Electronic Supplementary Material (ESI) for Nanoscale.
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Supporting Information

Self-Supported Nickel-Doped Molybdenum Carbide Nanoflower Clusters on Carbon Fiber Paper for Efficient Hydrogen Evolution Reaction

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The role of Ni in the formation of Mo_2C

When nickel nitrate solution was used as the nickel source, the nickel nitrate decomposed to nickel oxide (NiO) (Eq.1), NiO will be reduced to Ni by the released CO to promote the production of Mo_2C by driving the reaction 3 to the right (Eq.3 and 4), so the intensity of the Mo_2C peak increased gradually with the increasing of the concentration of nickel nitrate. When metallic nickel (<100 nm) was used as a dopant, we believe that the surface of raw Ni was easily oxidized to NiO (Eq.2), then, NiO reacted with CO to reduce to Ni, thereby promoting the formation of Mo_2C (Eq.3 and 4). The chemical reactions during the process can be described by the following equations:

$$2Ni(NO_3)_2 \cdot 6H_2O \rightarrow 2NiO + 4NO_2 + O_2 + 12H_2O \quad (1)$$

$$Ni + O_2 \rightarrow NiO \quad (2)$$

$$2MoO_3 + 7C \rightarrow Mo_2C + 6CO \quad (3)$$

$$NiO + CO \rightarrow Ni + CO_2 \quad (4)$$

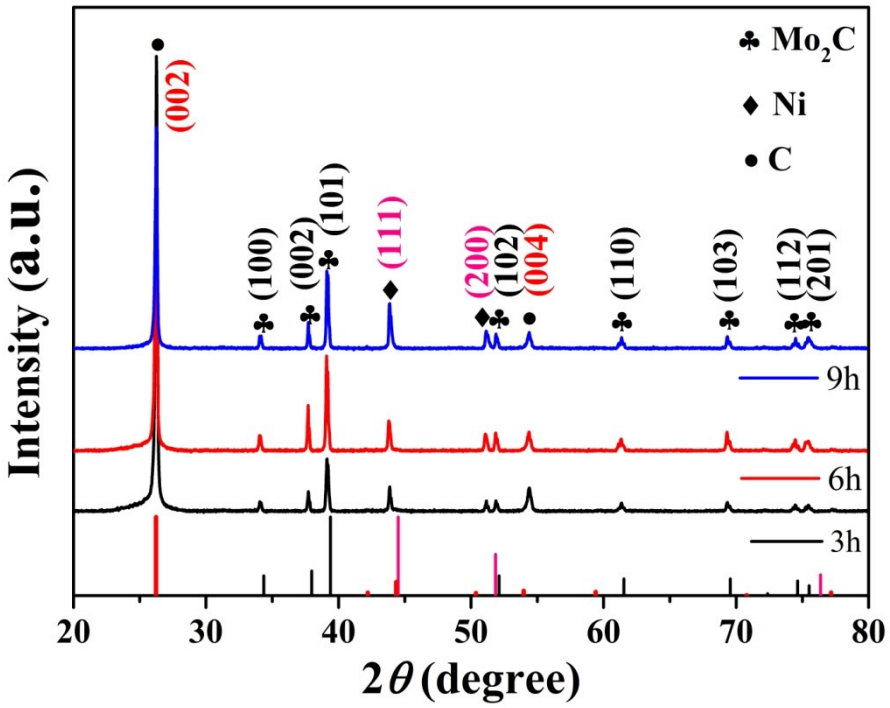

Figure S1. The XRD patterns of self-supported Mo_2C-3M $Ni(NO_3)_2$/CFP electrocatalysts obtained at the different annealing time from 3 to 9 h, standard crystal indices of Mo_2C (PDF# 35-0787), C (PDF#41-1487) and Ni (PDF#04-0850) are shown at the bottom.

