

## Supplementary Information

### **Three-Dimensional Porous MoNi<sub>4</sub> Networks Constructed by Nanosheets as Bifunctional Electrocatalysts for Overall Water Splitting**

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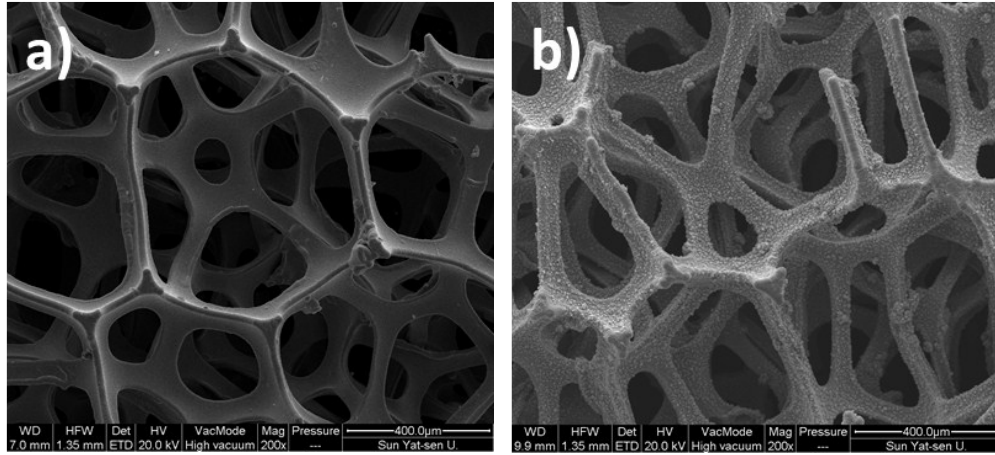
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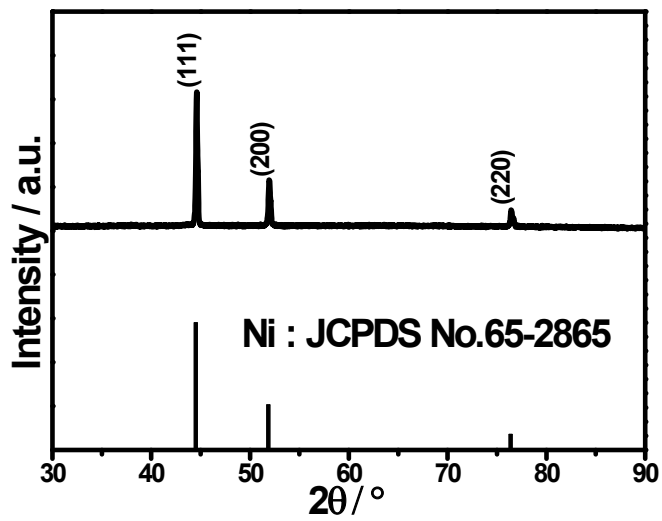
**Table S1.** HER, OER and overall water splitting activities of the porous MoNi<sub>4</sub> networks and reported catalysts.

Catalyst (mass loading)	Electrolyte	HER Potential vs. RHE (V) @ 10 mA cm <sup>-2</sup>	OER Potential vs. RHE (V) @ 10 mA cm <sup>-2</sup>	Overall Water Splitting Potential (V) @ 10 mA cm <sup>-2</sup>	Overall Water Splitting Onset Potential (V)
porous MoNi <sub>4</sub> networks (~1.09 mg/cm <sup>2</sup> )	1 M KOH	-0.028	1.51	1.58	1.45 <sup>this work</sup>
NiCo <sub>2</sub> O <sub>4</sub> hollow microcuboids <sup>[1]</sup> (~1 mg/cm <sup>2</sup> )	1 M KOH	-0.110	1.52	1.65	
NiSe nanowire film/Ni foam <sup>[2]</sup> (2.8 mg/cm <sup>2</sup> )	1 M KOH	-0.096		1.63	~1.5
Ni <sub>5</sub> P <sub>4</sub> Films/Ni foil <sup>[3]</sup> (~3.5 mg/cm <sup>2</sup> )	1 M KOH	-0.15	1.56	<1.7	~1.53
Ni <sub>2</sub> P nanoparticles <sup>[4]</sup> (0.14 mg/cm <sup>2</sup> )	1 M KOH		1.52	1.63	~1.5
Co-P films/Cu foil <sup>[5]</sup> (2.71 mg/cm <sup>2</sup> )	1 M KOH	-0.094	1.575	1.64	1.57
Porous Cobalt-Based Thin Film <sup>[6]</sup> (~0.1 mg/cm <sup>2</sup> )	1 M KOH	-0.38	1.53		
	0.5 M H <sub>2</sub> SO <sub>4</sub>	-0.15			
Ni <sub>3</sub> S <sub>2</sub> Nanosheet Arrays /Ni foam <sup>[7]</sup> (~1.6 mg/cm <sup>2</sup> )	1 M KOH	~-0.22	~1.49	~1.76(@ ~13 mA cm <sup>-2</sup> )	
	neutral media	~-0.17			

