

Supporting Information

MoS₂-Ni₃S₂ Heteronanorods as Efficient and Stable Bifunctional Electrocatalysts for Overall Water Splitting

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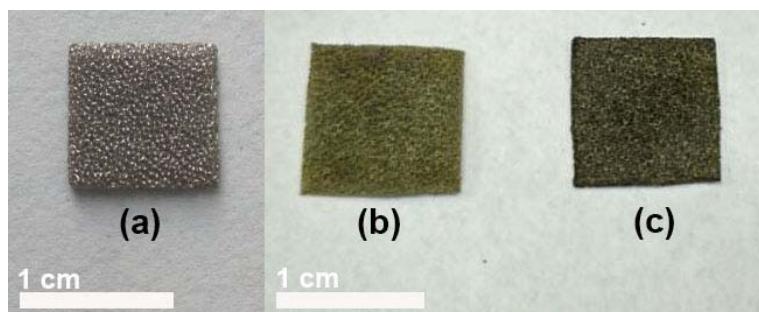


Figure S1. Photographs of (a) NF, (b) Ni₃S₂/NF, and (c) MoS₂-Ni₃S₂ HNRs/NF.

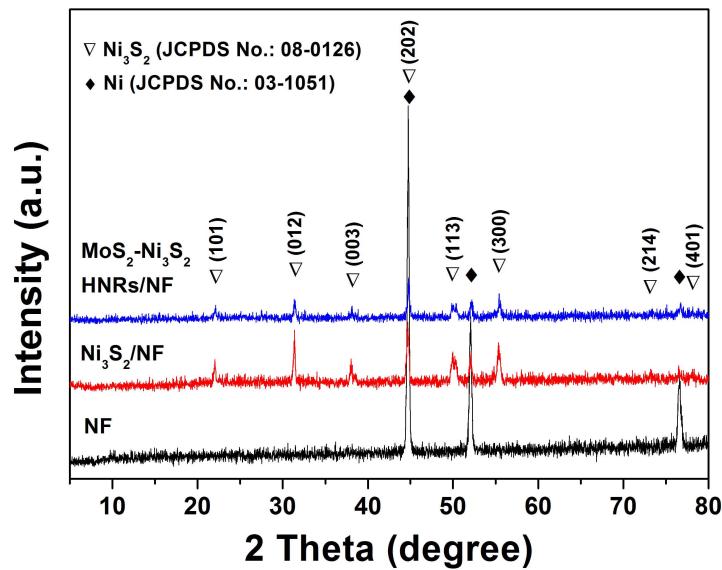


Figure S2. XRD patterns of NF, Ni_3S_2 /NF and MoS_2 - Ni_3S_2 HNRs/NF.

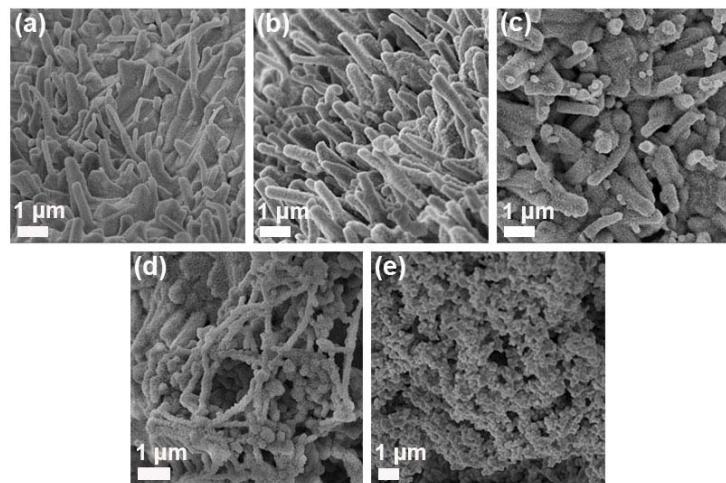


Figure S3. SEM images of various MoS_2 - Ni_3S_2 obtained with varied AHM/NF mass ratios of (a) 0.02, (b) 0.07, (c) 0.12, (d) 0.19, and (e) 0.28.