As shown in XRD patterns, The C, β-Mo_2C and Ni specials are all present as a result of the short annealing time of 3 h. The intensity of C at 3 h is higher than that of other annealing time conditions, while the peak intensity of Mo_2C and Ni are relatively weaker. At an annealing time of 9 h, the peak intensity of Mo_2C and Ni increase. The increase of Ni is much higher than that of Mo_2C, indicating that the content of Ni in the composite electrode has increased, which will make the electrode material more easily oxidized and reduce the activity.

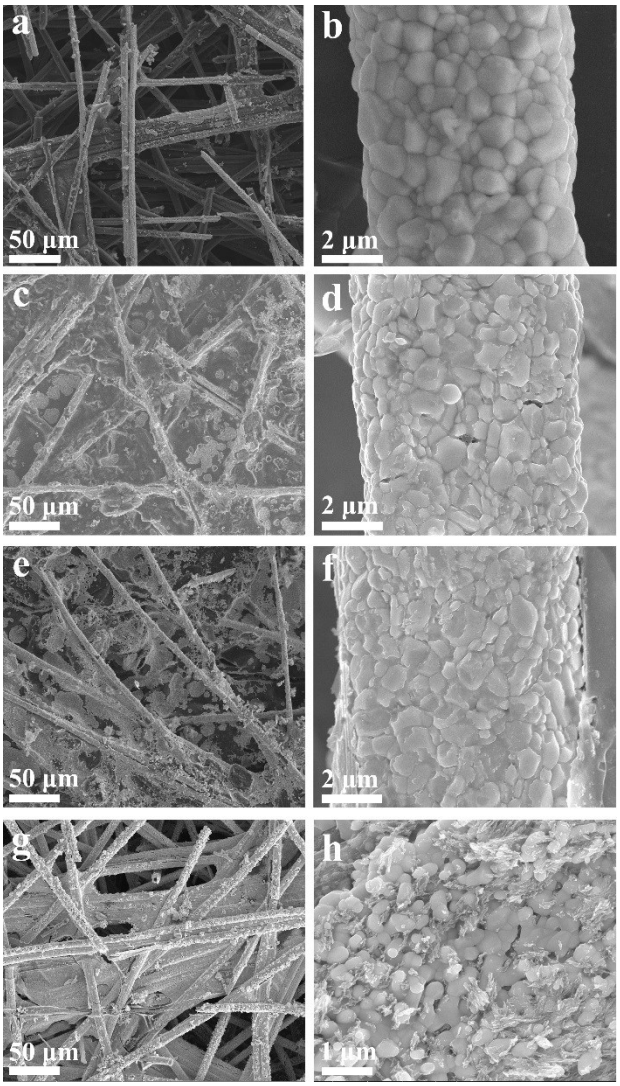

Figure S2. SEM images of (a, b) Mo_2C-0Ni/CFP, (c, d) Mo_2C-2Ni/CFP, (e, f) Mo_2C-5Ni/CFP and (g, h) Mo_2C-10Ni/CFP self-supported electrocatalysts obtained at 1000 °C for 6 h.

