

Electronic Supplementary Information

***In-situ* chemical etching of tunable 3D Ni₃S₂ superstructures for bifunctional electrocatalysts for overall water splitting**

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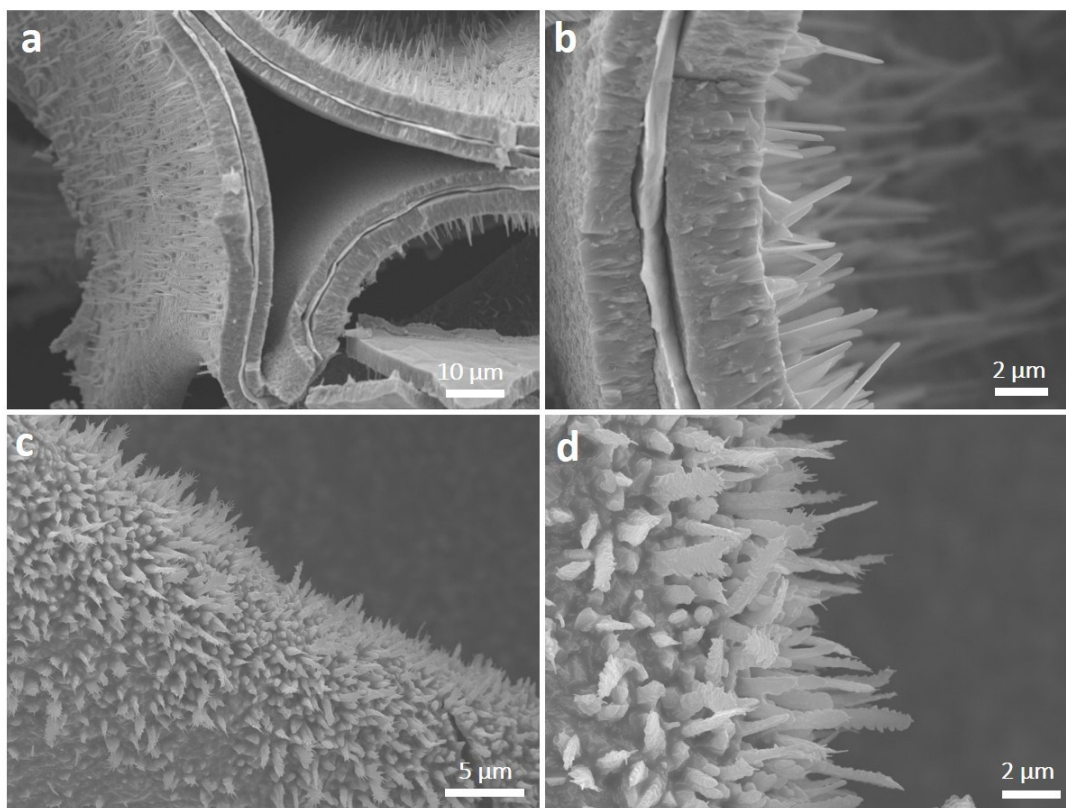


Fig. S1 SEM images of the NN@NF-2 (a and b) and NL@NF-2 (c and d).