Table S1. Comparison of the HER performance of MoS₂/Ni₃S₂ HNRs/NF with other reported non-precious HER electrocatalysts in basic electrolyte.

Catalysts	η_{10} (mV)	η_{onset} (mV)	Tafel Slope (mV dec ⁻¹)	Electrolyte	Ref.
MoS₂-Ni₃S₂ HNRs/NF	98	31	61	1.0 M KOH	<i>This work</i>
Ni₃S₂ nanosheet arrays/Ni foam	223	--	--	1.0 M KOH	¹
Ni₃S₂ particles	335	--	97	1.0 M KOH	²
Ni₃S₂ nanoparticles/CNTs	480	350	102	1.0 M KOH	³
NiSe nanowires/Ni foam	96	--	120	1.0 M KOH	⁴
NiCo-P hollow nanocubes	150	--	61	1.0 M KOH	⁵
Ni-Fe/nanocarbon	219	--	110	1.0 M KOH	⁶
Ni₁Mn₁ porous materials	360	150	--	1.0 M KOH	⁷
NiSe₂ nanosheets	184	90	184	1.0 M KOH	⁸
Ni₂P nanoparticles	230	150	100	1.0 M KOH	⁹
NiCo₂S₄ nanowires/ carbon cloth	--	230	141	1.0 M KOH	¹⁰
NiSn@C	--	100	145	1.0 M NaOH	¹¹
MoS₂/graphene/Ni foam	> 600	25	98	1.0 M KOH	¹²
MoS_{2+x} nanoparticles	310	200	84	1.0 M KOH	¹³
Co-Mo/Ti	75	--	--	1.0 M KOH	¹⁴
MoB nanoparticles	230	150	59	1.0 M KOH	¹⁵
Mo₂C nanoparticles	190	150	60	1.0 M KOH	¹⁵
Carbon paper/carbon tubes/Co-S	190	50	131	1.0 M KOH	¹⁶
Co/N-doped carbon	260	~45	91.2	1.0 M KOH	¹⁷
N, P, Co-doped graphene	> 600	> 350	145	1.0 M KOH	¹⁸
CoP nanowires/ carbon cloth	110	38	129	1.0 M KOH	¹⁹
WC nanoparticles/ CNT	137	16	106	1.0 M KOH	²⁰
WN nanowires/ carbon cloth	285	100	170	1.0 M KOH	²¹

Table S2. BET surface of NF, $\text{Ni}_3\text{S}_2/\text{NF}$ and $\text{MoS}_2\text{-}\text{Ni}_3\text{S}_2/\text{NF}$ determined by N_2 isothermal sorption.

Catalysts	BET surface area ($\text{m}^2 \text{ g}^{-1}$)
NF	14.8
$\text{Ni}_3\text{S}_2/\text{NF}$	10.1
$\text{MoS}_2\text{-}\text{Ni}_3\text{S}_2/\text{NF}$ (0.02)	3.9
$\text{MoS}_2\text{-}\text{Ni}_3\text{S}_2/\text{NF}$ (0.07)	4.1
$\text{MoS}_2\text{-}\text{Ni}_3\text{S}_2/\text{NF}$ (0.12)	4.0
$\text{MoS}_2\text{-}\text{Ni}_3\text{S}_2/\text{NF}$ (0.19)	3.8
$\text{MoS}_2\text{-}\text{Ni}_3\text{S}_2/\text{NF}$ (0.29)	4.0