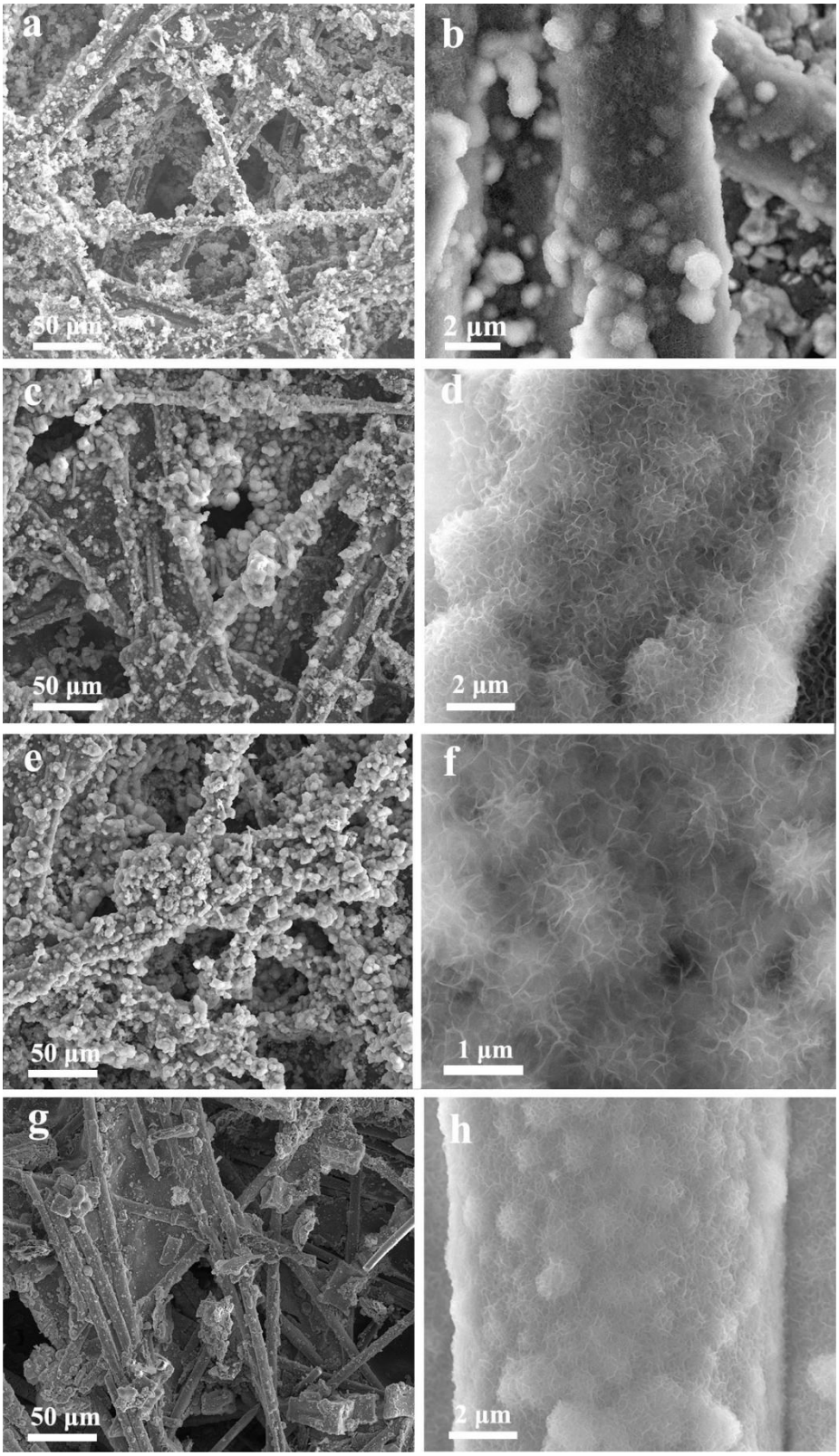

Figure S3. SEM images of (a, b) Mo_2C-1M $Ni(NO_3)_2$/CFP, (c, d) Mo_2C-2M $Ni(NO_3)_2$/CFP, (e, f) Mo_2C-3M $Ni(NO_3)_2$/CFP and (g, h) Mo_2C-4M $Ni(NO_3)_2$/CFP self-supported electrocatalysts obtained at 1000 °C for 6 h.

