

## Supporting Information

### **Integrated 3D self-supported Ni decorated MoO<sub>2</sub> nanowires as highly efficient electrocatalysts for ultra-highly stable and large-current-density hydrogen evolution**

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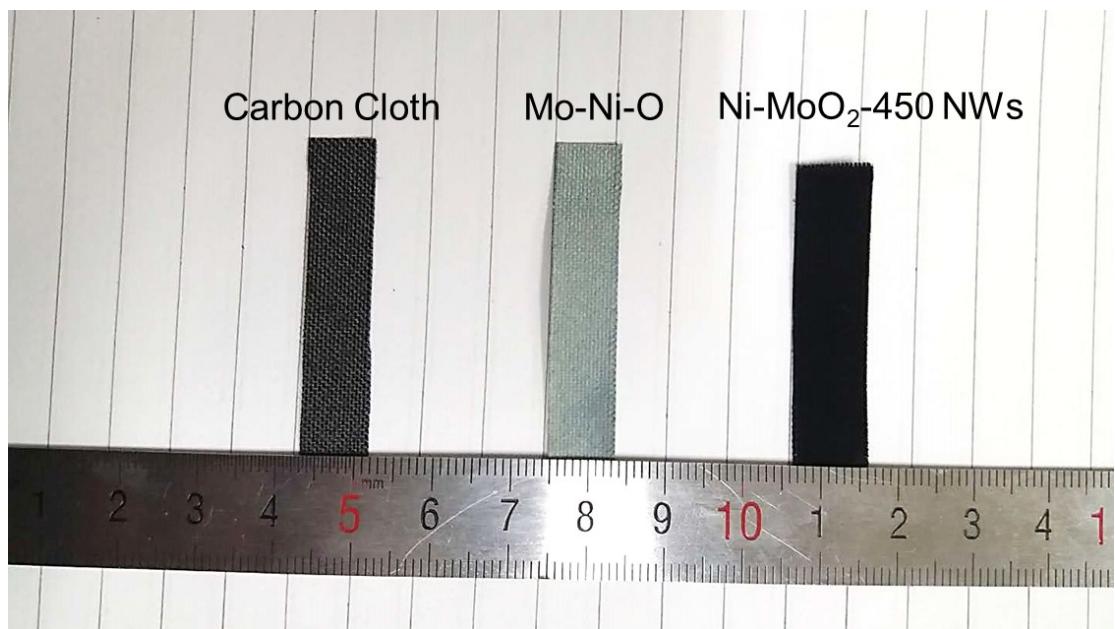
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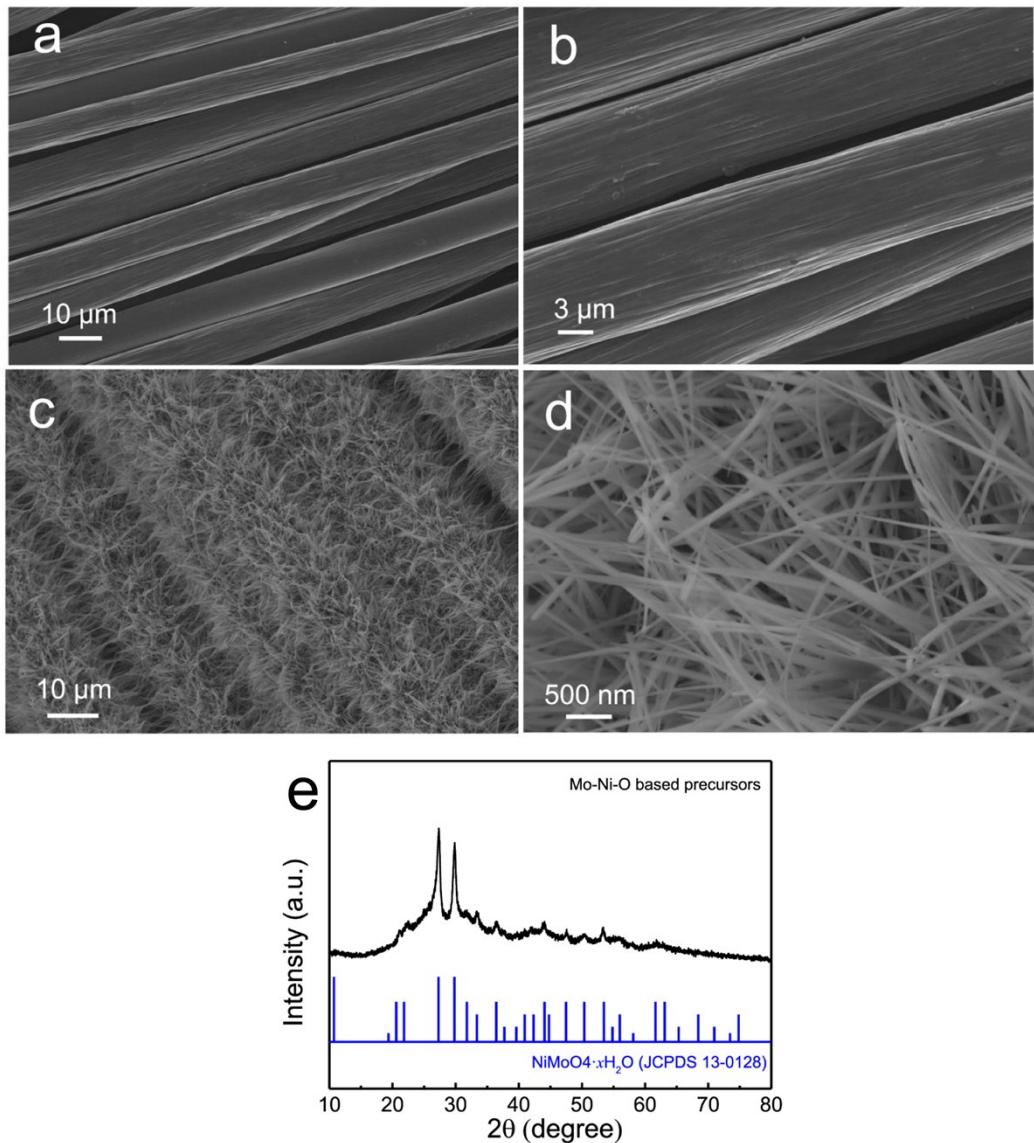
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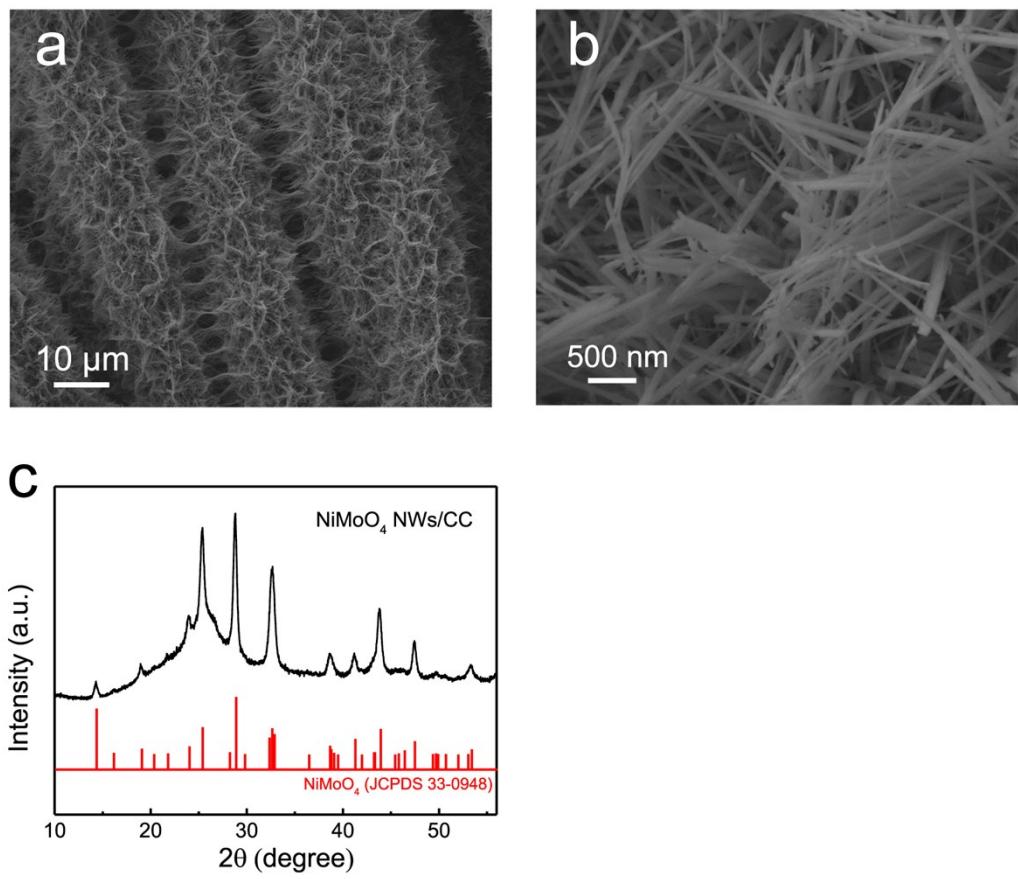
