

(Ni,Co)Se@Ni(OH)₂ heterojunction nanosheet as an efficient electrocatalyst for hydrogen evolution reaction

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Figure S1. (a) XPS spectra of the $\text{NC}_x\text{S@NH}$ ($x=1.5, 2, 2.5$): (a) Ni 2p, (b) Co 2p (c) Se 3d and (d) S 2p spectrum.

Table S1. Comparison of HER activity of $(\text{NiCo}_2)\text{Se@Ni(OH)}_2$ catalyst with other reported transition metal selenides catalysts.

Figure S2. XRD of the NCS@NH and the NCS@NH after 2000 cycles.

Figure S3. SEM images of the NCS@NH after 2000 cycles.

Figure S4. (a) XPS spectra of the NCS@NH and NCS@NH after 2000 cycles: (a) Ni 2p, (b) Co (c) Se 3d and (d) S 2p spectrum.

Figure S5. (a) TEM images and (b) HRTEM images of the NCS@NH after it test.

Figure S6. Cyclic voltammetry curves of the $\text{NiCo}_2\text{S}_4\text{@NH}$ in 1.0 M KOH under different scan rate in a region of 0.8 to 0.85 V vs RHE.

Figure S7. XRD of the $\text{CoNiSe}_2\text{@CoO}$.

Figure S8. SEM images of the $\text{CoNiSe}_2\text{@CoO}$.

Figure S9. Electrochemical performances: (a) HER polarization curves, (b) the Tafel plots and (c) Nyquist plots of $\text{CoNiSe}_2\text{@CoO}$ and NCS@NH .

Figure S10. XRD of the NCS_x ($x=1, 1.5$).

Figure S11. SEM images of the $\text{NCS}_{1.5}$.

Figure S12. Electrochemical performances: (a) HER polarization curves, (b) the Tafel plots and (c) Nyquist plots of NCS@NH and $\text{NCS}_{1.5}$.

Experiment

Electrochemical measurements

Electrochemical measurements were performed in 1.0 M KOH solution at 25°C, and used a three-electrode system with graphite rod as the counter electrode and Hg/HgCl₂ (SCE, CHI104, China) electrode, The NCS@NH and other samples electrodes immersed into electrolyte was 1 × 1 cm², which were used as working electrodes. In alkaline solution, $E(\text{RHE}) = E(\text{SCE}) + 0.243 \text{ V} + 0.0592 * \text{pH}$.

Characterization

Phase analysis of all as-prepared samples was measured with X-ray powder diffraction with Rigaku D-MAX-2500/PC using Cu K α radiation. The morphologies and structures of the samples was observed with scanning electron microscopy (SEM) with Zeiss sigma-500, transmission electron microscopy (TEM; FEI, Tecnai G2 F20) and high-resolution transmission electron microscope (HRTEM). The surface element analysis were confirmed by using X-ray photoelectron spectroscopy (XPS; Thermo Fisher Scientific, Escalab 250Xi).