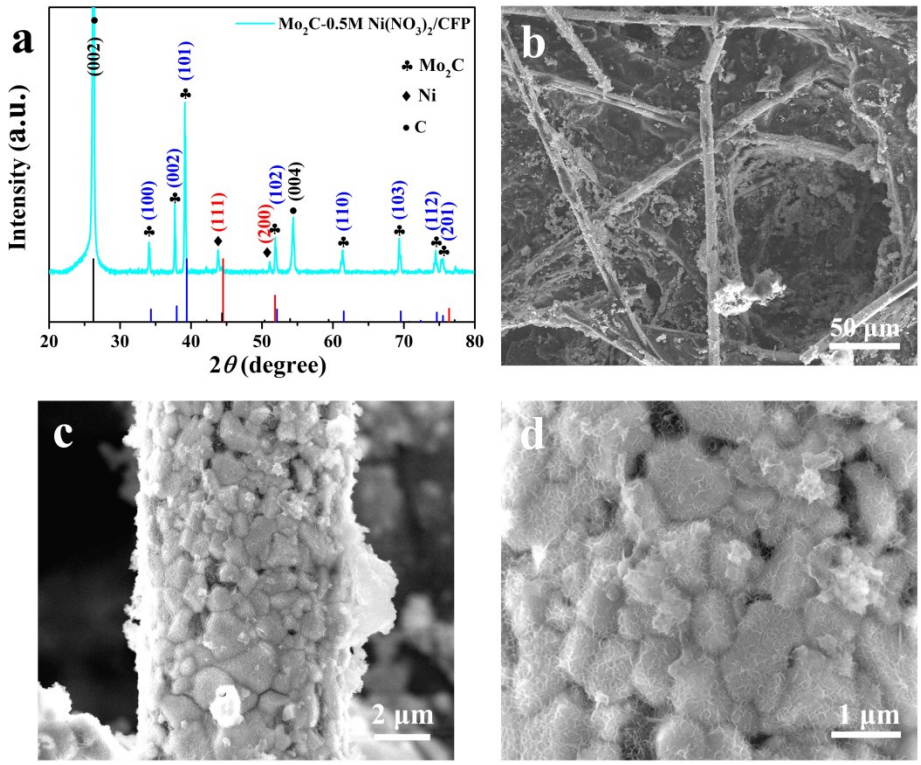

Figure S4. (a) XRD pattern and (b, c, d) SEM images of Mo_2C-0.5M $Ni(NO_3)_2$/CFP electrocatalysts obtained at 1000 °C for 6 h.

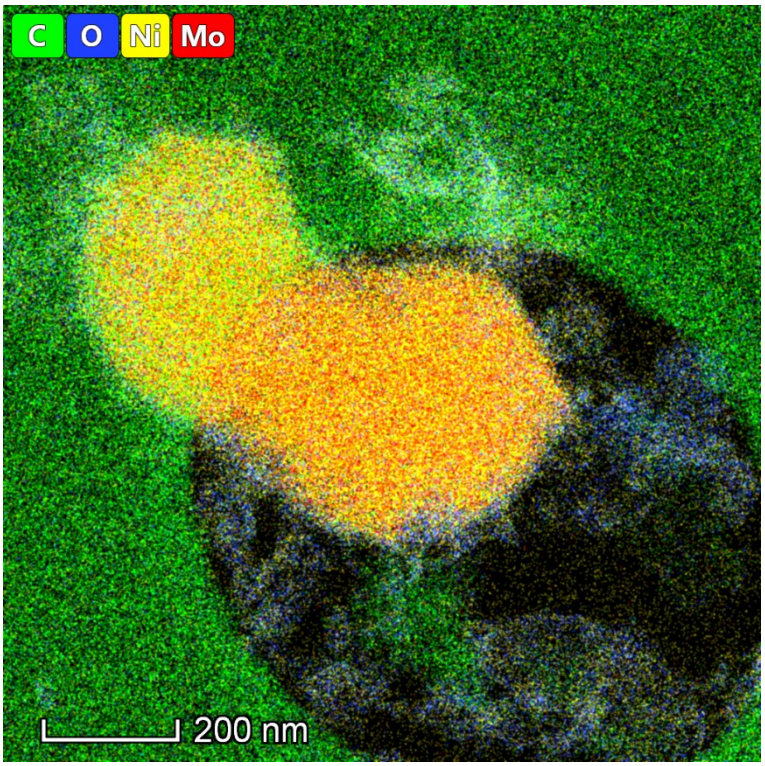

Figure S5. EDS mapping of the agglomeration of nickel in the sample of Mo_2C-4M $Ni(NO_3)_2$/CFP electrocatalysts.