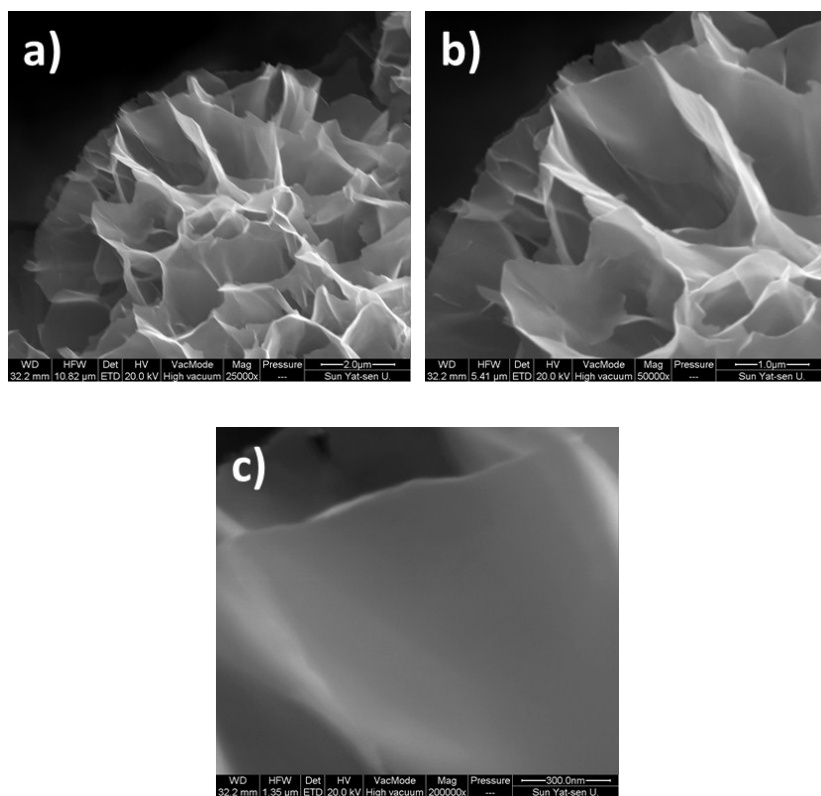
NiFeO <sub>x</sub> /CFP after two lithium galvanostatic cycles <sup>[8]</sup> (~1.6 mg/cm <sup>2</sup> )	1M KOH	-0.088	1.46	1.55	~1.5
				1.51 (increasing the mass loading)	



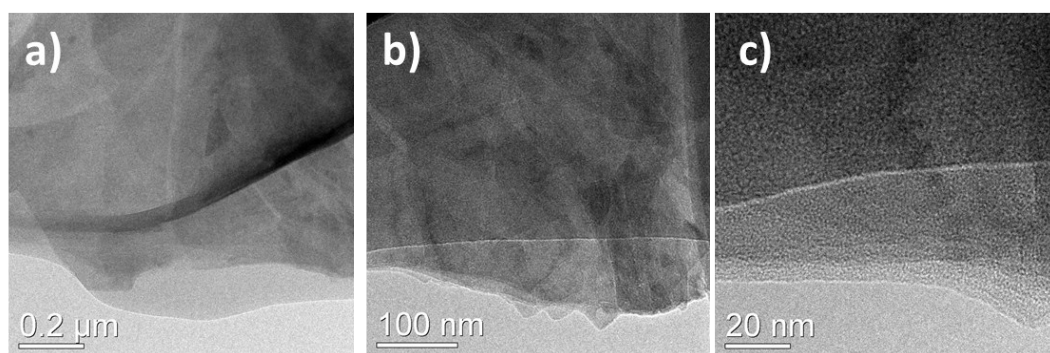
**Figure S1.** SEM images of (a) nickel foam, (b) porous MoNi<sub>4</sub> networks annealed at 450°C at low magnification.



