du, *Inorg. Chem. Front.*, 2024, **11**, 6064-6071.

6. A. T. N. Nguyen, M. Kim and J. H. Shim, *RSC Adv.*, 2022, **12**, 12891-12901.
7. T. M. Pham, M. Plevova, S. Bartling, N. Rockstroh, A. Springer, A. Slabon, J. Hnat, A.-E. Surkus and R. Francke, *J. Catal.*, 2024, **438**, 115675.
8. Y. Lao, X. Huang, L. Liu, X. Mo, J. Huang, Y. Qin, Q. Mo, X. Hui, Z. Yang and W. Jiang, *Chem. Eng. J.*, 2024, **481**, 148428.
9. H. Wu, Q. Lu, Y. Li, J. Wang, Y. Li, R. Jiang, J. Zhang, X. Zheng, X. Han, N. Zhao, J. Li, Y. Deng and W. Hu, *Nano Lett.*, 2022, **22**, 6492-6500.
10. H. He, P. Kou, Z. Zhang, D. Wang, R. Zheng, H. Sun, Y. Liu and Z. Wang, *J. Colloid Interface Sci.*, 2024, **653**, 179-188.
11. L. Zhu, C. Li, R. Zheng, W. Cheng, Y. He, C. Gong, M. Liu, Y. Huang, X. Zhu and Y. Sun, *Int. J. Hydrogen Energy*, 2024, **51**, 638-647.
12. L. Zhao, J. Yan, H. Huang, X. Du, H. Chen, X. He, W. Li, W. Fang, D. Wang, X. Zeng, J. Dong and Y. Liu, *Adv. Funct. Mater.*, 2024, **34**, 2310902.
13. S.-J. Huang, S. Balu, N. R. Barveen and R. Sankar, *Colloids Surf., A*, 2022, **654**, 130024.
14. A. Junaid, M. Abdullah, N. Bano, F. Noreen, S. I. A. Shah, R. A. Alshgari, S. Mohammad, S. Manzoor, M. F. Ehsan and M. N. Ashiq, *J. Korean Ceram. Soc.*, 2024, **61**, 469-481.