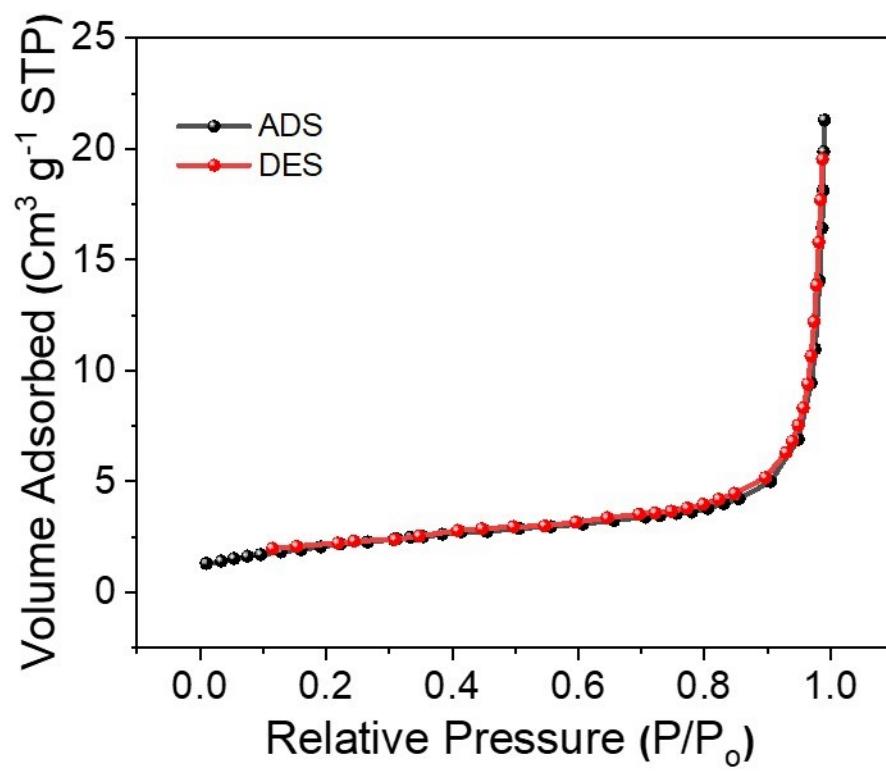


Supporting Information

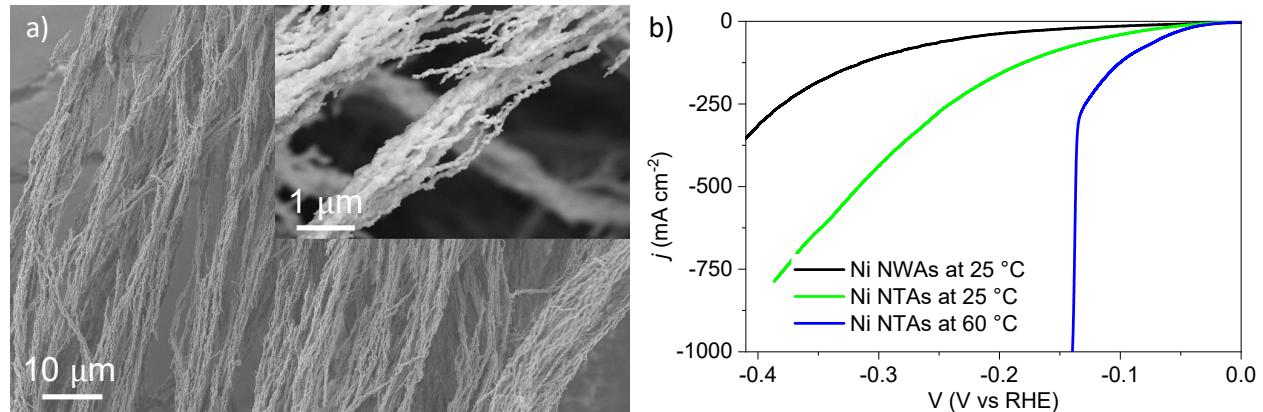
**Coupling of Thermal and Electrochemical Activated Ni Nanothorn Array Electrode For Highly Robust Hydrogen Generation**

