Supplementary Information (SI) for Dalton Transactions.

Supporting Information

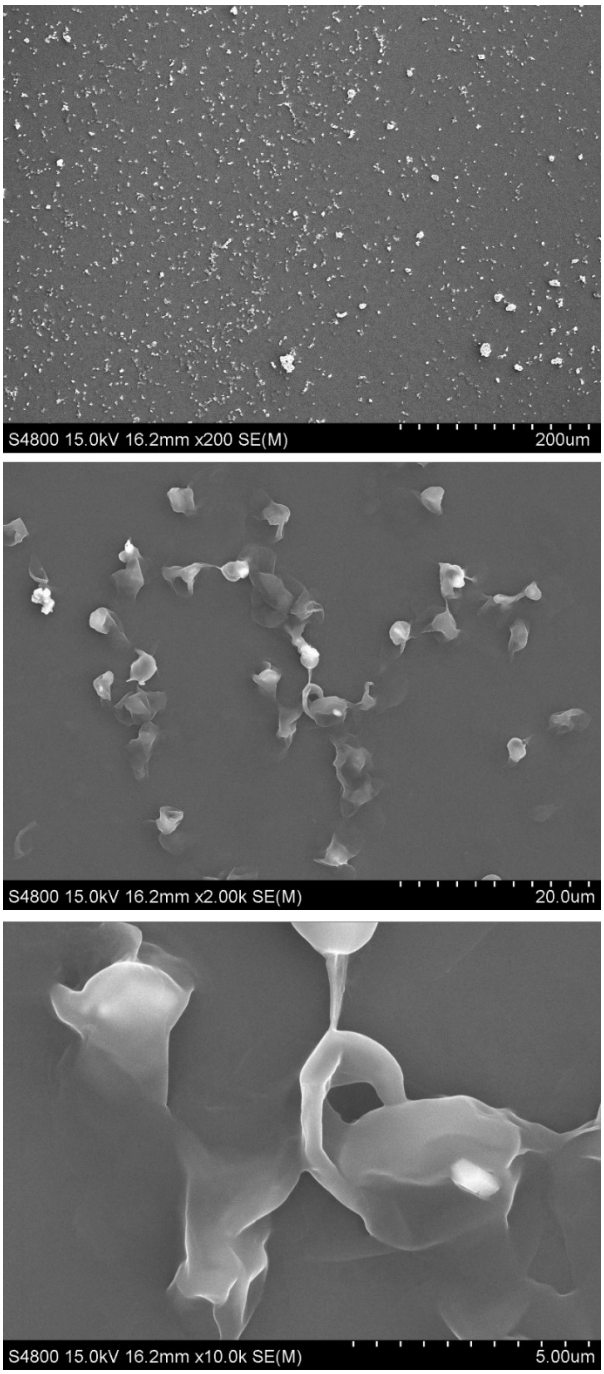

Figure S1. SEM photos of niv-NiS/$NiSe_2$ at various magnifications.

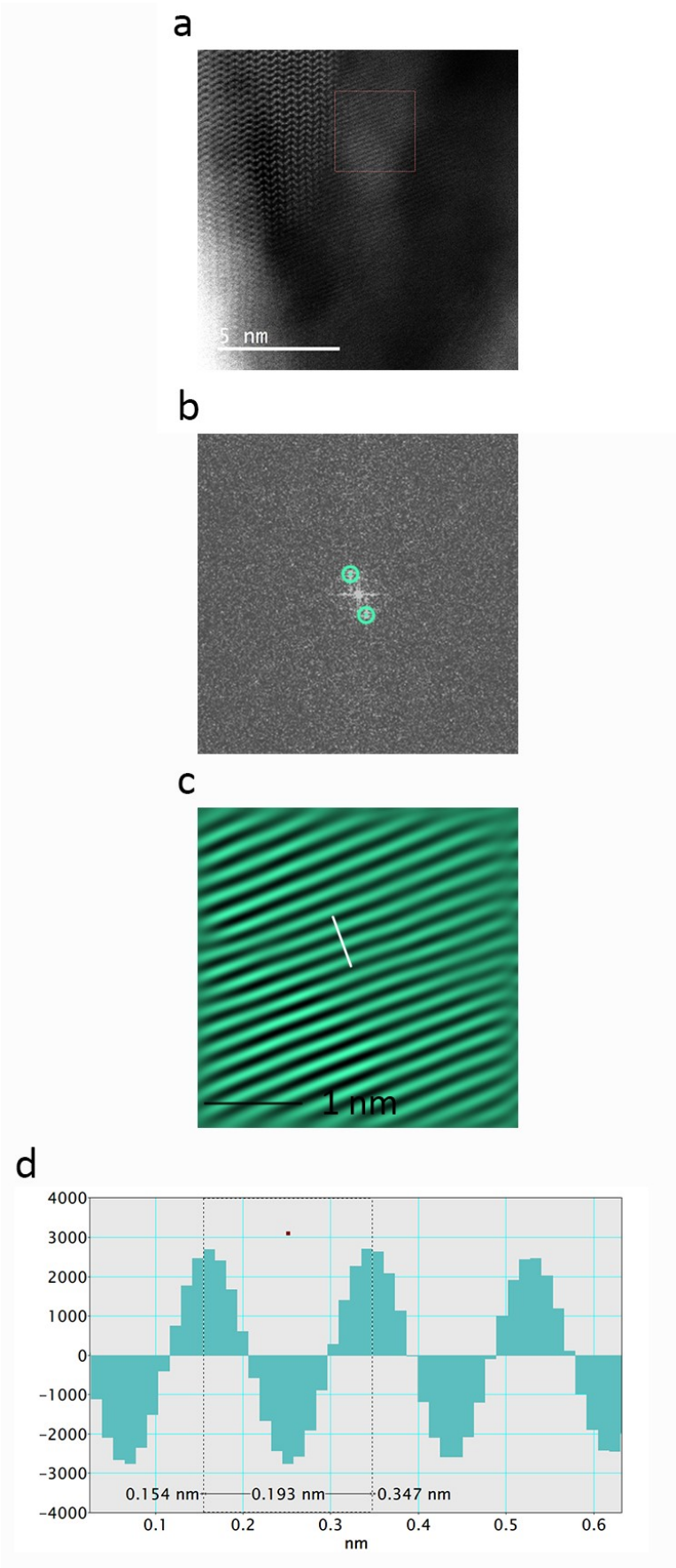

Figure S2. TEM photos of niv-NiS/$NiSe_2$.