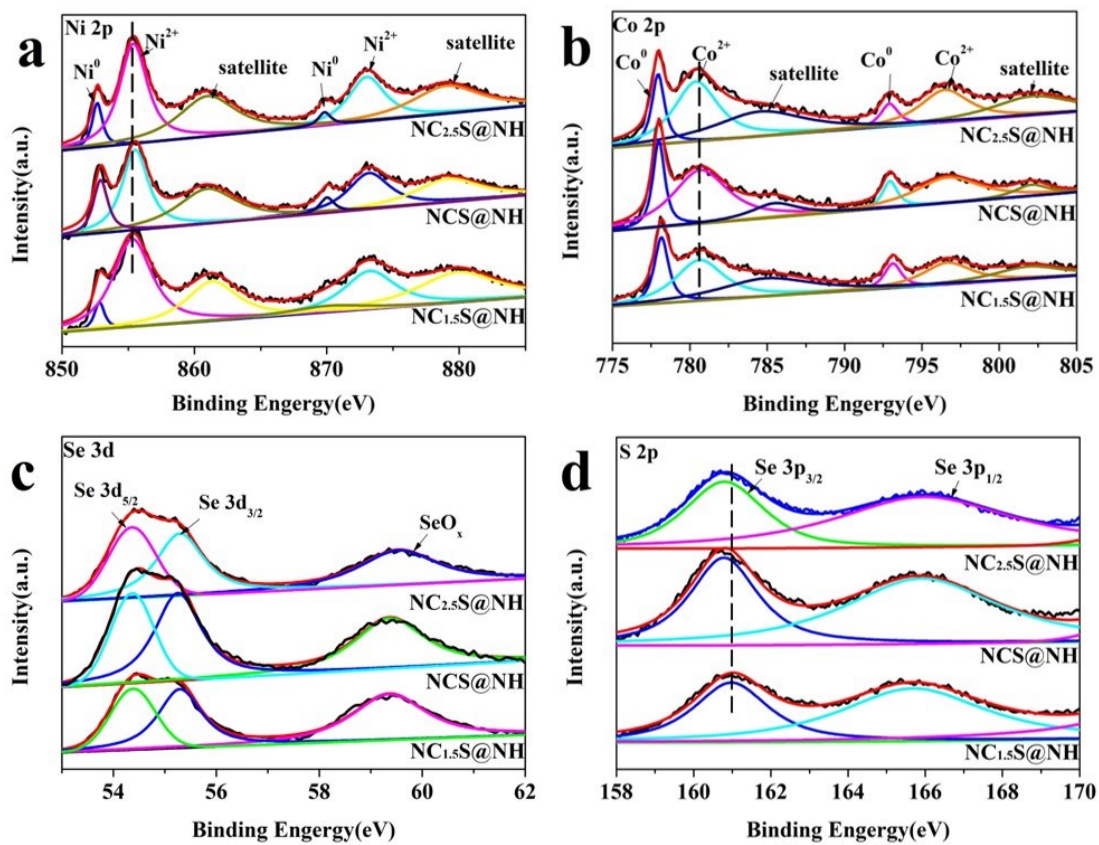


Figure S1. (a) XPS spectra of the $\text{NC}_x\text{S@NH}$ ($x=1.5, 2, 2.5$): (a) Ni 2p, (b) Co 2p (c) Se 3d and (d) S 2p spectrum.

Table S1 Comparison of HER activity of (NiCo₂)Se@Ni(OH)₂ catalyst with other reported transition metal selenides catalysts.

Samples	η_{10} (V vs. RHE)	electrolyte	References
(NiCo ₂)Se@Ni(OH) ₂	130.8 mV	1 M KOH	This work
NiCo ₂ S ₄ @Ni(OH) ₂	148.6 mV	1 M KOH	This work
(NiCo _{1.5})Se@Ni(OH) ₂	167.1 mV	1 M KOH	This work
(NiCo _{2.5})Se@Ni(OH) ₂	130.7 mV	1 M KOH	This work
(NiCo ₂)Se _{1.5}	153.8 mV	1 M KOH	This work
CoNiSe ₂ @CoO	155.6 mV	1 M KOH	This work
Ni-Se-Cu	136 mV	1 M KOH	[S1]
Ni-Se _{1.2} -S _{0.8}	144 mV	1 M KOH	[S2]
Ni _{0.85} Se@NC	135 mV	1 M KOH	[S3]
CoSe ₂ /MoSe ₂	168 mV	1 M KOH	[S4]
NiSe ₂ @NC	162 mV	1 M KOH	[S5]
30wt%MWCNTs/Co _{0.85} Se	266 mV	0.5 M H ₂ SO ₄	[S6]
Ni _{0.54} W _{0.26} Se	162 mV	1 M KOH	[S7]
3 at. % Zn-doped MoSe ₂	231 mV	0.5 M H ₂ SO ₄	[S8]
P-1T/2H-MoSe ₂ -1	174 mV	0.5 M H ₂ SO ₄	[S9]
Ni ₃ Se ₂ /NiSe NWs	198 mV	1 M KOH	[S10]