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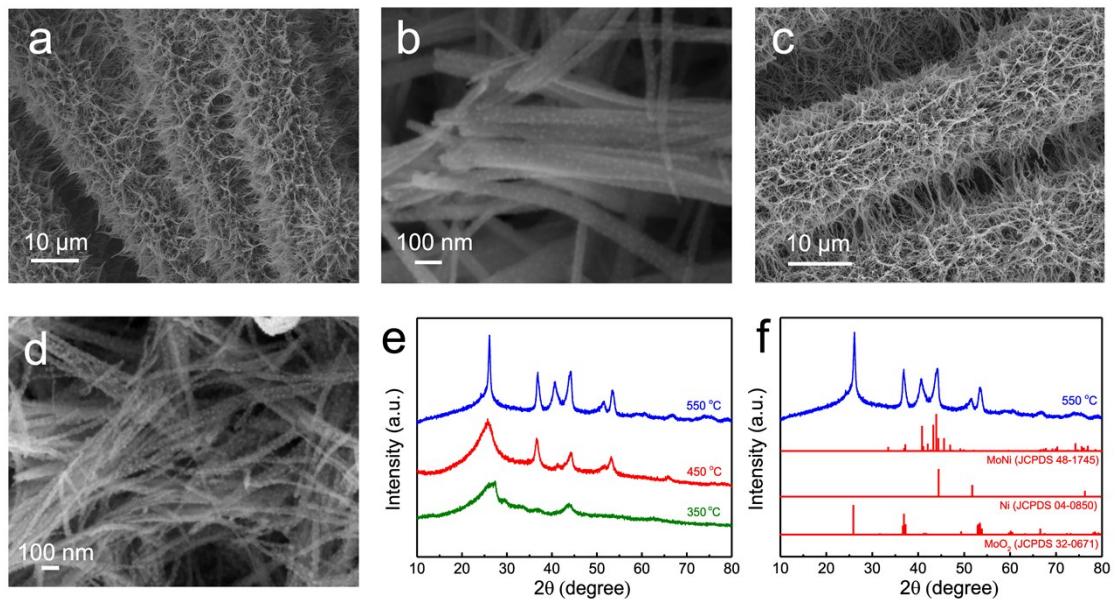
**Figure S1.** Optical photograph of bare CC (left), Mo-Ni-O based precursors (middle), and Ni-MoO<sub>2</sub>-450 NWs/CC (right).