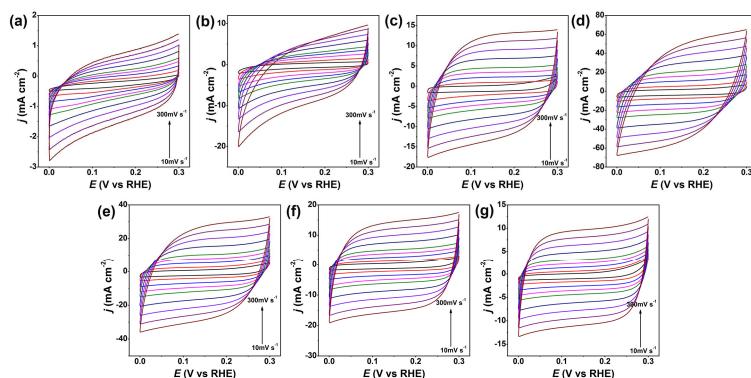


Figure S4. Cyclic voltammograms of (a) Ni foam, (b) $\text{Ni}_3\text{S}_2/\text{NF}$, and of various $\text{MoS}_2\text{-}\text{Ni}_3\text{S}_2$ obtained with different AHM/NF mass ratios of (c) 0.02, (d) 0.07, (e) 0.12, (f) 0.19, and (g) 0.28.

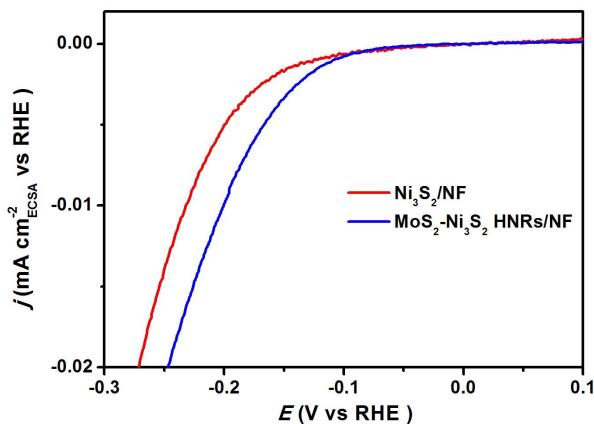


Figure S5. Specific HER activity of $\text{Ni}_3\text{S}_2/\text{NF}$ and $\text{MoS}_2\text{-}\text{Ni}_3\text{S}_2$ HNRs/NF in 1.0 M KOH. The specific capacitance for a flat surface (1 cm^2) is generally found to be in the range of $20\text{-}60 \mu\text{F cm}^{-2}$, and it is assumed as $40 \mu\text{F cm}^{-2}$ in the following calculations of ECSA. The ECSA is determined via dividing C_{dl} by $40 \mu\text{F cm}^{-2}$, and the specific HER activity is calculated via normalizing the current by the corresponding ECSA.

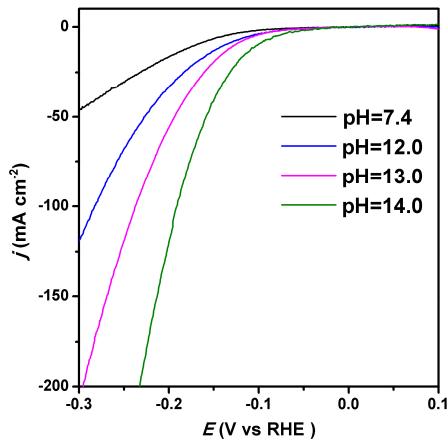


Figure S6. HER performance on MoS₂-Ni₃S₂ HNRs/NF at different pH level.