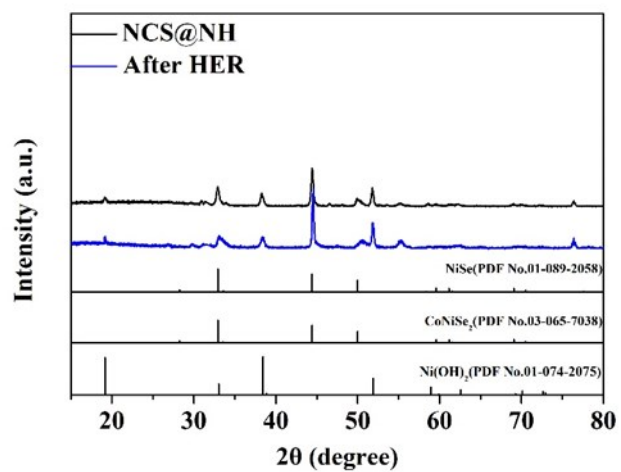


Figure S2. XRD of the NCS@NH and the NCS@NH after 2000 cycles.

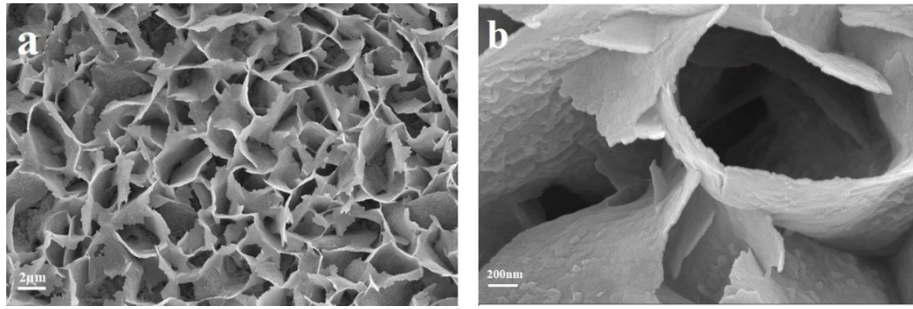


Figure S3. SEM images of the NCS@NH after 2000 cycles.

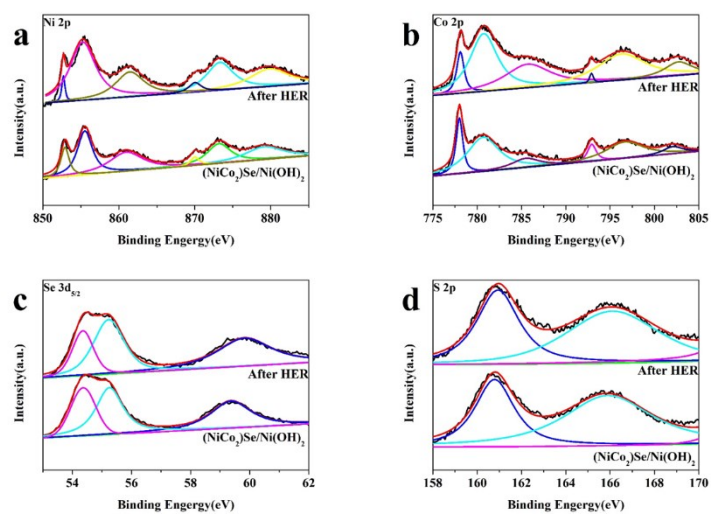


Figure S4. (a) XPS spectra of the NCS@NH and NCS@NH after 2000 cycles: (a) Ni 2p, (b) Co (c) Se 3d and (d) S 2p spectrum.