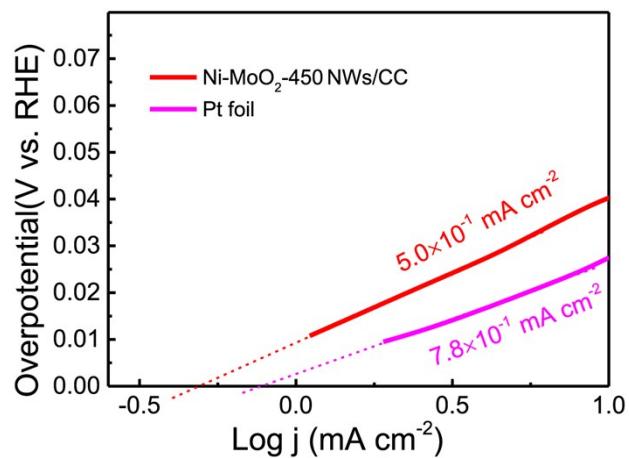
**Figure S2.** a) Low- and b) high-magnification SEM images of carbon cloth. c) Low- and d) high-magnification SEM images of Mo-Ni-O based precursors. e) XRD pattern of Mo-Ni-O based precursors.



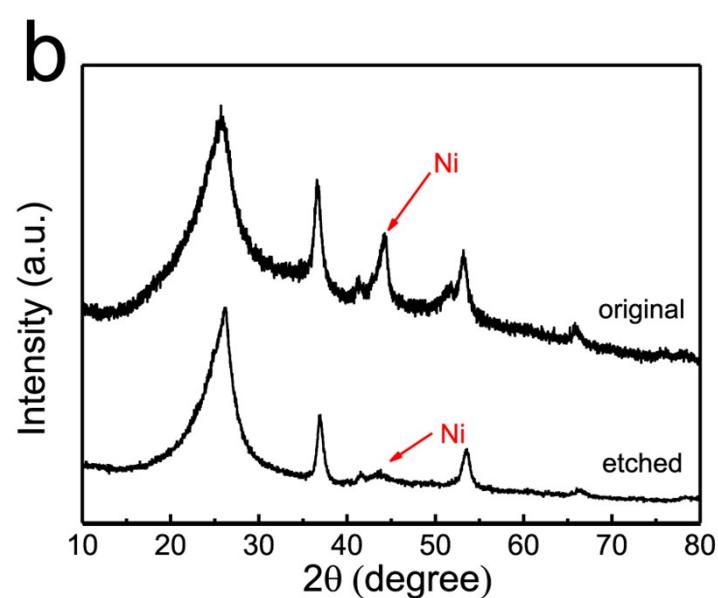
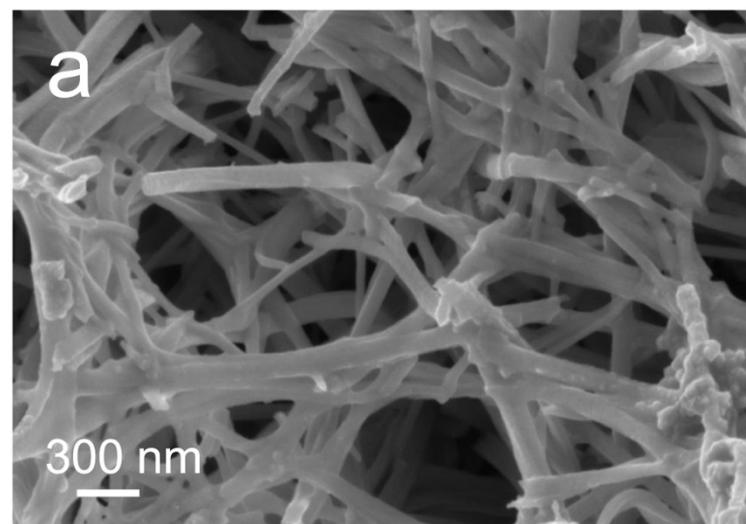
**Figure S3.** a) Low- and b) high-magnification SEM images of  $\text{NiMoO}_4$  NWs/CC. c) XRD pattern of  $\text{NiMoO}_4$  NWs/CC.