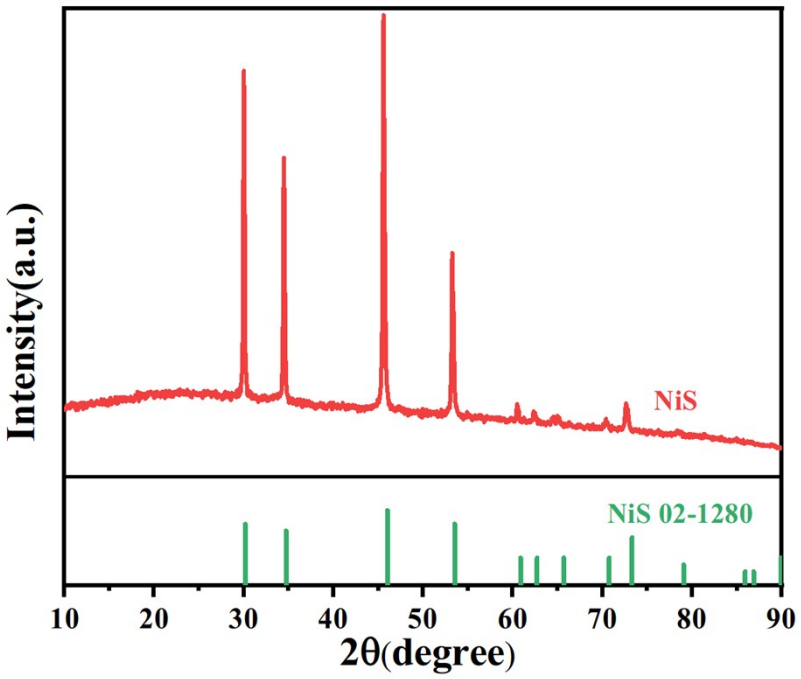

Figure S3. PXRD of NiS.

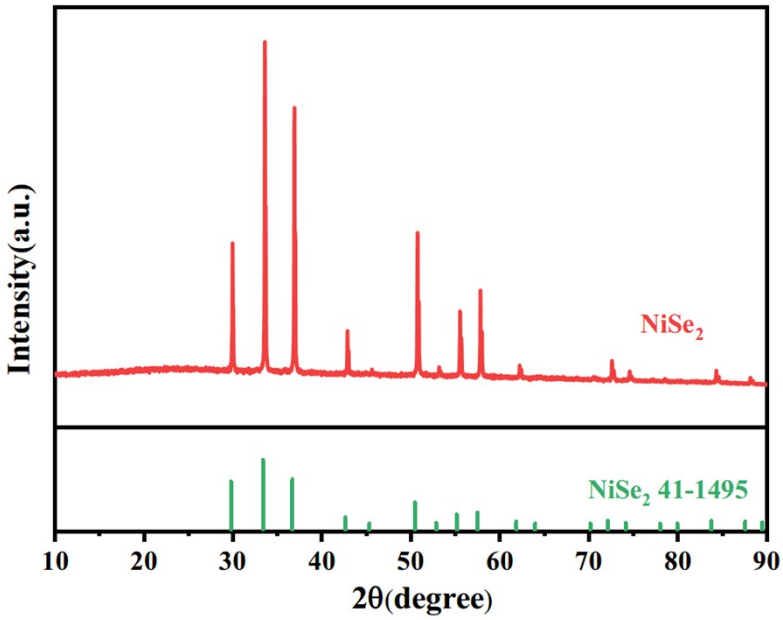

Figure S4. PXRD of $NiSe_2$.

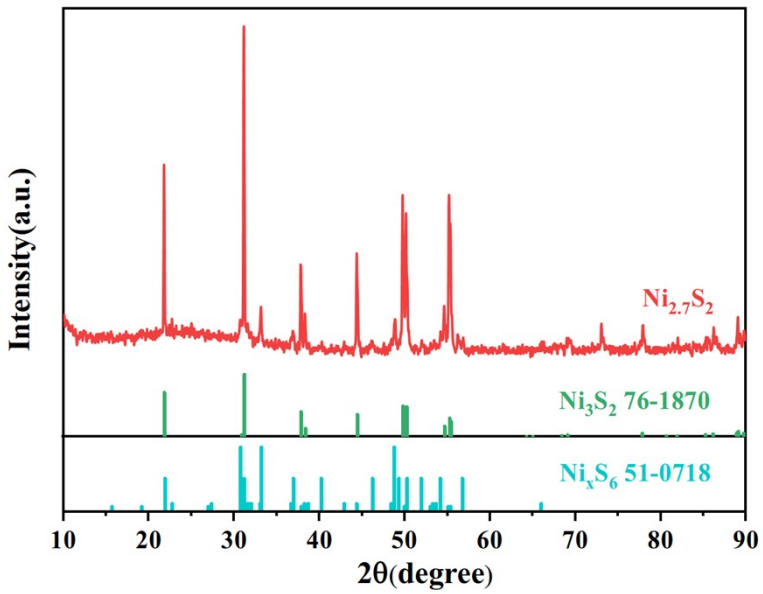

Figure S5. PXRD of Ni2.7S.