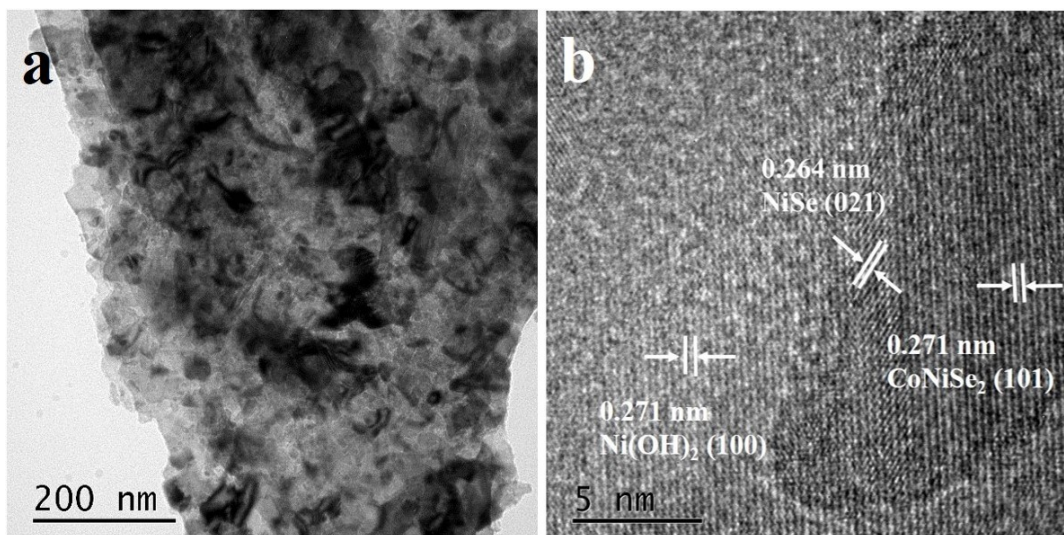


Figure S5. (a)TEM images and (b) HRTEM images of the NCS@NH after it test.

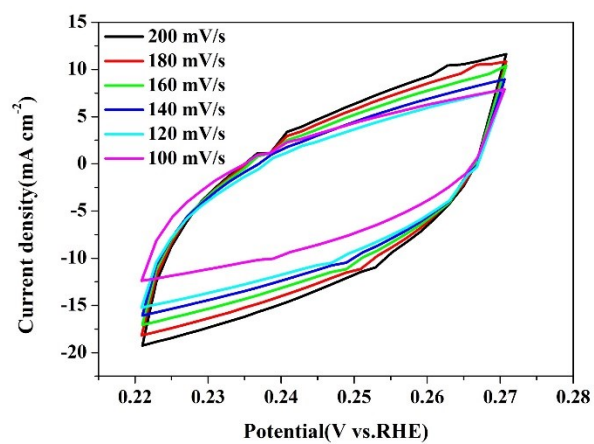


Figure S6. Cyclic voltammetry curves of the NiCo₂S₄@NH in 1.0 M KOH under different scan rate in a region of 0.8 to 0.85 V vs RHE.