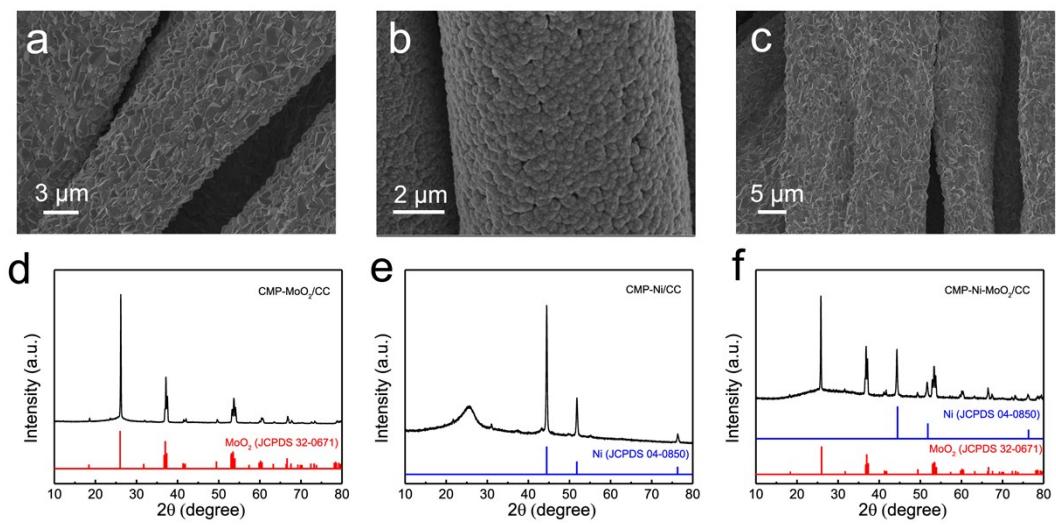
**Figure S4.** a) Low- and b) high-magnification SEM images of Ni-MoO<sub>2</sub>-350 NWs/CC. c) Low- and d) high-magnification SEM images of Ni-MoO<sub>2</sub>-550 NWs/CC. e) XRD pattern of Ni-MoO<sub>2</sub> NWs/CC annealed at different temperature. f) XRD pattern of Ni-MoO<sub>2</sub>-550 NWs/CC with the standard crystallographic spectrum of MoNi (JCPDS 48-1745), Ni (JCPDS 04-0850) and MoO<sub>2</sub> (JCPDS 32-0671).



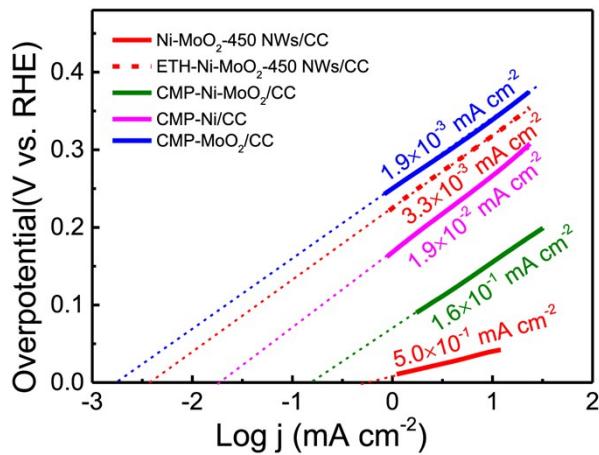
**Figure S5.** Exchange current densities for Ni-MoO<sub>2</sub>-450 NWs/CC and Pt foil in 1 M KOH, which were calculated from Tafel plots by extrapolation method.