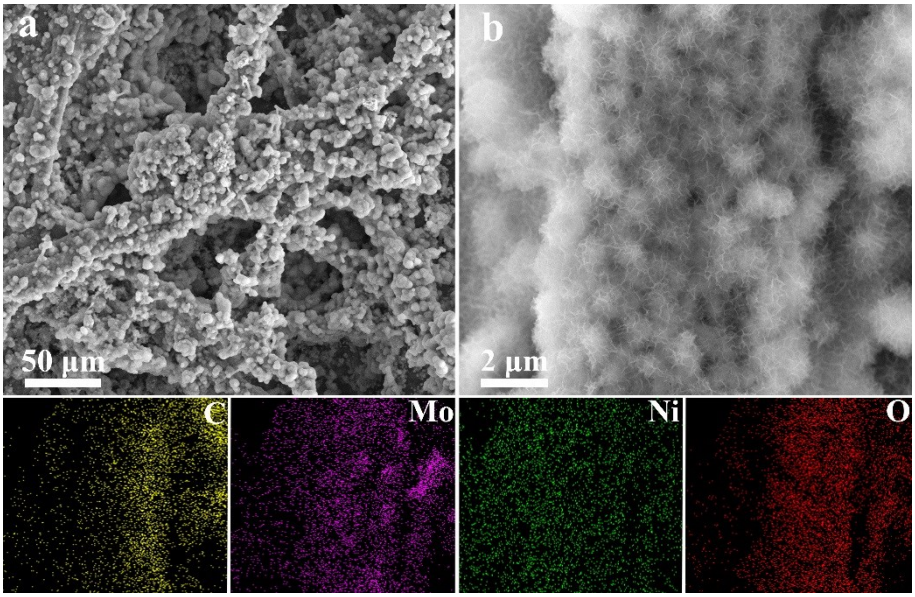

Figure S6. (a, b) SEM images and the corresponding EDS mappings of Mo_2C-3M $Ni(NO_3)_2$/CFP electrocatalysts obtained at 1000 °C for 6 h.

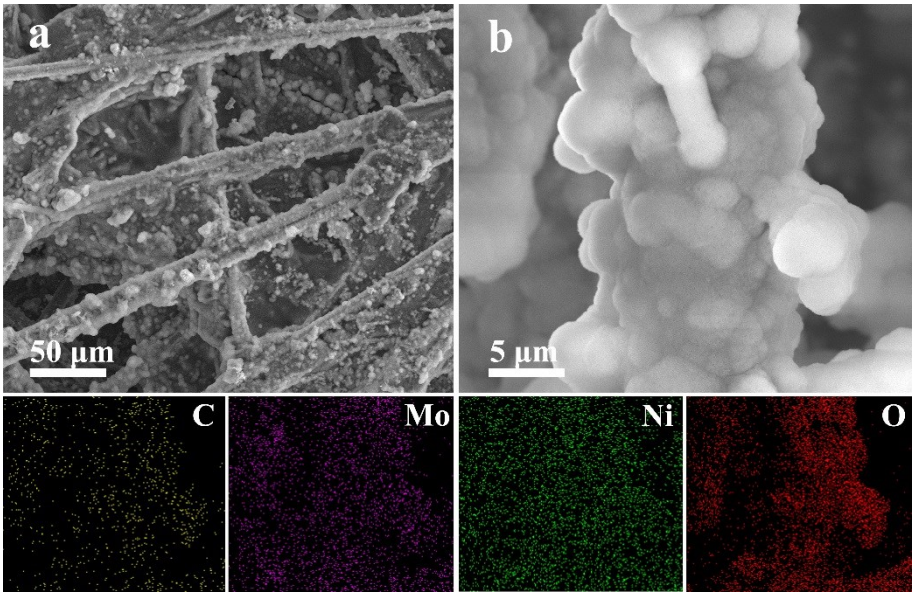

Figure S7. (a, b)SEM images and the corresponding EDS mappings of Mo_2C-3M $Ni(NO_3)_2$/CFP electrocatalysts obtained at 1000 °C for 3 h.