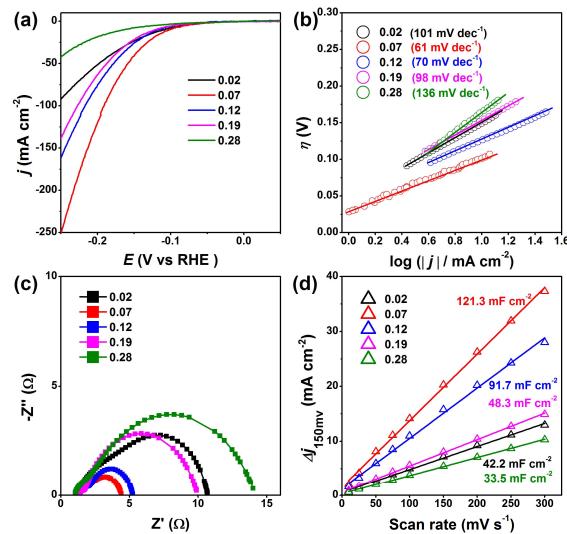


Figure S7. (a) Polarization curves and (b) the corresponding Tafel plots of a series of MoS₂-Ni₃S₂/NF in 1M KOH solution, which are synthesized with varied feeding AHM/NF ratios (0.02 ~ 0.28). (c) Nyquist plots (at $\eta = 200$ mV), and (d) Estimation of C_{dl} by plotting the current density variation ($\Delta j = (j_a - j_c)/2$, at 150 mV vs. RHE; data obtained from the CV in Figure S4) against scan rate to fit a linear regression.

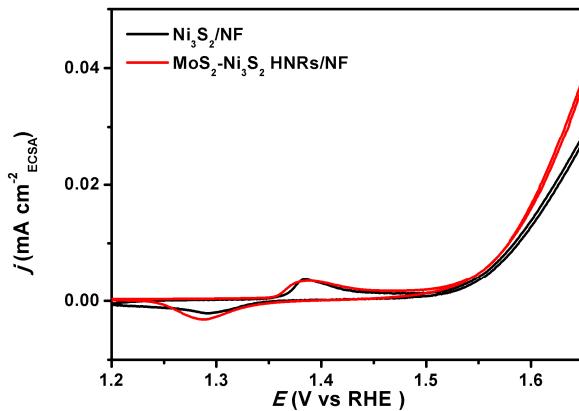


Figure S8. Specific OER activity of $\text{Ni}_3\text{S}_2/\text{NF}$ and $\text{MoS}_2\text{-Ni}_3\text{S}_2$ HNRs/NF in 1.0 M KOH. The specific capacitance for a flat surface (1 cm^2) is generally found to be in the range of $20\text{-}60 \mu\text{F cm}^{-2}$, and it is assumed as $40 \mu\text{F cm}^{-2}$ in the following calculations of ECSA. The ECSA is determined via dividing C_{dl} by $40 \mu\text{F cm}^{-2}$, and the specific OER activity is calculated via normalizing the current by the corresponding ECSA.

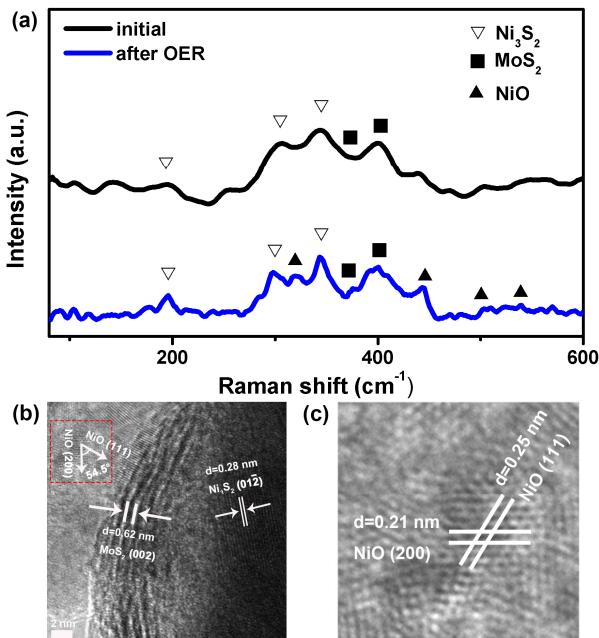


Figure S9. (a) Raman spectra of $\text{MoS}_2\text{/Ni}_3\text{S}_2$ HNRs/NF before and after OER test, (b) HR-TEM images of $\text{MoS}_2\text{/Ni}_3\text{S}_2$ HNRs/NF after OER test, and (c) HR-TEM image of the area highlighted by red box in (b). The Raman spectra clearly identifies the present of NiO species in the $\text{MoS}_2\text{/Ni}_3\text{S}_2$ HNRs/NF, which is also observed by TEM investigation.

