## Supporting information for

## Sustainable and Energy-Saving Hydrogen Production via Binder-free and In-situ Electrodeposited Ni-Mn-S Nanowires on Ni-Cu 3-D Substrate

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Table S1: Composition of electrolyte for deposition of Ni-Cu nano-micro dendrites

Materials	<b>Concentration (M)</b>
NiSO <sub>4</sub> .6 H <sub>2</sub> O	0.5
$CuSO_4.5 H_2O$	0.01
HCl	1
$H_2SO_4$	1.5

Table S2: Composition of electrolyte for deposition of Ni-Cu nano-micro dendrites

Materials	Concentration
NiCl <sub>2</sub> .6 H <sub>2</sub> O	5 mM
$MnCl_2.4 H_2O$	5 mM
$H_2NCSNH_2$	0.075 M



Fig. S1. FESEM and EDX images of Ni-Mn-S/Ni-Cu samples fabricated at different coating cycles: (a) 3, (b) 5, and (c) 20 cycles.



Figure S2: LSV curves of different electrodes.



Figure S3: Nyquist curves at different overpotentials of optimized electrode.



Figure S4: dynamic specific resistance at fixed frequency.

Catalyst	Substrate	Tafel slope (mV dec-1)	Overpotential (mV)	Stability	Ref.
Mo-NiSx/NF	NF	88.0	$\eta 10 = 155$	50 h at 10 mA cm-2	[1]
V-Ni3N	NF	28.7	$\eta 10 = 15$	24 h at 10 mA cm-2	[2]
NiCu/NiMn(OH)2	NF	31.0	$\eta 10 = 17$	50 h at 10 mA cm-2	[3]
S-Ni@Ni(OH)2/NF	NF	74.0	$\eta 10 = 50$	15 h at 80 mV	[4]
Ni-Co-Fe-P	NF	67.0	$\eta 10 = 64$	100 h at 100 mA cm-2	[5]
MnCo/NiSe	NF	45.1	$\eta 10 = 22$	200 h at 500 mA cm-2	[6]
NiMo@Ni(OH)2MoOx	GR	115.0	$\eta 100 = 160$	24 h at 100 mA cm-2	[7]
NiCoSeP	NF	59.0	$\eta 10 = 52$	15 h at 500 mA cm-2	[8]
P-doped NiSe	NF	117.0	$\eta 10 = 90$	100 h at 100 mA cm-2	[9]
Nanoporous Ni-Se	GR	126.0	$\eta 10 = 100$	12 h at 100 mA cm-2	[10]
Ni-P/Ni(OH)2 NTs	NF	58.0	$\eta 10 = 55$	30 h at 10 mA cm-2	[11]
NiMn1.5PO4/NF	NF	43.0	$\eta 10 = 72$	50 h at 10 mA cm-2	[12]
O-NiCoP/Ni2P	NF	68.8	$\eta 10 = 58$	24 h at 10 mA cm-2	[13]
Ni-Mo-O/Ni4Mo@NC	СР	99.0	$\eta 10 = 61$	15 h at 10 mA cm-2	[14]
V-doped NiSe/Ni3Se2	NF	70.0	$\eta 100 = 175$	11 h at 100 mA cm-2	[15]
NiSe2-Ni2P/NF	NF	68.0	$\eta 10 = 102$	25 h at 150 mV	[16]
N: M. S/NI: C/10	NIE	01.0	10 54	24 h at 100 mA	This
N1-MIN-S/N1-Cu/10 NF	81.0	η10 =64	cm-2	work	

Table S3: Comparison of HER properties for different electrocatalysts in 1.0 M KOH solution.

Catalyst	Substrate	Solution	Tafel slope (mV dec <sup>-1</sup> )	Potential vs. RHE (V)	Stability	Ref.
Co <sub>2</sub> P/NiMoO <sub>4</sub> /NF	NF	1.0 M KOH + 0.50 M urea	75.0	$E_{10} = 1.34$	50 h at 1.37 V	[17]
Ni <sub>3</sub> N/Mo <sub>2</sub> N	NF	1.0 M KOH + 0.33 M urea	34.7	E <sub>100</sub> = 1.36	40 h at 120 mA cm <sup>-2</sup>	[18]
Ni-Mn-Se	NF	1.0 M KOH + 0.33 M urea	58.2	E <sub>100</sub> = 1.44	50 h at 200 mA cm <sup>-2</sup>	[19]
W-NiS <sub>2</sub> /MoO <sub>2</sub> @CC	CC	1.0 M KOH + 0.33 M urea	24.1	$E_{10} = 1.30$	24 h at 1.40 V	[20]
NF/PPy <sub>700</sub> -Ni <sub>3</sub> S <sub>2</sub> -8-Ar	NF	1.0 M KOH + 0.33 M urea	20.0	E <sub>20</sub> = 1.35	12 h at 20 mA cm <sup>-2</sup>	[21]
FeNi <sub>3</sub> -MoO <sub>2</sub> /NF	NF	1.0 M KOH + 0.50 M urea	30.1	$E_{10} = 1.29$	120 h at 500 mA cm <sup>-2</sup>	[22]
Mo-doped $Ni_3S_2$	NF	1.0 M KOH + 0.30 M urea	28.1	E <sub>10</sub> = 1.33	120 h at 10 mA cm <sup>-2</sup>	[23]
Ni <sub>9</sub> S <sub>8</sub> /CuS/Cu <sub>2</sub> O	NF	1.0 M KOH + 0.33 M urea	64.0	$E_{10} = 1.36$	20 h at 1.36 V	[24]
NiCo <sub>2</sub> S <sub>4</sub> /CC	CC	1.0 M KOH + 0.33 M urea	172.0	$E_{50} = 1.43$	10 h at 1.37 V	[25]
NiCo-BDC/Ni-S	NF	1.0 M KOH + 0.33 M urea	58.2	$E_{10} = 1.31$	52 h at 10 mA cm <sup>-2</sup>	[26]
P-CoS <sub>x</sub> (OH) <sub>y</sub> NN/Ti	TM	1.0 M KOH + 0.50 M urea	104.0	$E_{10} = 1.30$	40 h at 1.48 V	[27]
Ni(OH)₂@NF	NF	1.0 M KOH + 0.30 M urea	24.4	E <sub>10</sub> = 1.35	40 h at 10 mA cm <sup>-2</sup>	[28]
$Ni_4N/Cu_3N/CF$	CF	1.0 M KOH + 0.50 M urea	55.7	$E_{10} = 1.34$	10 h at 100 mA cm <sup>-2</sup>	[29]
Ni <sub>3</sub> N/NF	NF	1.0 M KOH + 0.50 M urea	41.0	$E_{10} = 1.34$	36 h at 1.37 V	[30]
NiFeCo LDH/NF	NF	1.0 M KOH + 0.33 M urea	31.0	E <sub>10</sub> = 1.35	50 h at 10 mA cm <sup>-2</sup>	[31]
NiFe(OH) <sub>2</sub> -SD/NF	NF	1.0 M KOH + 0.50 M urea	41.0	E <sub>10</sub> = 1.32	24 h at 10 mA cm <sup>-2</sup>	[32]
Ni-Mn-S/Ni-Cu/10	NF	1.0 M KOH + 0.33 M urea	87.0	E <sub>10</sub> = 1.247	24 h at 100 mA cm $^{-2}$	This work