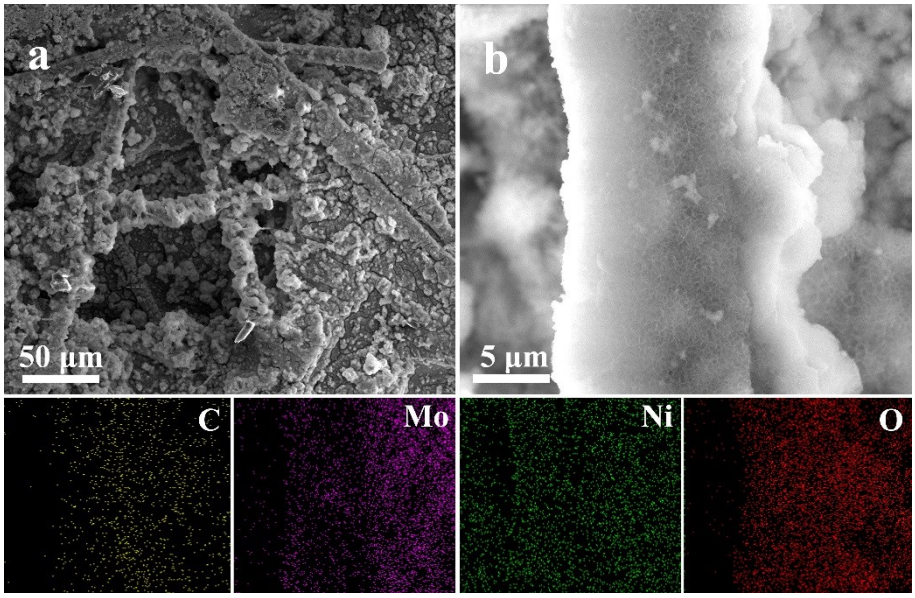

Figure S8. (a, b) SEM images and the corresponding EDS mappings of Mo_2C-3M $Ni(NO_3)_2$/CFP electrocatalysts obtained at 1000 °C for 9 h.

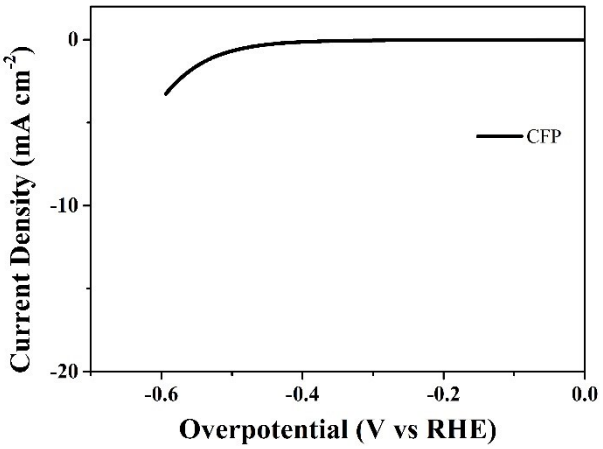

Figure S9. The HER polarization curves of bare CFP.