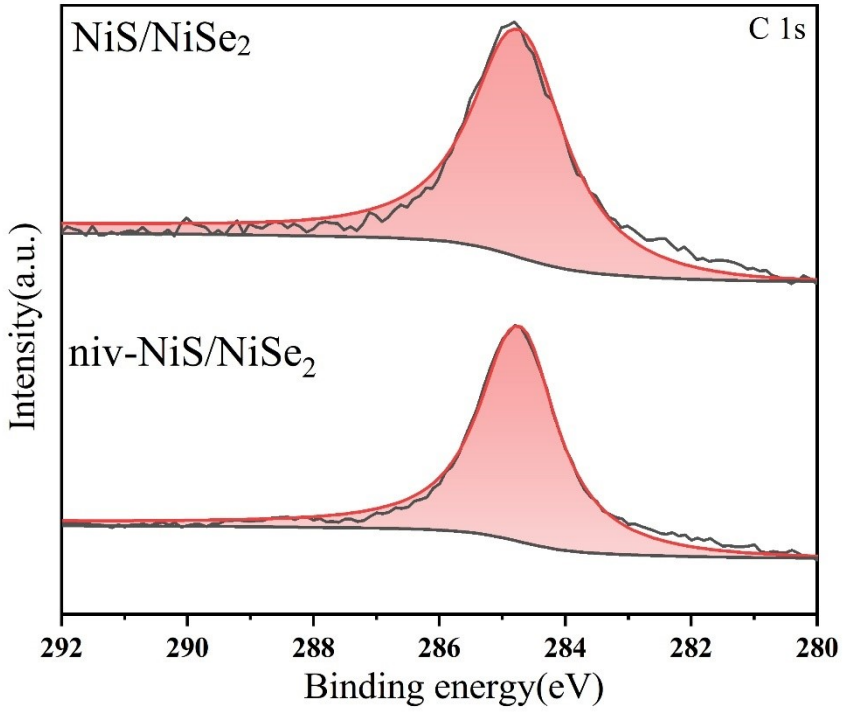

Figure S6. C 1s XPS spectra of $NiS/NiSe_2$ and niv-$NiS/NiSe_2$, respectively.

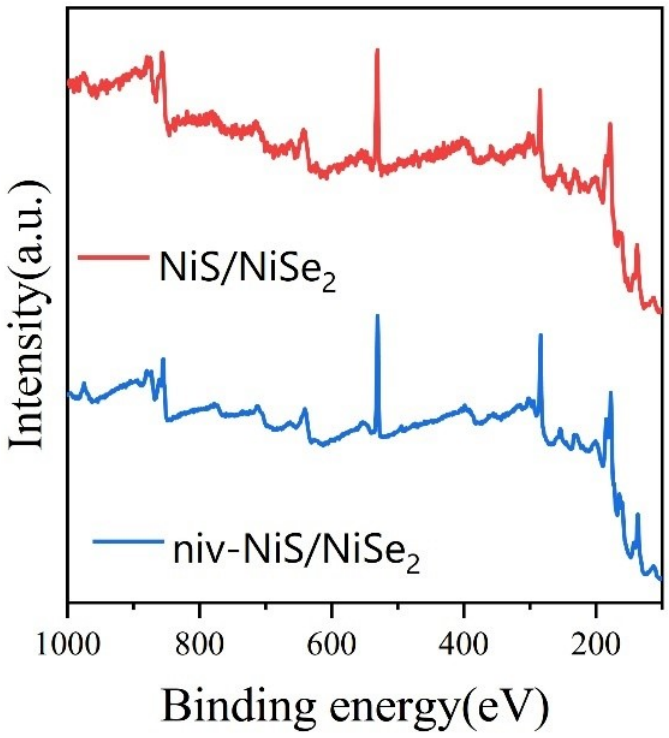

Figure S7. XPS survey of $NiS/NiSe_2$ and niv-$NiS/NiSe_2$, respectively.

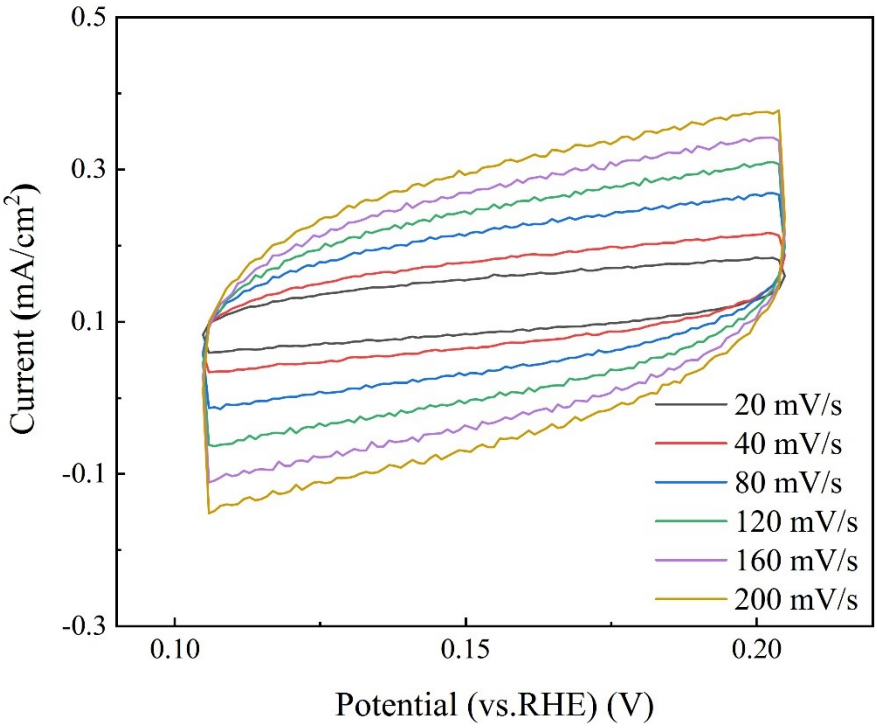

Figure S8. CV sweeps of Ni_3S_2.