Table S4: Comparison of UOR properties for different electrocatalysts.

Catalyst	Substrate	Solution	Cell potential vs. RHE (V)	Stability	Ref.
Ni <sub>3</sub> N/Mo <sub>2</sub> N	NF	1.0 M KOH + 0.33 M urea	$\Delta E_{10} = 1.36$	50 h at 10 mA cm <sup>-2</sup>	[18]
Ni-Mn-Se	NF	1.0 M KOH + 0.33 M urea	ΔE <sub>100</sub> = 1.62	50 h at 50 mA cm <sup>-2</sup>	[19]
W-NiS <sub>2</sub> /MoO <sub>2</sub> @CC	CC	1.0 M KOH + 0.33 M urea	ΔE <sub>10</sub> = 1.37	24 h at 1.40 V	[20]
NF/PPy <sub>700</sub> -Ni <sub>3</sub> S <sub>2</sub> -8-Ar	NF	1.0 M KOH + 0.33 M urea	ΔE <sub>20</sub> = 1.50	20 h at 1.60 V	[21]
FeNi <sub>3</sub> -MoO <sub>2</sub> /NF	NF	1.0 M KOH + 0.50 M urea	ΔE <sub>10</sub> = 1.37	70 h at 100 mA cm <sup>-2</sup>	[22]
Mo-doped $Ni_3S_2$	NF	1.0 M KOH + 0.30 M urea	ΔE <sub>10</sub> = 1.45	120 h at 10 mA cm <sup>-2</sup>	[23]
Ni <sub>9</sub> S <sub>8</sub> /CuS/Cu <sub>2</sub> O	NF	1.0 M KOH + 0.33 M urea	ΔE <sub>10</sub> = 1.47	20 h at 1.47 V	[24]
NiCo <sub>2</sub> S <sub>4</sub> /CC	CC	1.0 M KOH + 0.33 M urea	ΔE <sub>10</sub> = 1.45	15 h at 1.51 V	[25]
NiCo-BDC/Ni-S	NF	1.0 M KOH + 0.33 M urea	ΔE <sub>10</sub> = 1.46	50 h at 10 mA cm <sup>-2</sup>	[26]
P-CoS <sub>x</sub> (OH) <sub>y</sub> NN/Ti	ТМ	1.0 M KOH + 0.50 M urea	ΔE <sub>10</sub> = 1.30	40 h at 1.29 V	[27]
Ni(OH) <sub>2</sub> @NF	NF	1.0 M KOH + 0.30 M urea	ΔE <sub>50</sub> = 1.45	40 h at 20 mA cm <sup>-2</sup>	[28]
Ni₄N/Cu₃N/CF	CF	1.0 M KOH + 0.50 M urea	$\Delta E_{10} = 1.48$	10 h at 100 mA cm <sup>-2</sup>	[29]
Ni <sub>3</sub> N/NF	NF	1.0 M KOH + 0.50 M urea	ΔE <sub>100</sub> = 1.42	20 h at 1.37 V	[30]
NiFeCo LDH/NF	NF	1.0 M KOH + 0.33 M urea	ΔE <sub>10</sub> = 1.49	50 h at 10 mA cm <sup>-2</sup>	[31]
Ni(OH)S/NF	NF	1.0 M KOH + 0.33 M urea	ΔE <sub>10</sub> = 1.36	40 h at 20 mA cm <sup>-2</sup>	[33]
Ni-Mn-S/Ni-Cu/10	NF	1.0 M KOH + 0.33 M urea	ΔE <sub>10</sub> = 1.302	24 h at 50 mA cm <sup>-2</sup>	This work

Table S5: Comparison of overall urea electrolysis properties for different electrocatalysts.

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