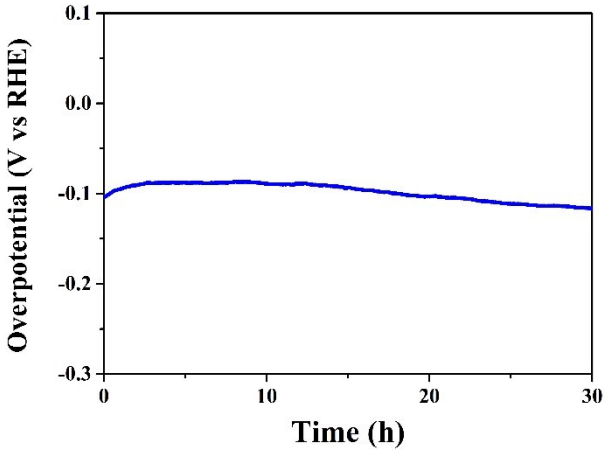

Figure S10. The stability test for Mo_2C-10Ni/CFP electrocatalyst obtained at 1000 °C for 6 h.

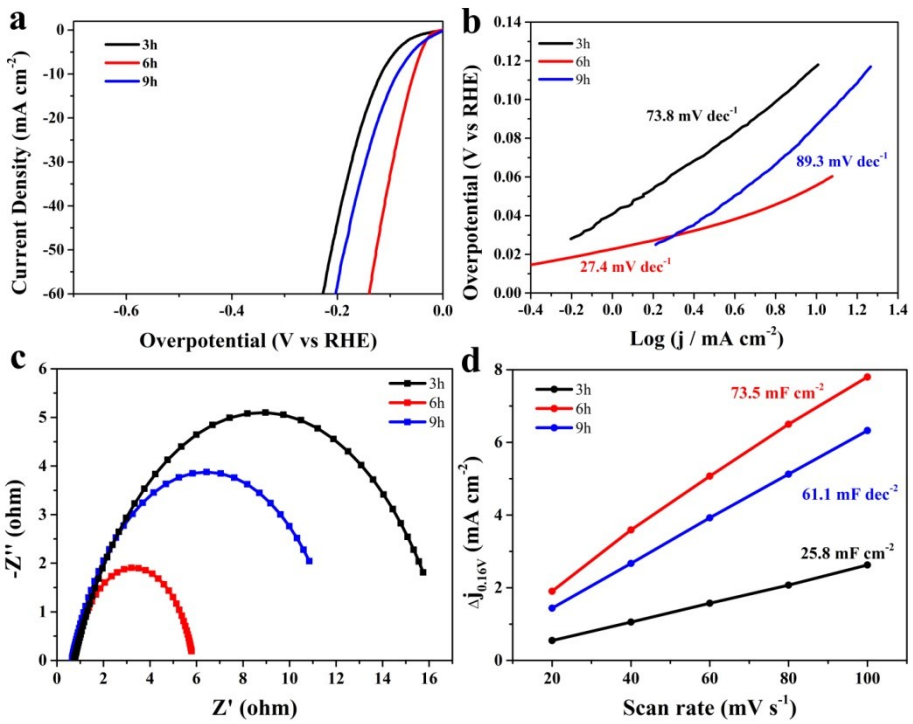

Figure S11. HER performance of Mo_2C-3M $Ni(NO_3)_2$/CFP electrocatalysts obtained at the different annealing time from 3 to 9 h. (a) LSV, (b) Tafel plots, (c) EIS Nyquist plots obtained at -100 mV and (d) The capacitive currents at different scan rates.