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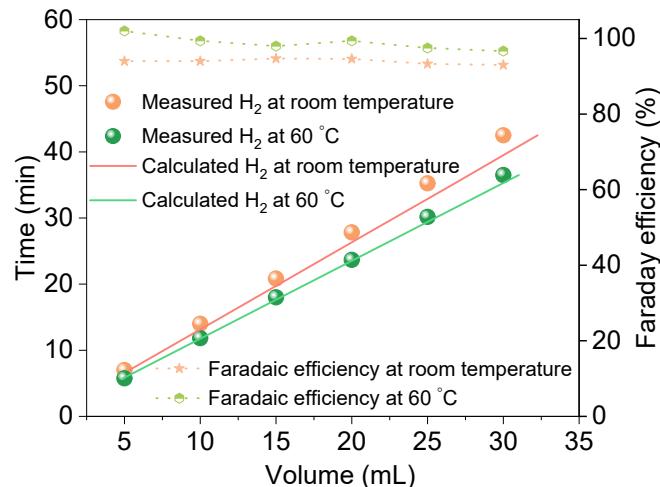
Institute of Functional Porous Materials, School of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, China.



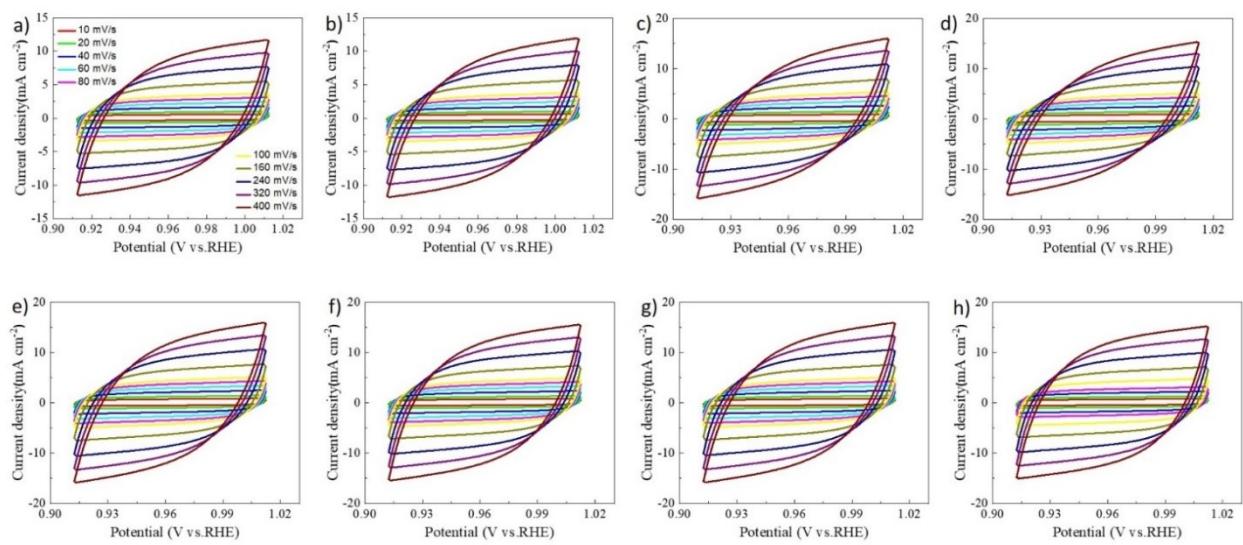
**Figure S1.**  $\text{N}_2$  adsorption-desorption isotherms of fabricated Ni NTAs electrode.