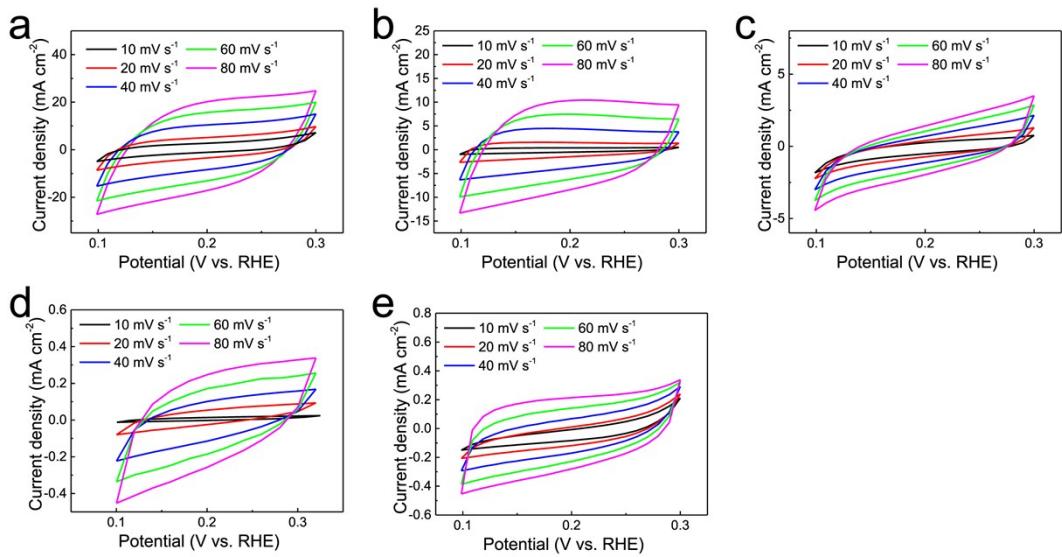
**Figure S6.** a) SEM image and b) XRD pattern of ETH-Ni-MoO<sub>2</sub>-450 NWs/CC.



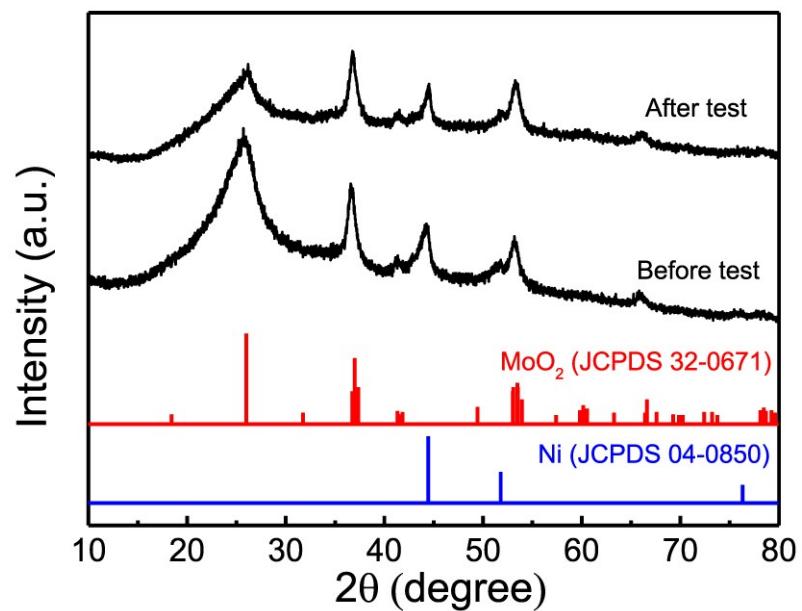
**Figure S7.** SEM images of a) CMP-MoO<sub>2</sub>/CC, b) CMP-Ni /CC, and c) CMP-Ni-MoO<sub>2</sub>/CC. XRD pattern of a) CMP-MoO<sub>2</sub>/CC, b) CMP-Ni /CC, and c) CMP-Ni-MoO<sub>2</sub>/CC.