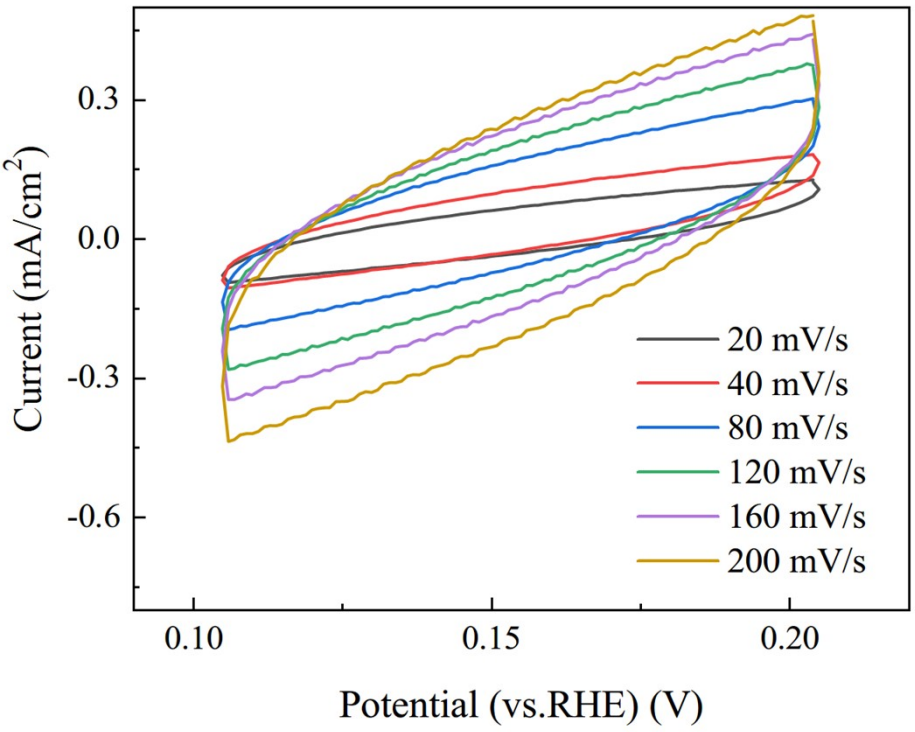

Figure S9. CV sweeps of $Ni_{2.8}S_2$.

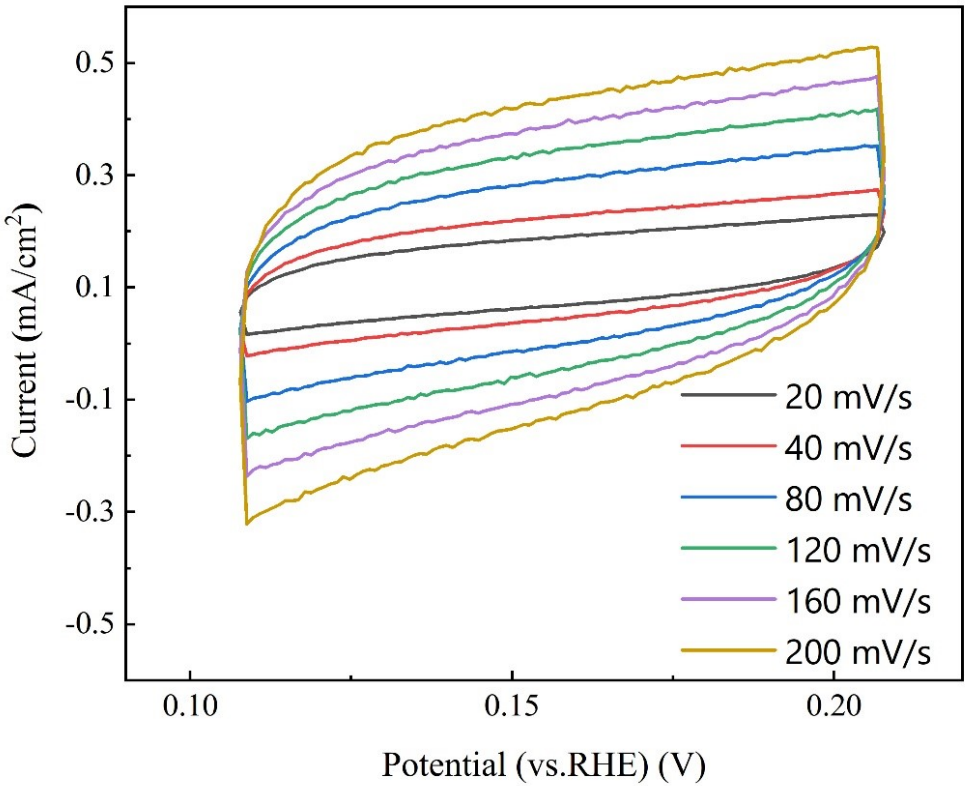

Figure S10. CV sweeps of $NiS/NiSe_2$.