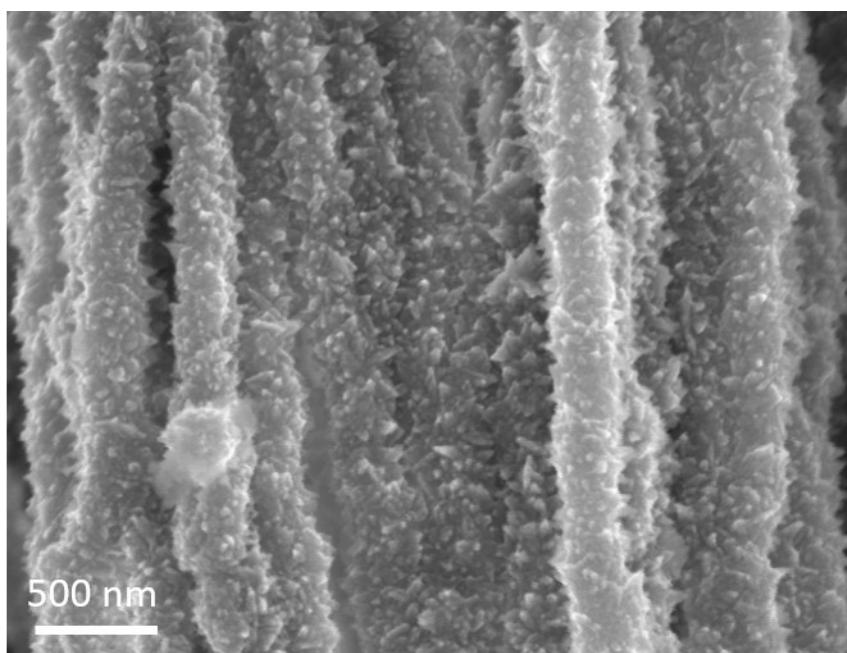
**Figure S2.** a) The scanning electron microscope image of Ni NWAs (without thorns). b) Polarization curves of Ni NWAs at 25 °C, and Ni NTAs at 25 °C and 60 °C towards HER.



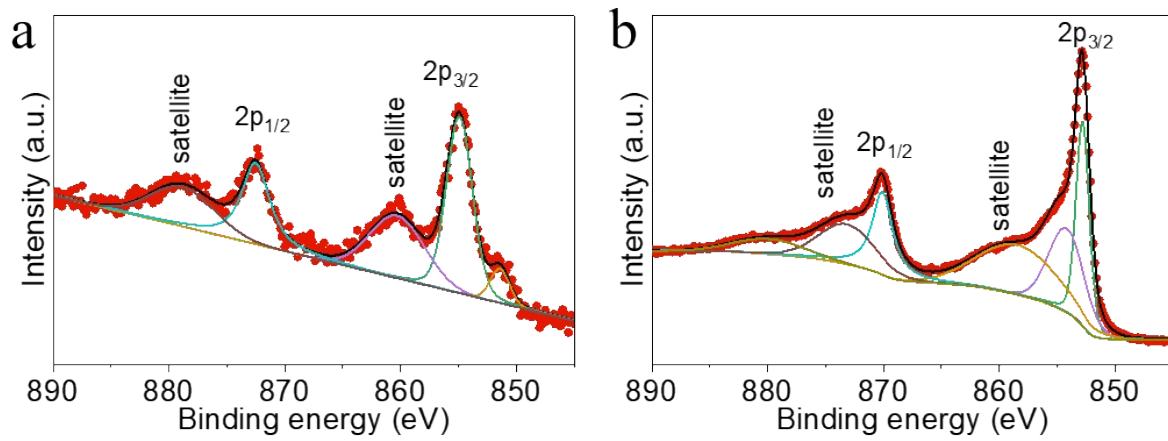
**Figure S3.** Faradaic efficiency of Ni NTAs by water displacement method in 1 M KOH at room temperature and 60 °C at a fixed current density of 100 mA cm<sup>-2</sup>.