Table S3. Comparison of the OER performance of MoS₂/Ni₃S₂ HNRs/NF with other reported OER electrocatalysts in basic electrolyte.

Catalysts	η_{10} (mV)	η_{onset} (mV)	Tafel Slope (mV dec ⁻¹)	Electrolyte	Ref.
MoS₂-Ni₃S₂ HNRs/NF	249	195	66	1.0 M KOH	<i>This work</i>
Ni₃S₂/Ni foam	260	-	-	1.0 M KOH	¹
carbon sheets @Ni-Mn	270	250	40	1.0 M KOH	²²
(Ni, Co)_{0.85}Se@NiCo-LDH	216	-	77	1.0 M KOH	²³
NiO_x/NiOOH	320	240	58	1.0 M NaOH	²⁴
CoNi-LDH/Fe-porphyrin-layer-by-layer	264	230	37.6	1.0 M KOH	²⁵
nickel–iron oxide/C	310	-	42	1.0 M KOH	²⁶
FeOOH/CeO₂HLNTs-NF	~230	210	92.3	1.0 M NaOH	²⁷
Ni_{0.75}V_{0.25}-LDH	350	250	50	1.0 M KOH	²⁸
Ni_xCo_{2x}(OH)_{6x}@Ni	305	263	78	1.0 M KOH	²⁹
Ni₄₅Fe₅₅ oxyhydroxide	310	-	35	0.1 M KOH	³⁰
FeNi-rGO LDH	206	195	39	1.0 M KOH	³¹
NiFe LDHs	305	-	40	1.0 M KOH	³²
Ni_xCo_{3-x}O₄	~620	-	66	1.0 M NaOH	³³
MoO₂-CoO-Carbon	270	240	36.7	1.0 M KOH	³⁴
Au@Co₃O₄	390	-	60	0.1 M KOH	³⁵
3D- Co/ cobaltphtyate nanoplates	265	-	69	1.0 M KOH	³⁶
CoCr LDH nanosheets	340	240	81	1.0 M NaOH	³⁷
FeOOH/Co/FeOOH	~245	-	32	1.0M NaOH	³⁸
Co₅Mn-LDH/MWCNT	300	-	73.6	1.0 M KOH	³⁹
RuO₂	350	~250	85	1.0 M KOH	⁴⁰

Table S4. Comparison of overall water splitting performance of MoS₂/Ni₃S₂ HNRs/NF with recently reported bi-functional electrocatalysts in basic electrolyte.