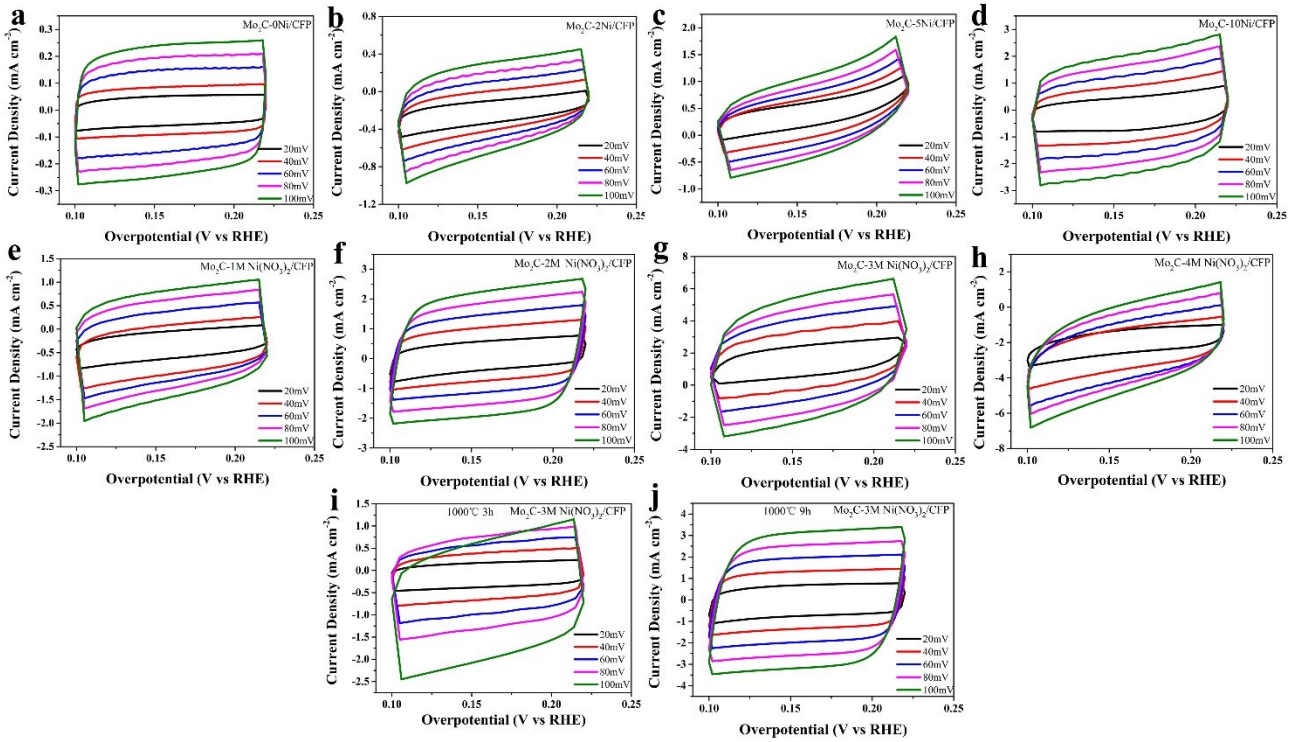

Figure S12. CV curves at different scan rates in the non-Faradaic potential region (0.1-0.22 V vs. RHE) for the samples: (a) Mo_2C-0Ni/CFP, (b) Mo_2C-2Ni/CFP, (c) Mo_2C-5Ni/CFP, (d) Mo_2C-10Ni/CFP, (e) Mo_2C-1M $Ni(NO_3)_2$/CFP, (f) Mo_2C-2M $Ni(NO_3)_2$/CFP, (g) Mo_2C-3M $Ni(NO_3)_2$/CFP, (h) Mo_2C-4M $Ni(NO_3)_2$/CFP, (i) Mo_2C-3M $Ni(NO_3)_2$/CFP-3h and (j) Mo_2C-3M $Ni(NO_3)_2$/CFP-9h.

Table S1. Fitting parameters (peak position, peak area and species percentage) for both Mo 3d profiles taken on Mo_2C-0Ni/CFP and Mo_2C-3M $Ni(NO_3)_2$/CFP from Figure 3 in the manuscript.

Samples	species	B.E (eV)		Mo^{2+} (%)	Mo^{4+} (%)	Mo^{6+} (%)
Mo_2C-0Ni/CFP	Mo^{2+}	228.8	232.0	6.0		
	Mo^{4+}	231.6	234.8		1.4	
	Mo^{6+}	233.2	236.4			92.6
Mo_2C-3M $Ni(NO_3)_2$/CFP	Mo^{2+}	228.6	231.8	23.9		
	Mo^{4+}	231.3	234.5		46.9	
	Mo^{6+}	233.0	236.2			20.5