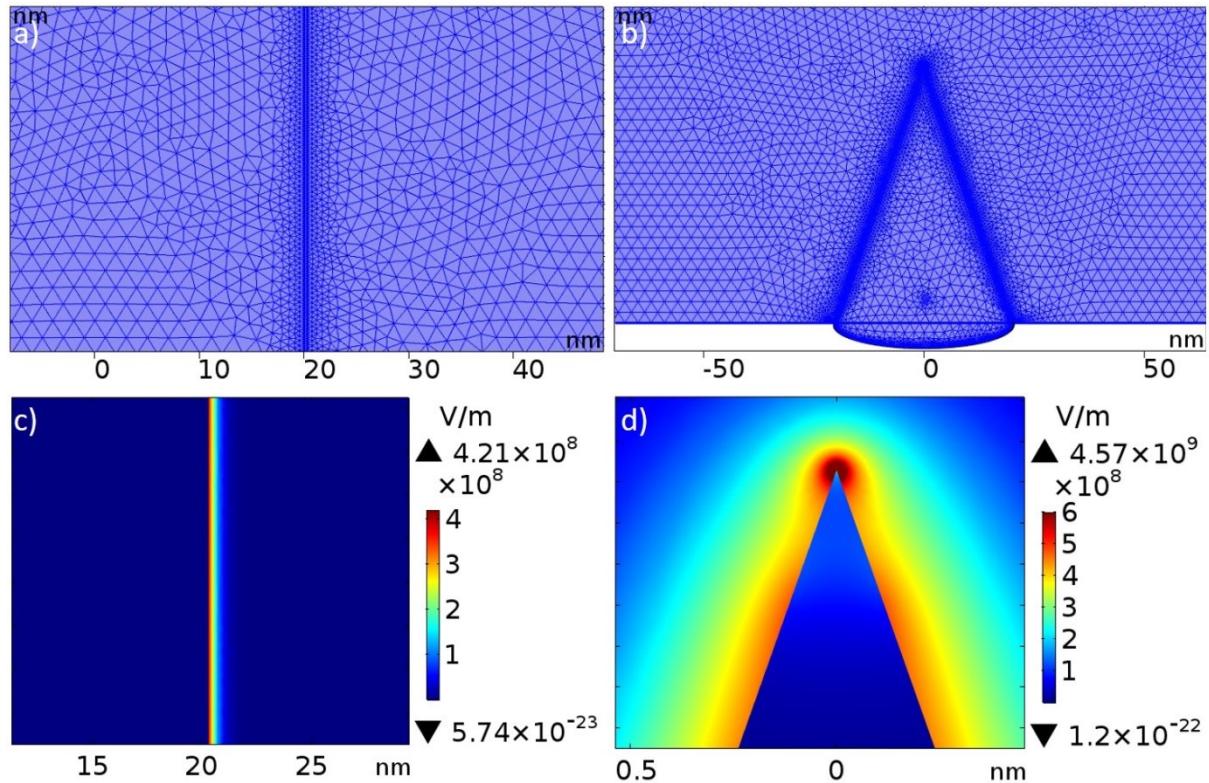
**Figure S4.** Cyclic voltammetry curves of Ni NTAs electrode measured at different temperatures, a) 25 °C, b) 30 °C, c) 35 °C, d) 40 °C, e) 45 °C, f) 50 °C, g) 55 °C, and h) 60 °C.



**Figure S5.** SEM micrograph of Ni NTAs at 60 °C after long-term stability test showing good morphology control after 60 h stability test.



**Figure S6.** XPS spectra of Ni 2p from Ni NTAs after 60 h long-term stability test (a) Ni 2p surface (b) Ni 2p after depth etching.



**Figure S7.** The COMSOL mesh for a) a smooth nanowire and b) nanothorn structure. c) The electric field distribution on the smooth nanowire. d) The electric field distribution around the tip of a nanothorn structure.