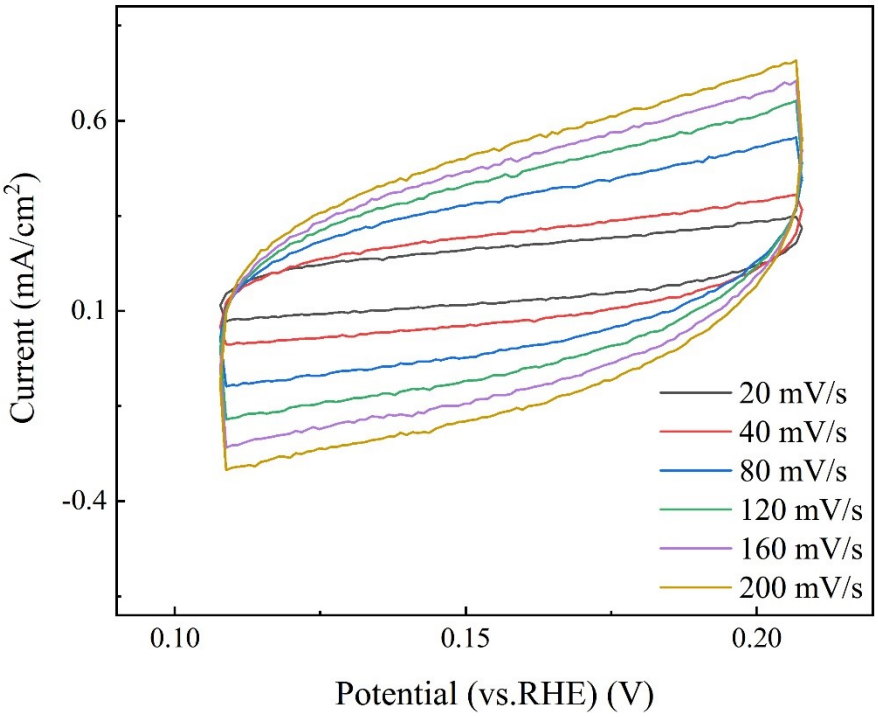

Figure S11. CV sweeps of niv-NiS/$NiSe_2$.

Table S1. Summary of the electrochemical data of various electrocatalysts in 0.5 M H_2SO_4.

Sample	HER Activity		C_{dl} (mF cm^{-2})	EIS	
	h_{10} (mV)	Tafel Slope (mV dec^{-1})		R_s (Ω)	R_{ct} (Ω)
Ni_3S_2	348	179.8	0.81	3.67	863.8
$Ni_{2.8}S_2$	252	84.1	1.05	3.60	428.3
$NiS/NiSe_2$	200	58.4	1.22	3.05	199.6
niv-$NiS/NiSe_2$	96	41.3	1.61	3.69	102

η_{10}: the overpotential at the current density of 10 mA cm^{-2}; C_{dl}: double layer capacitance; R_s and R_{ct}: electrolyte resistivity and electron transfer resistivity fitted from EIS analysis, respectively.

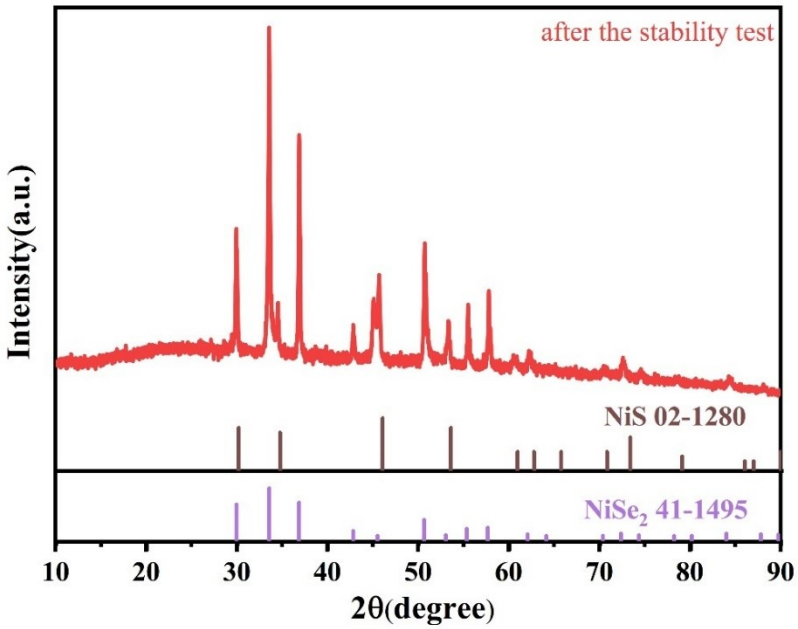

Figure S12. PXPD of niv-NiS/$NiSe_2$ after the stability test, respectively.

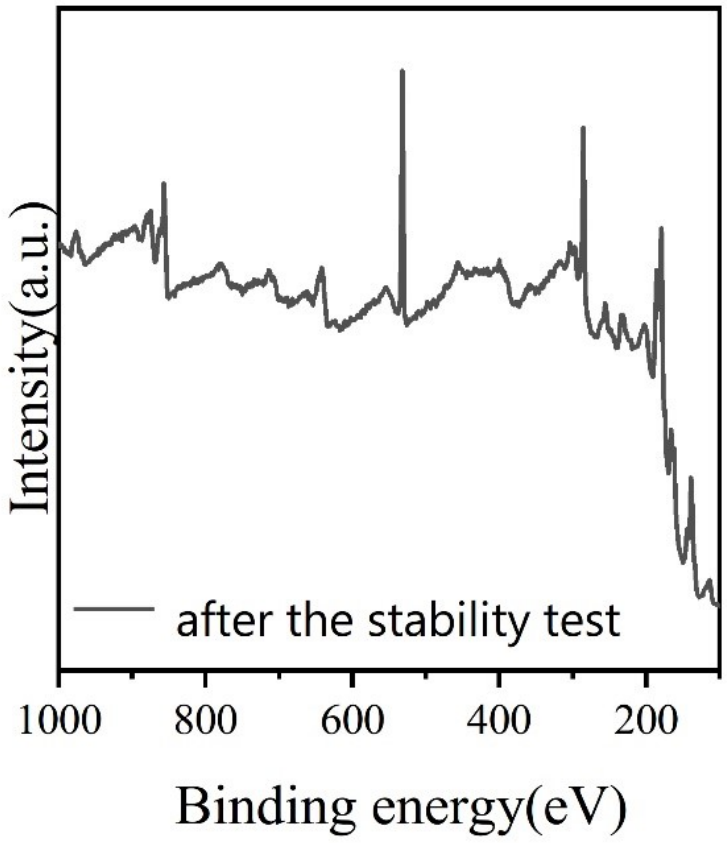

Figure S13. XPS survey of niv-NiS/$NiSe_2$ after the stability test, respectively.