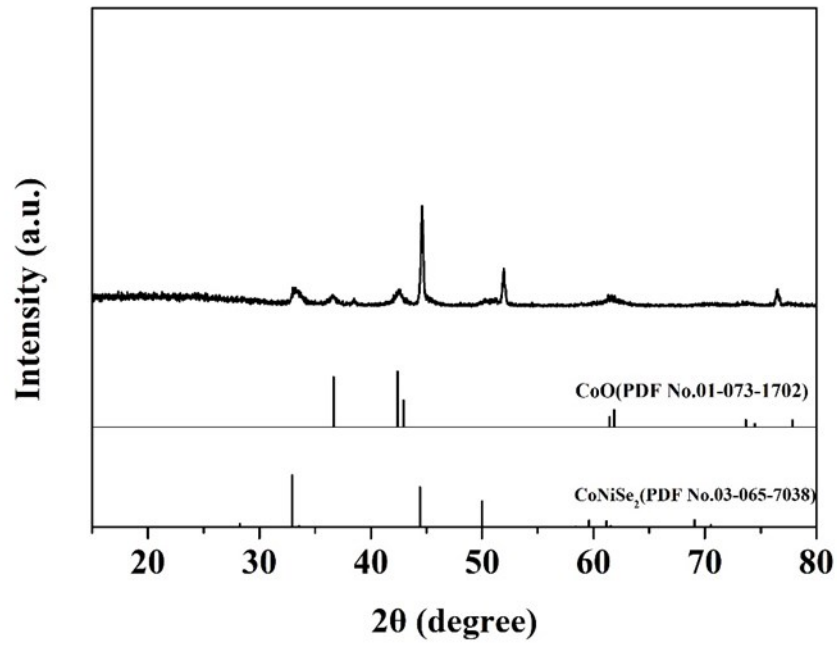


Figure S7. XRD of the CoNiSe₂@CoO.

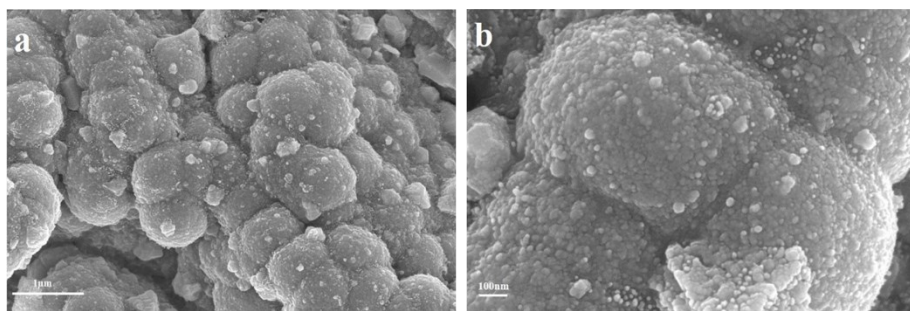


Figure S8. SEM images of the $\text{CoNiSe}_2@\text{CoO}$.

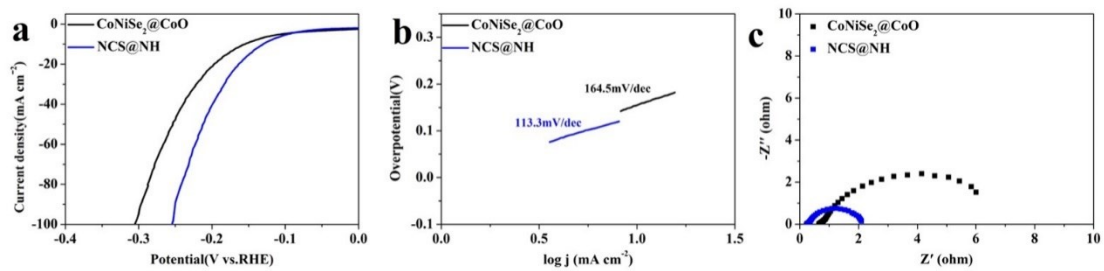


Figure S9. Electrochemical performances: (a) HER polarization curves, (b) the Tafel plots and (c) Nyquist plots of CoNiSe₂@CoO and NCS@NH.

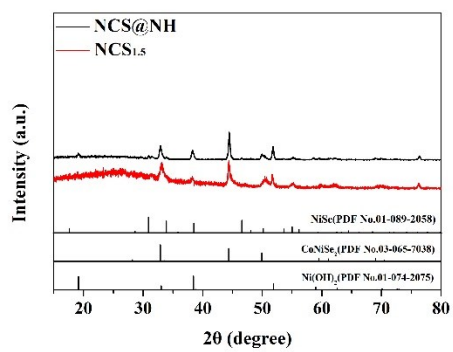


Figure S10. XRD of the NCS_x (x=1, 1.5).