Catalyst	Substrate	Mass loading (mg cm <sup>-2</sup> )	Current density (mA cm <sup>-2</sup> )	Overpotential (mV)	Tafel slope (mV dec <sup>-1</sup> )	References
Ni NTAs	Ni Foam	1.8	10 100 500 1000	27 90 137 140	47.1	This Work
Ni <sub>3</sub> N@2M-MoS <sub>2</sub>	2M-MoS <sub>2</sub>	NA	50 100 500 1000	31 97 152 155	43.2	Adv. Mater. 34, (2022), 2108505.
NiP <sub>2</sub> /NiSe <sub>2</sub>	Carbon fiber	3.5	10 100	93 160	65.7	Appl. Catal. B-Environ. 282, (2020), 119584.
(Fe <sub>0.74</sub> Co <sub>0.26</sub> )P/Ni <sub>3</sub> N	Ni foam	NA	100 1000	113 ~215	31.8	Small (2023), 2207082
CuMo <sub>6</sub> S <sub>8</sub> /Cu	Cu foam	10	1000	334	NA	Nature Comm. 13, (2022) 6382.
Ni/NiFe-Oxide	Ni foam	NA	10 100	29 ~180	82	Chem. Eng. J. 426, (2021), 131827.
CoSA-MoS <sub>2</sub> /TiN NRs	Carbon cloth	NA	10 50	131.9 232.8	56.9	Adv. Funct. Mater. 31, (2021), 2100233.
PNiMoHZ	Ni foam	NA	10 1000	23 210	44	Nature Comm. 12, (2021) 5960.
HC-Mo <sub>2</sub> S/Mo <sub>2</sub> C	Cu foam	10	1000	412	60	Nature Comm. 11, (2020), 3724.
LiCoBPO	Ni foam	~3	10 100 1000	121 274 391	98	Energy Environ. Sci., 12, (2019), 988.
NaCoBPO	Ni foam	~3	10 100 1000	207 307 506	124	Energy Environ. Sci., 12, (2019), 988.
Ni <sub>3</sub> N-V <sub>2</sub> O <sub>3</sub>	Ni foam	1.6	10	57	50	Appl. Catal. B-Environ. 283, (2021), 119590.
Mo <sub>2</sub> N-Mo <sub>2</sub> C/HGr-3	Glassy carbon	0.337	10 100	154 ~400	68	Adv. Mater. 30, (2018), 1704156.
Ni-MoO <sub>2</sub> @BC	Glassy carbon	0.375	10	169	63	Chem. Eng. Sci. 246, (2021), 116868.
N-NiCo <sub>2</sub> S <sub>4</sub>	Ni foam	NA	10 100	28 ~130	37	Nature Comm. 9, (2018), 1425.
MoO <sub>2</sub> -Ni	Carbon cloth	17.17 mg	10 80	46 ~125	56.9	Sci. China. Chem. 63, (2020), 841.
Ni/La-Ce oxide	Glassy carbon	10 mg	10 25	114 130	72.7	ACS Sustainable Chem. Eng. 9, (2021), 12508.
Ni(Cu)	Ni foam	NA	10 100	27 ~110	33.3	Small, 14, (2018) 1704137.

**Table S1.** Comparison of Ni NTAs catalytic performance based on the geometric surface area with some recently reported HER electrocatalysts in an alkaline medium.

MoO <sub>2</sub> -Ni	Ni foam	~0.85	10 100	50.48 ~175	65.52	ACS Appl. Mater. Interfaces 13 (2021), 39470.
NiCo <sub>2</sub> S <sub>4</sub>	Ni foam	NA	10 100	65 ~210	84.5	Nano Energy, 24, (2016), 139.
NiFeO <sub>x</sub>	Carbon fiber	1.6	10 100	88 ~210	150	Nature Comm. 6, (2015), 7261.
FeP/Ni <sub>2</sub> P	Ni foam	8	10 100	14 140	24.2	Nat. Commun., 9, (2018), 2551.
Hierarchical nickel–carbon composite	Fe foam	7.3±0.3	10 100	37 210	57	Energy Environ. Sci., 11(2018): 2363.