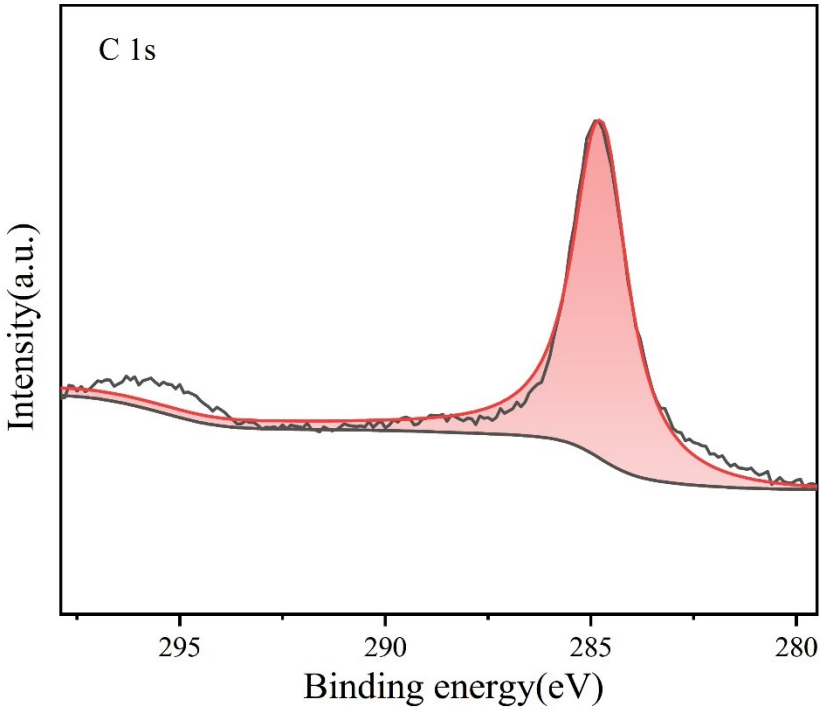

Figure S14. C 1s XPS spectra of niv-NiS/$NiSe_2$ after the stability test, respectively.

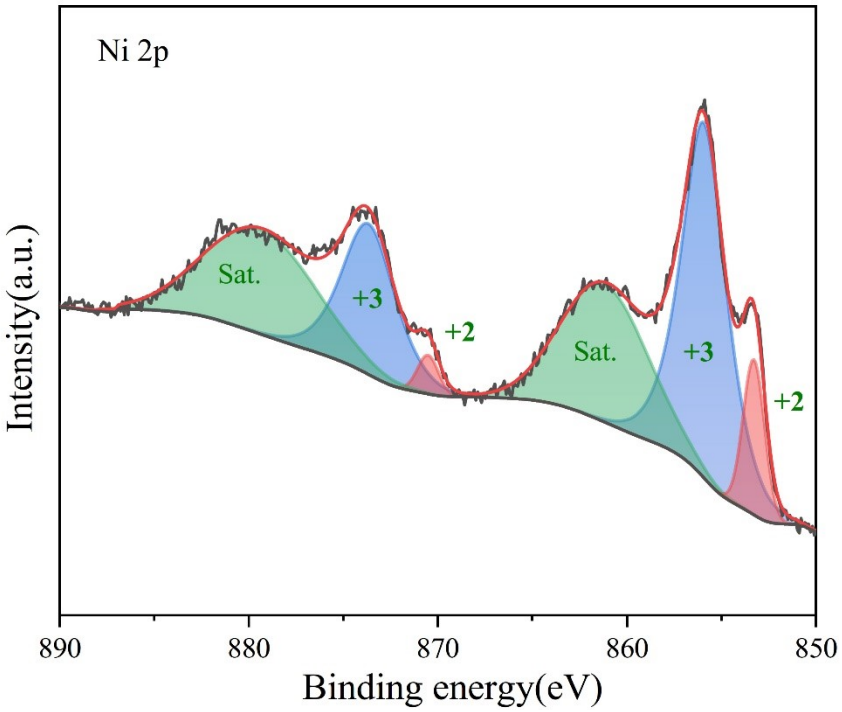

Figure S15. Ni 2p XPS spectra of niv-NiS/$NiSe_2$ after the stability test, respectively.