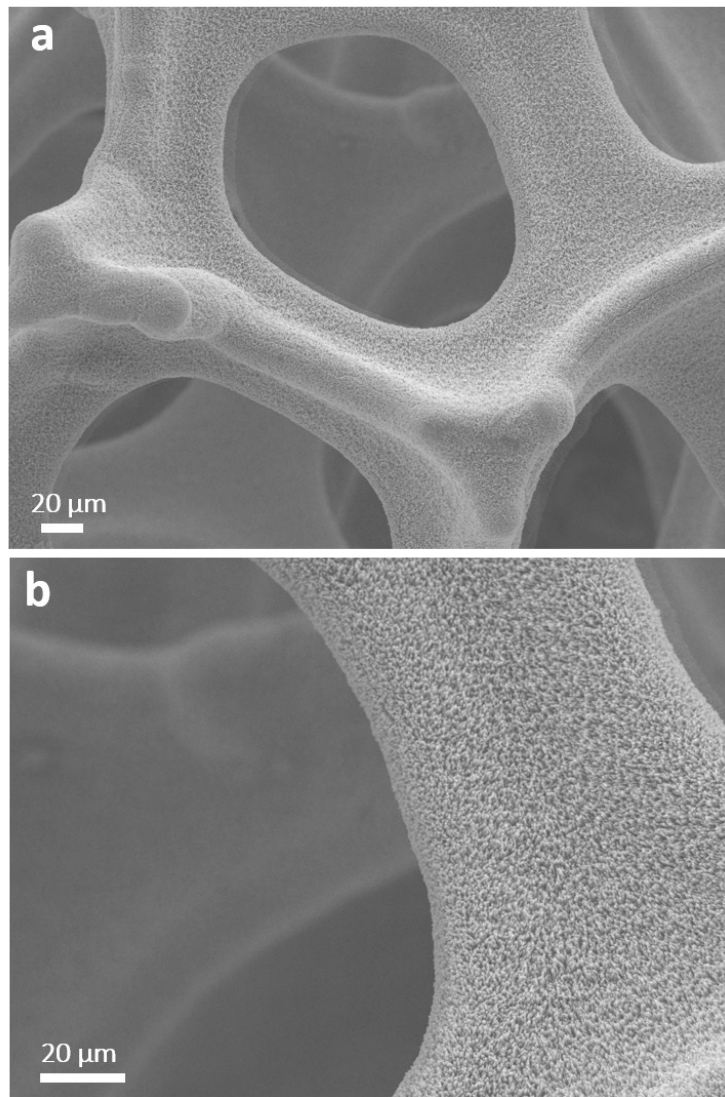


Fig. S2 Low (a) and high (b) magnification of SEM images of the needle array (NN@NF-1) grown on the outmost surface of NF.

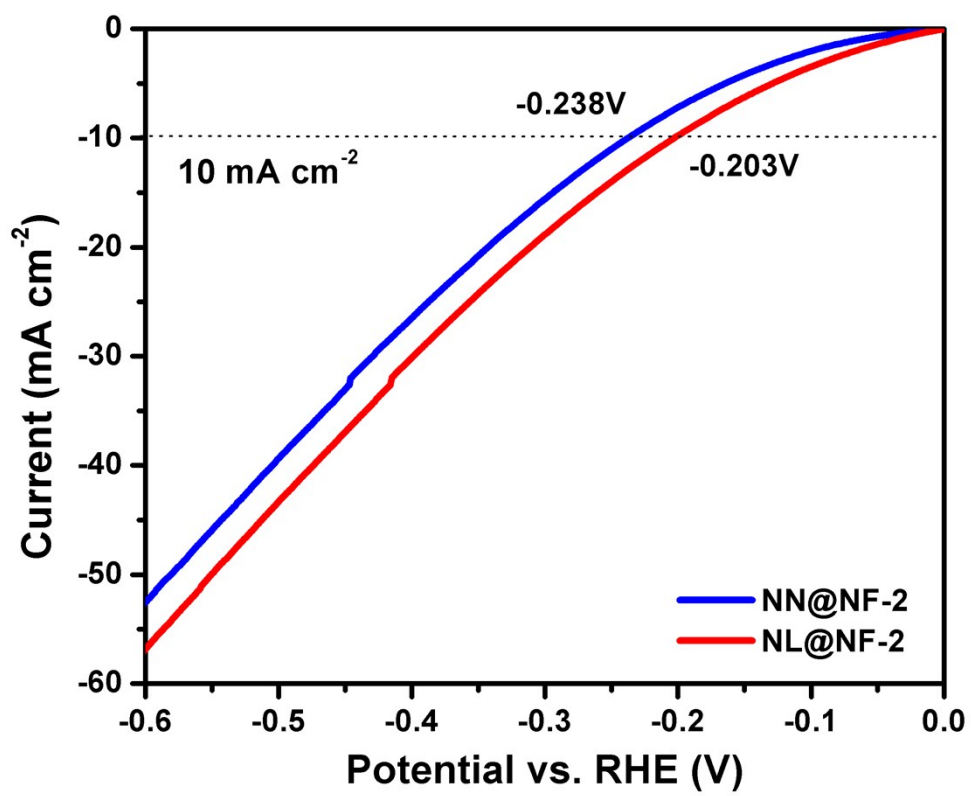


Fig. S3 LSV curves of the NN@NF-2 and NL@NF-2 for HER.