Catalysts	HER η_{10} (mV)	OER η_{10} (mV)	Overall water splitting cell voltage (V, @10 mA cm ⁻²)	Electrolyte	Ref.
MoS₂-Ni₃S₂ HNRs/NF	98	249	1.50	1.0 M KOH	<i>This work</i>
MoS₂/Ni₃S₂ particles	110	218	1.56	1.0 M KOH	⁴¹
NiS/Ni foam	158 mV 20 mA cm ⁻²	335 mV 50 mA cm ⁻²	1.64	1.0 M KOH	⁴²
NiFe nanosheets/NiCo₂O₄ nanoflakes/NF	105	250	1.67	1.0 M KOH	⁴³
Ni₂P/Ni/NF	98	200	1.49	1.0 M KOH	⁴⁴
Ni@NC	190	390	-	0.1 M KOH	⁴⁵
Ni₃FeN nanoparticles	158	280	-	1.0 M KOH	⁴⁶
Ni₃Se₂ nanoforest/Ni foam	203	353 mV 100 mA cm ⁻²	1.612	1.0M KOH	⁴⁷
EG/Ce_{0.85}Se/NiFe-LDH	260	270 mV 150 mA cm ⁻²	1.67	1.0M KOH	⁴⁸
β-Ni(OH)₂-OER and NiSe₂	184	415	~1.78	1.0M KOH	⁸
carbon fiber paper (CP) @Ni-P	117	180 mV 20 mA cm ⁻²	1.63	1.0 M KOH.	⁴⁹
Bi₂Te₃@CoNiMo on Ni foam	-	80	1.41	0.9 M KOH	⁵⁰
Ni_{2.5}Co_{0.5}Fe/NF	~150	275	1.62	1.0 M KOH	⁵¹
Ni/NiP	130	270 mV 30 mA cm ⁻²	1.61	1.0 M KOH	⁵²
NiMn-rGO	~428	260	-	1.0 M KOH	⁵³
Ni_xCo_{3-x}O₄/NiCo/NiCoO_x	155	337	1.75	1.0 M KOH	⁵⁴
Ni_xP_y-325	160 mV 20 mA cm ⁻²	320	1.57	1.0 M KOH	⁵¹
NiFeP/Ni₂P	183	277	-	1.0 M KOH	⁵⁵
Ni-P foam	135	1.45	1.64	1.0 M KOH	⁵⁶
V/NF	176	292	1.74	1.0 M KOH	⁵⁷

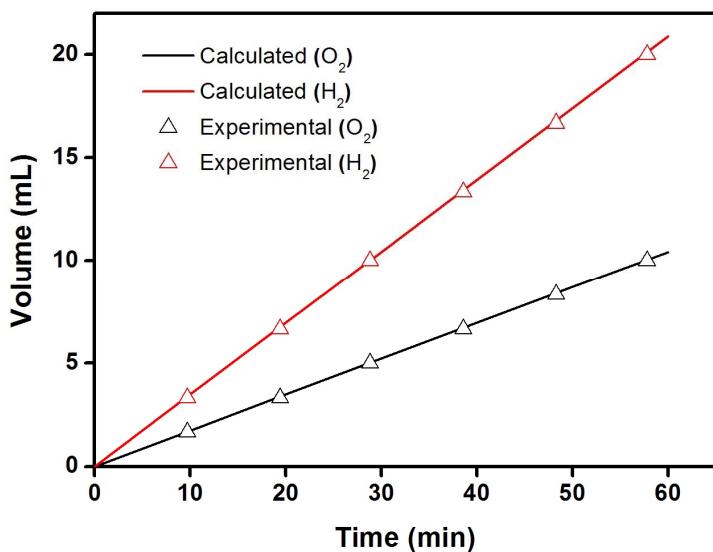


Figure S10. The amount of gas theoretically calculated and experimentally measured versus time of overall water splitting on $\text{MoS}_2/\text{Ni}_3\text{S}_2$ HNRs/NF.

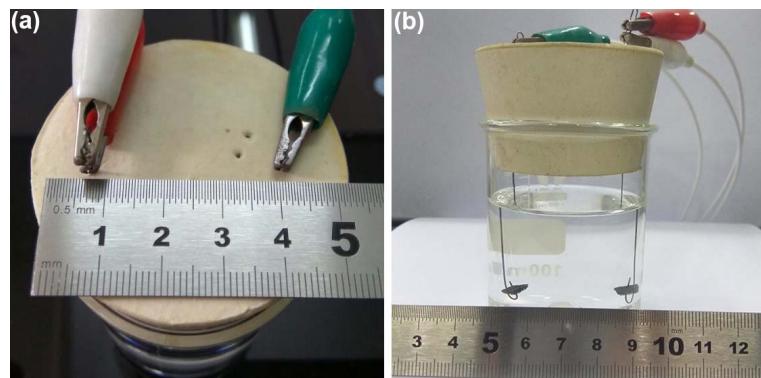


Figure S11. Photograph of the setup used for overall water splitting.

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