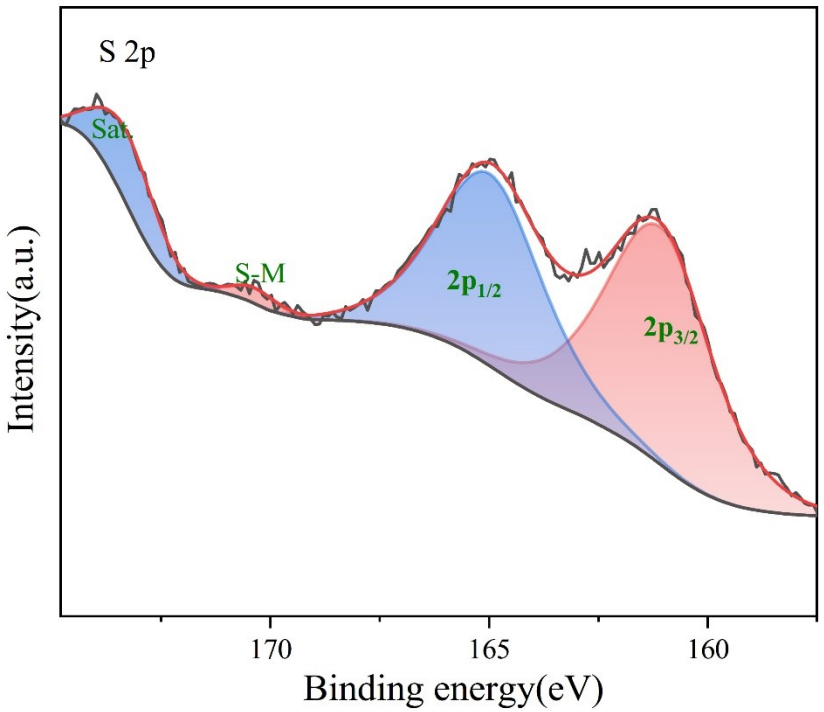

Figure S16. S 2p XPS spectra of niv-NiS/$NiSe_2$ after the stability test, respectively.

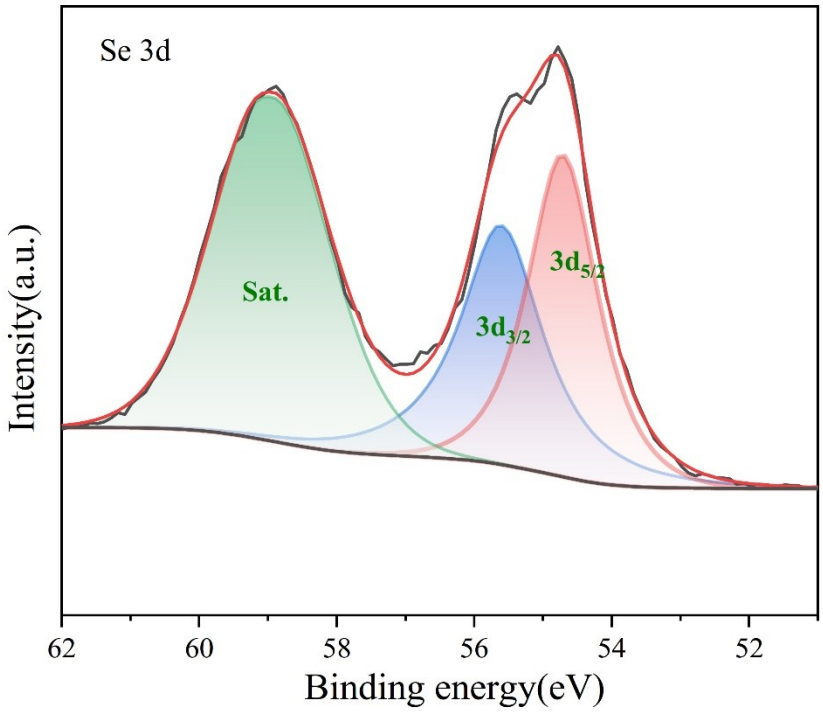

Figure S17. Se 3d XPS spectra of niv-NiS/$NiSe_2$ after the stability test, respectively.

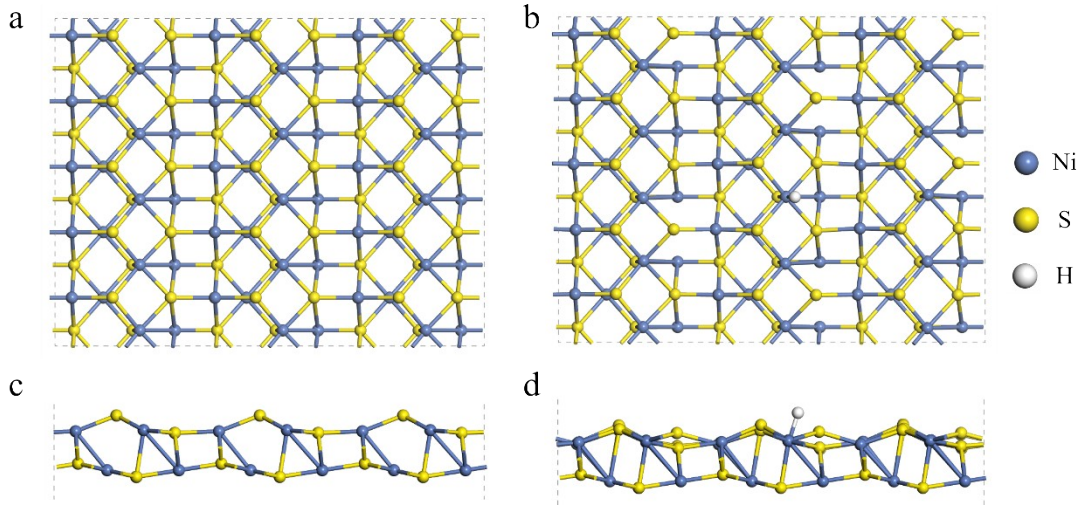

Figure S18. (a), (c) Top and side view of NiS(102). (b), (d) Top and side view of NiS(102) adsorbing H atom. Ni, S and H atom are marked by blue, yellow and white balls, respectively.

