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Supporting Information

## Nickel Sulfides for Electrocatalytic Hydrogen Evolution under Alkaline Conditions: A Case Study of Crystalline NiS, NiS<sub>2</sub>, and Ni<sub>3</sub>S<sub>2</sub> Nanoparticles

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Figure S1.  $N_2$  sorption isotherms of NiS (black), NiS<sub>2</sub> (blue), and Ni<sub>3</sub>S<sub>2</sub> (red).



**Figure. S2.** Rotation rate dependence of linear sweep voltammograms of (a) NiS, (b) NiS<sub>2</sub>, and (c) Ni<sub>3</sub>S<sub>2</sub> in 1.0 M KOH.



**Figure S3.** Cyclic voltammograms of (a) NiS and (b)  $NiS_2$  in 0.11 – 0.21 V vs RHE at scan rates from 1 to 10 mV/s in 1.0 M KOH.



Figure S4. Bode plots (circles) and corresponding fitting curves (solid) of (a) NiS, (b) NiS<sub>2</sub>, and (c) Ni<sub>3</sub>S<sub>2</sub>.

Table 1. The geometry structure, space group, lattice parameter, electronic band gap, and magnetic ground state of NiS, NiS<sub>2</sub> and Ni<sub>3</sub>S<sub>2</sub>.

Sample	Geometry structure	Space	Lattice	Electronic	Magnetic ground
		group	parameter		state
NiS		P63/mmc	a = b = 3.499 Å; c=5.483 Å	semiconductor band gap ~1.1 eV.	antiferromagnetic
NiS₂		Pa-3	a= b = c = 5.755 Å	semiconductor band gap ~0.4 eV.	antiferromagnetic
Ni₃S₂		R32	a = b = c = 4.037 Å	metallic	non-magnetic