## Supporting Information

## In-situ growth of MOF derived ultrafine molybdenum carbides nanoparticles supported on Ni foam as efficient hydrogen evolution electrocatalysts

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**Fig. S1.** The XRD spectra of the powder sample of CoMo hydroxides/oxides. The peaks at 17.7 °and 25.5 °correspond to the planes (002) and (102) of CoMo oxides, respectively. (PDF # 34-0511) The peaks at 27.3 °, 28.0 °, 29.4 °, 31.3 °, 32.0 °, 33.6 °, 34.6 °, and 58.9 ° correspond to CoMo hydroxides. (PDF # 14-0087)



Fig. S2. The SEM images of the framework of NF.



Fig. S3. HRTEM images of Mo<sub>x</sub>Co<sub>y</sub>C/NF. (0.226 nm, CoO (200))



Fig. S4. HRTEM images of  $Mo_xCo_yC/NF$ . (0.199 nm,  $Co_2C$  (210))



Fig. S5. HRTEM images of  $Mo_xCo_yC/NF$ . (0.246 nm,  $MoO_2$  (100))



Fig. S6. The mapping image of  $Mo_xCo_yC/NF$ .



Fig. S7. The LSV curves of  $Mo_xCo_yC/NF$ ,  $W_xCo_yC/NF$ , and  $Co_xC/NF$  (without iR compensation).



Fig. S8. The LSV curves of  $Mo_x Co_y C/NF$ , and Pt/C/NF (qualitatively normalized).



**Fig. S9** a) CV curves of  $Mo_xCo_yC/NF$ , and b) half of the capacitive current density as a function of scan rates, measured in 1.0 M KOH solution.



Fig. S10 a) CV curves of  $W_x Co_y C/NF$ , and b) half of the capacitive current density as a function of scan rates, measured in 1.0 M KOH solution.



Fig. S11 a) CV curves of  $Co_xC/NF$ , and b) half of the capacitive current density as a function of scan rates, measured in 1.0 M KOH solution.



Fig. S12 The faradic efficiency of  $Mo_xCo_yC/NF$  electrode.



Fig. S13 SEM image of  $Mo_xCo_yC/NF$  electrode after the long-term stability test.



Fig. S14 high-resolution XPS spectrum of  $Mo_xCo_yC/NF$  (Mo 3d) after the long-term stability test.



Fig. S15 high-resolution XPS spectrum of  $Mo_xCo_yC/NF$  (Co 2p) after the long-term stability test.



Fig. S16 high-resolution XPS spectrum of  $Mo_xCo_yC/NF$  (N 1s) after the long-term stability test.

catalysts	η <sub>10</sub> (mV)	η <sub>100</sub> (mV)	ref
Mo <sub>x</sub> Co <sub>y</sub> C/NF	33.5	124	This work
MoC-Mo <sub>2</sub> C/PNCDs	121	182	1
Mo <sub>2</sub> C@NC	60		2
NiMo <sub>2</sub> C@C	181		3
Mo <sub>2</sub> C@2D-NPC	45		4
Co-NC@Mo <sub>2</sub> C	99		5
MoNi <sub>4</sub> /MoO <sub>2</sub> @Ni	15		6
NiMo <sub>2</sub> C/NF		150	7
Mo <sub>2</sub> C@ NC NPs/CC	123		8

**Table S1.** The comparison of the electrocatalytic activities of Mo<sub>x</sub>Co<sub>y</sub>C/NF with some representative carbide-based HER electrocatalysts recently reported in 1.0 M KOH solution

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