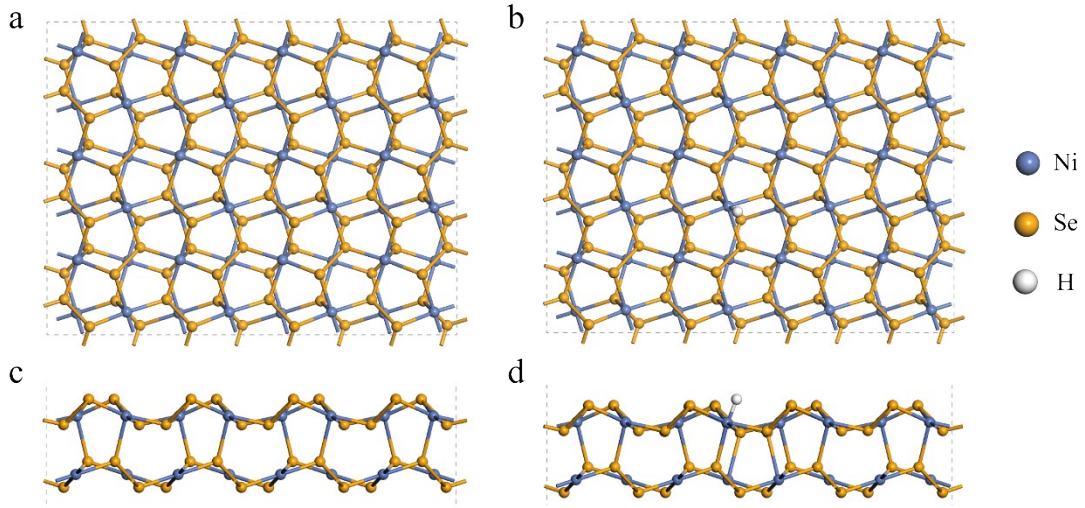

Figure S19. (a), (c) Top and side view of NiSe2(010). (b), (d) Top and side view of NiSe2(010) adsorbing H atom. Ni, Se and H atom are marked by blue, orange and white balls, respectively.

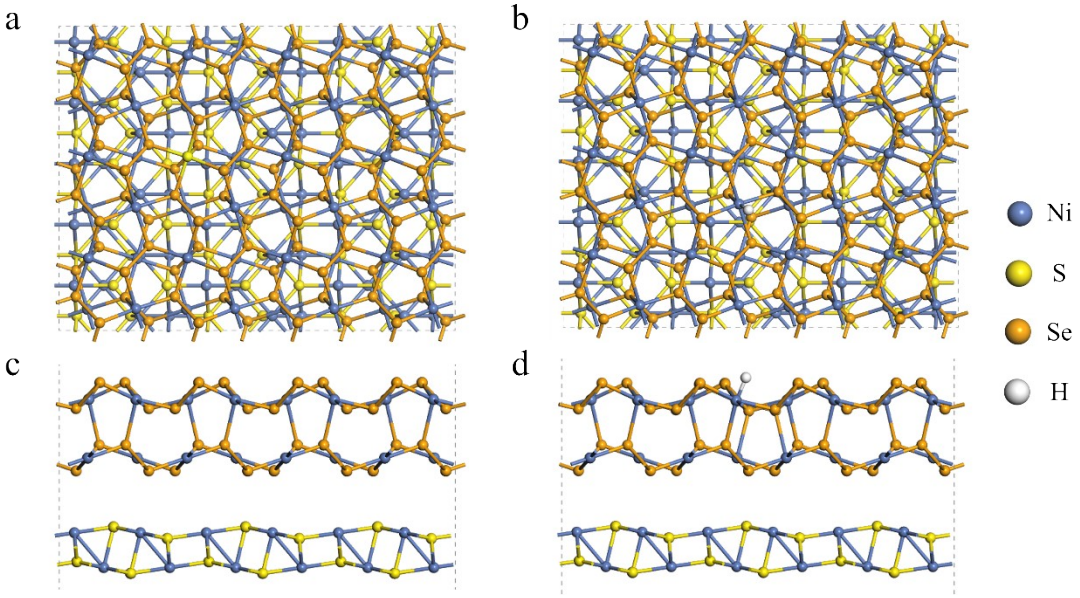

Figure S20. (a), (c) Top and side view of heterostructure of $NiSe_2$/NiS. (b), (d) Top and side view of heterostructure of $NiSe_2$/NiS adsorbing H atom. Ni, S, Se and H atom are marked by blue, yellow, orange and white balls, respectively.

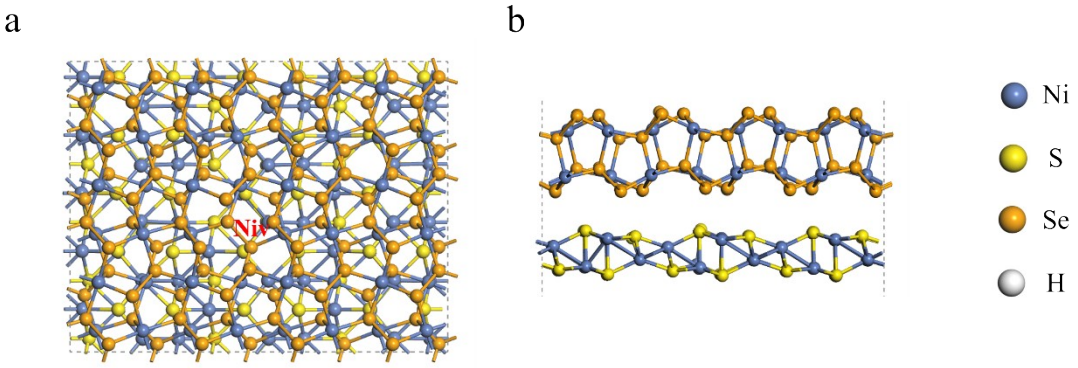

Figure S21 (a), (b) Top and side view of heterostructure of niv-$NiSe_2$/NiS. Ni vacancy was marked in (a).