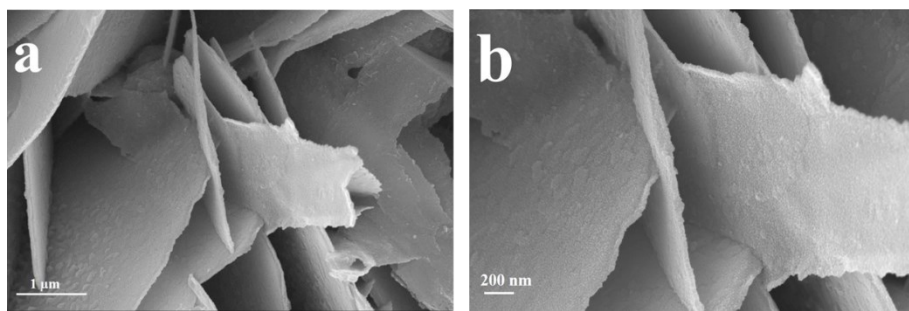


Figure S11. SEM images of the NCS_{1.5}.

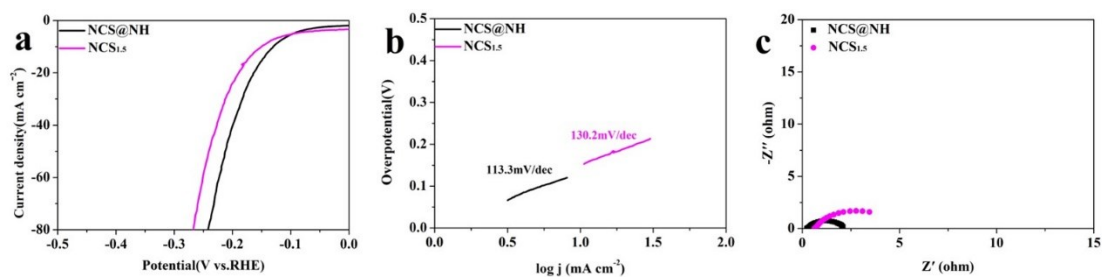


Figure S12. Electrochemical performances: (a) HER polarization curves, (b) the Tafel plots and (c) Nyquist plots of NCS@NH and NCS_{1.5}.

References

- [S1] Y. Gao, Y. Wu, H. He and W. Tan, *Journal of Colloid and Interface Science*, 2020, **578**, 555-564.
- [S2] J. Sun, X. Hu, Z. Huang, T. Huang, X. Wang, H. Guo, F. Dai and D. Sun, *Nano Research*, 2020, **13**, 2056-2062.
- [S3] Z. Huang, B. Xu, Z. Li, J. Ren, H. Mei, Z. Liu, D. Xie, H. Zhang, F. Dai, R. Wang and D. Sun, *Small*, 2020, **16**, 2004231.
- [S4] X. Tang, J-Y. Zhang, B. Mei, X. Zhang, Y. Liu, J. Wang and W. Li, *Chemical Engineering Journal*, 2021, **404**, 126529.
- [S5] Z. Huang, S. Yuan, T. Zhang, B. Cai, B. Xu, X. Lu, L. Fan, F. Dai and Da. Sun, *Applied Catalysis B: Environmental*, 2020, **272**, 118976.
- [S6] X. Sun, N. Habibul and H. Du, *Chinese Journal of Catalysis*, 2021, **42**, 235-243.
- [S7] Y. Zhao, G. Mao, Y. Du, G. Cheng and W. Luo, *Chemistry-An Asian Journal*, 2018, **13**, 2040-2045.
- [S8] J. Qian, T. Wang, B. Xia, P. Xi and D. Gao, *Electrochimica Acta*, 2019, **296**, 701-708.
- [S9] L. Chen, Y. Zhu, J. Li, H. Feng, T. Li, X. Zhang, S. Wang, M. Gu, P. Zhang and C. Zhao, *Energy Technology*, 2020, **8**, 1901503.
- [S10] H-B. Wang, Y-S. Sun, F. Ma, L. Zhou, H-F. Li, L. Zhang, G-J. Chen, Y-K. Xu, Y-N. Chen, K-W. Xu and D-Y. Ma, *Journal of Alloys and Compounds*, 2020, **819**, 153056.