## **Supporting Information**

## Controllable Synthesis of Nickel Sulfide Nanocatalysts and their Phase-Dependent Performance for Overall Water Splitting

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Figure S1 EDX spectra of  $Ni_3S_2$ , NiS and  $NiS_2$  nanocrystals.



Figure S2 XPS survey spectrum of  $Ni_3S_2$  nanocrystals.



Figure S3 Cycle voltammograms from 1.067 to 1.167 V vs RHE in 0.1 M KOH at different scan rates of (a-b)  $Ni_3S_2$ , (c-d) NiS and (e-f)  $NiS_2$  electrodes.



Figure S4 EIS Nyquist plots for  $Ni_3S_2$ , NiS and  $NiS_2$  electrocatalysts.



Figure S5 HRTEM images of (a)  $Ni_3S_2$ , (b) NiS, and (c)  $NiS_2$  nanocrystals after 1000 CV cycles.

Catalysts	Electrode	Tafel (mV dec <sup>-1</sup> )	Overpotential (mV) at10 mA cm <sup>-2</sup>	Refs
Ni <sub>3</sub> Se <sub>2</sub> film	Cu foam	98	100	1
Co-NiSe <sub>2</sub>	Ti plate	63	64	2
CoNiSe <sub>2</sub>	Ni foam	40	120	3
α-NiOOH	Ni foam	119	240	4
MoS <sub>2</sub> /Ni <sub>3</sub> S <sub>2</sub>	Ni foam	88	280	5
NiSe/NF	Ni foam	120	150	6
Ni <sub>2</sub> P/NiFe	Ni foam	67	75	7
NiFe-LDH	Ni foam	70	160	8
$Ni_{1-x}Co_xSe_2$	Ni foam	52	140	9
$CoS_{2x}Se_{2(1-x)}$	Carbon paper	44	120	10
Ni <sub>3</sub> S <sub>2</sub>	Carbon cloth	67	112	TW*
NiS	Carbon cloth	93	160	TW*
NiS <sub>2</sub>	Carbon cloth	110	227	TW*

**Table S1** Comparison of HER performances of transition metal compoundselectrocatalysts that previously reported in 1.0 M KOH.

Catalysts	Electrode	Tafel	Overpotential	Refs	
		$(mV dec^{-1})$	(mV) at 50 mA cm <sup>-2</sup>		
Ni <sub>3</sub> Se <sub>2</sub> film	Cu foam	80	310	1	
Co-NiSe <sub>2</sub>	Ti plate	94	300	2	
CoNiSe <sub>2</sub>	Ni foam	79	260	3	
α-ΝίΟΟΗ	Ni foam	76	350	4	
MoS <sub>2</sub> /Ni <sub>3</sub> S <sub>2</sub>	Ni foam	83	110	5	
NiSe/NF	Ni foam	75	300	6	
Ni <sub>2</sub> P/NiFe	Ni foam	32	210	7	
NiFe LDH/NF	Ni foam	86	280	8	
Ni-CoSe <sub>2</sub>	FTO	78	380	11	
NiSe <sub>2</sub>	Carbon cloth	84	310	12	
Ni <sub>3</sub> S <sub>2</sub>	Carbon cloth	52	330	TW*	
NiS	Carbon cloth	92	410	TW*	
NiS <sub>2</sub>	Carbon cloth	138	490	TW*	

**Table S2** Comparison of OER performances of transition metal compoundselectrocatalysts that previously reported in 1.0 M KOH.

Table S3. Hall measurement data of  $\ensuremath{\text{NiS}_x}$  electrocatalysts.

Catalyst	Resistivity / $\Omega$ cm	Carrier concentration / cm <sup>3</sup>
Ni <sub>3</sub> S <sub>2</sub>	0.852	$2.360  imes 10^{19}$
NiS	4.783	$6.937  imes 10^{18}$
NiS <sub>2</sub>	7.561	3.752× 10 <sup>18</sup>

Catalysts	Electrode	Current density (mA cm <sup>-2</sup> )	Potential (V)	Refs
Ni <sub>3</sub> Se <sub>2</sub> film	Cu foam	10	1.65	1
Co-NiSe <sub>2</sub>	Ti plate	10	1.62	2
CoNiSe <sub>2</sub>	Ni foam	10	1.59	3
α-NiOOH	Ni foam	10	1.66	4
MoS <sub>2</sub> /Ni <sub>3</sub> S <sub>2</sub>	Ni foam	10	1.56	5
NiSe/NF	Ni foam	10	1.63	6
Ni <sub>2</sub> P/NiFe	Ni foam	10	1.51	7
NiFe-LDSH	Ni foam	10	1.53	8
Co <sub>2</sub> P	Ni foam	10	1.57	13
Co-NiSe <sub>2</sub> /C	Ni foam	10	1.61	14
Ni <sub>3</sub> S <sub>2</sub>	Carbon cloth	10	1.63	TW*
NiS	Carbon cloth	10	1.74	TW*
NiS <sub>2</sub>	Carbon cloth	10	1.85	TW*

**Table S4** Overall watersplitting performances of transition metal compoundselectrocatalysts that previously reported in 1.0 M KOH.

## **Supplementary References**

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