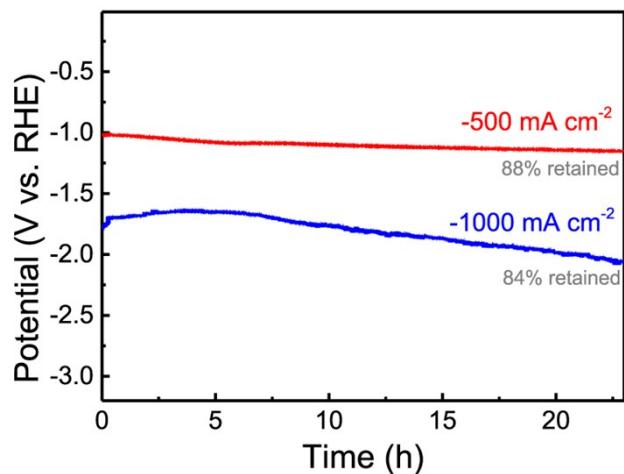
**Figure S8.** Exchange current densities for Ni-MoO<sub>2</sub>-450 NWs/CC, ETH-Ni-MoO<sub>2</sub>-450 NWs/CC, CMP-Ni-MoO<sub>2</sub>/CC, CMP-MoO<sub>2</sub>/CC, and CMP-Ni/CC in 1 M KOH, which were calculated from Tafel plots by extrapolation method.



**Figure S9.** Electrochemically active surface area measurements. CV curves measured from 10 to 80  $\text{mV s}^{-1}$  in 1 M KOH of CV curves measured from 10 to 80  $\text{mV s}^{-1}$  of a) Ni-MoO<sub>2</sub>-450 NWs/CC, b) ETH-Ni-MoO<sub>2</sub>-450 NWs/CC, c) CMP-Ni-MoO<sub>2</sub>/CC, d) CMP-MoO<sub>2</sub>/CC, and e) CMP-Ni/CC.



**Figure S10.** XRD patterns of Ni-MoO<sub>2</sub>-450 NWs/CC before and after the multi-current-step measurement.



**Figure S11.** Chronoamperometry measurement at a static current density of  $-500$  and  $-1,000 \text{ mA cm}^{-2}$  in  $1 \text{ M KOH}$  for more than  $20$  hours without  $iR$  correction.

**Table S1.** Summary of Ni-MoO<sub>2</sub> NWs/CC annealed at different temperature.

Materials	Annealing temperature (°C)	Crystallinity	Chemical composition	$\eta_{10}$ (mV)	Tafel slope (mV dec <sup>-1</sup> )
Ni-MoO <sub>2</sub> -350 NWs/CC	350	Low	Ni/MoO <sub>2</sub>	56	42
Ni-MoO <sub>2</sub> -450 NWs/CC	450	Middle	Ni/MoO <sub>2</sub>	40	30
Ni-MoO <sub>2</sub> -550 NWs/CC	550	High	MoNi/Ni/MoO <sub>2</sub>	55	38

**Table S2.** The HER activities of the Ni-MoO<sub>2</sub>-450 NWs/CC and reported catalysts in 1 M KOH.

Materials	Onset overpotential (mV)	Overpotential at 10 mA cm <sup>-2</sup> (mV)	Tafel slope (mV dec <sup>-1</sup> )	Reference
Ni-MoO <sub>2</sub> -450 NWs/CC	0	40	30	<b>This work</b>
MoNi <sub>4</sub> on MoO <sub>2</sub>	0	15	30	1
MoS <sub>2</sub> /Ni <sub>3</sub> S <sub>2</sub>	50	110	83	2
Ni(OH) <sub>2</sub> /MoS <sub>2</sub>	20	80	60	3
MoC-Mo <sub>2</sub> C	33	120	42	4
Ni-MoC	-	123	83	5
MoP	50	130	48	6
Ni <sub>2</sub> P/Ni	41	~75	50	7
N,P-doped Mo <sub>2</sub> C@carbon nanospheres	0	50	71	8
NiMoN	50	109	95	9
Ni-WN	0	47	71	10
Co/Co <sub>3</sub> O <sub>4</sub>	30	~90	44	11

## References

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