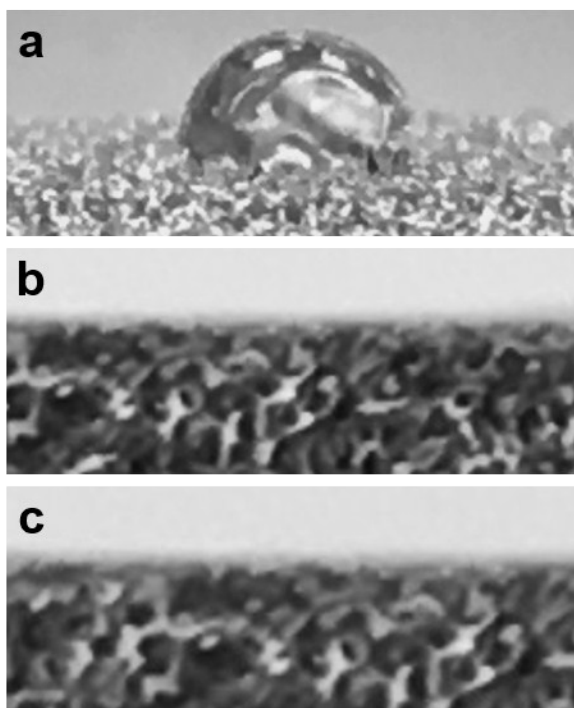


Fig. S4 Processed digital photos of the hydrophilic property test for pure NF (a), NL@NF-1 (b) and NN@NF-1 (c).

Table S1 A comparison of HER activity of nickel sulfide based electrocatalysts in previous work

Catalysts	Substrate	Electrolyte	η (mV) at 10 mA cm ⁻²	Tafel slope (mV dec ⁻¹)	Reference
Ni ₃ S ₂ leaves	Ni foam	1 M KOH	182	89	This work
Ni ₃ S ₂ Nanorod Array	Ni foam	1 M KOH	200	107	<i>Electrochimica Acta</i> , 2015, 174 , 297–301
Ni ₃ S ₂ Nanosheets array	Ni foam	1 M KOH	123	110	<i>Int. J. Hydrogen Energy</i> , 2015, 40 , 4727–4732
Iron-nickel sulfide nanosheets	N.A.	0.5 M H ₂ SO ₄	117	40	<i>J. Am. Chem. Soc.</i> , 2015, 137 , 11900–11903
NiS nanoparticles	N.A.	0.5 M H ₂ SO ₄	~250	88	<i>Nanoscale</i> , 2015, 7 , 5157–5163
NiS nanocrystals	N.A.	0.5 M H ₂ SO ₄	186	51	<i>RSC Adv.</i> , 2015, 5 , 104740–104749
NiS ₂ nanosheets	Graphite	0.5 M H ₂ SO ₄	240	41	<i>RSC Adv.</i> , 2015, 5 , 32976–32982.
NiS microspheres	Ni foam	0.1 M KOH	158 ^a	83	<i>Chem. Commun.</i> , 2016, 52 , 1486–1489
Ni ₃ S ₂ Nanosheets array	Ni foam	1 M KOH	170	N.A.	<i>J. Am. Chem. Soc.</i> , 2015, 137 , 14023–14026
Nickel sulfide film	FTO	Neutral water	330	77	<i>J. Mater. Chem. A</i> , 2014, 2 , 19407–19414
Ni-Mo-S nanosheets	Carbon fiber	0.5 M Sodium phosphate	~200	85	<i>Sci. Adv.</i> , 2015, 1 :e1500259

^a η needed to achieve 20 mA cm⁻².

Table S2 A comparison of OER activity of nickel sulfide based electrocatalysts in previous work

Catalysts	Substrate	Electrolyte	η (mV) at 10 mA cm ⁻²	Tafel slope (mV dec ⁻¹)	Reference
Ni ₃ S ₂ leaves	Ni foam	1 M KOH	340	150	This work
Ni ₃ S ₂	Ni foam	0.1 M KOH	400	331	<i>Electrochimica Acta</i> , 2015, 174 , 297–301
Ni ₃ S ₂ nanorods	Ni foam	0.1 M KOH	187	159	<i>Energy Environ. Sci.</i> , 2013, 6 , 2921–2924
Fe doped Ni ₃ S ₂ particles	Ni foam	1M KOH	253 ^a	65	<i>J. Mater. Chem. A</i> , 2015, 3 , 23207–23212
NiS nanosheets	Stainless steel mesh	0.1 M KOH	297	47	<i>ACS Appl. Mater. Interfaces</i> , 2016, 8 , 5509–5516
Hierarchical nickel sulfide	Ni foam	1 M KOH	180	96	<i>Adv. Energy Mater.</i> , 2016, 6 , 1502333
NiS microspheres	Ni foam	1 M KOH	335 ^b	89	<i>Chem. Commun.</i> , 2016, 52 , 1486--1489
Ni ₃ S ₂	N-doped carbon	1 M KOH	390	196	<i>Dalton Trans.</i> , 2016, 45 , 6352-6356
Ni ₃ S ₂ Nanosheets array	Ni foam	1 M KOH	260	N.A.	<i>J. Am. Chem. Soc.</i> , 2015, 137 , 14023–14026

^a η needed to achieve 100 mA cm⁻².^b η needed to achieve 50 mA cm⁻².