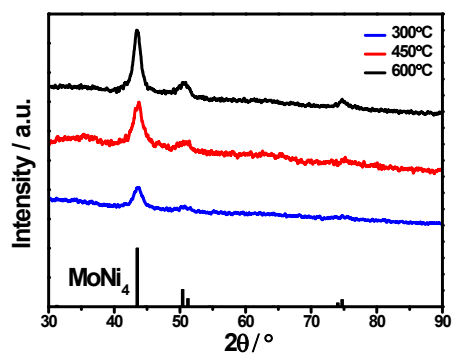
**Figure S2.** XRD patterns of nickel foam.



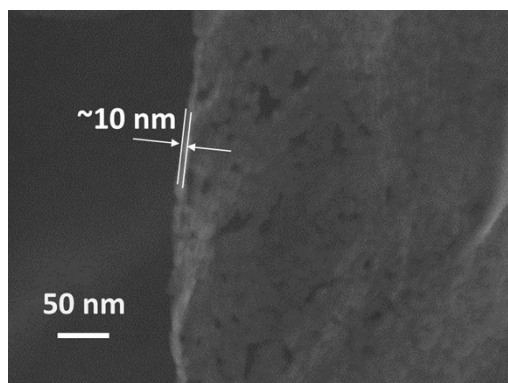
**Figure S3.** SEM images of Mo-Ni based precursors at different magnifications.



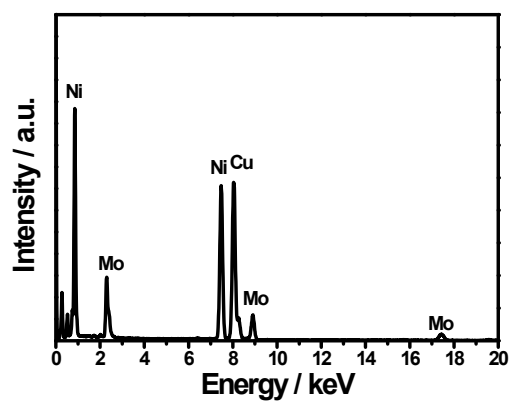
**Figure S4.** TEM images of Mo-Ni based precursors at different magnifications.



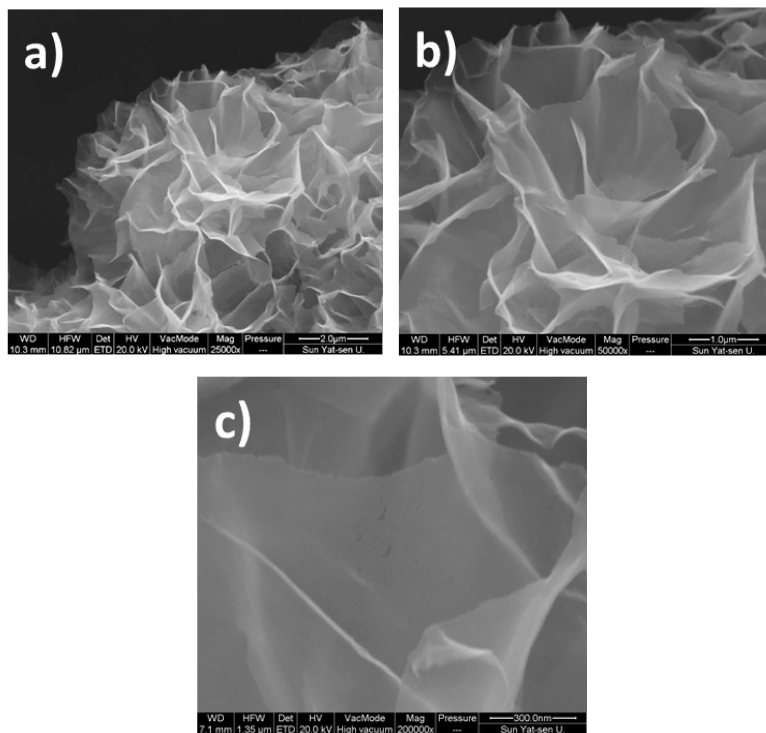
**Figure S5.** XRD patterns of the porous MoNi<sub>4</sub> networks annealed at 300°C, 450°C and 600°C.



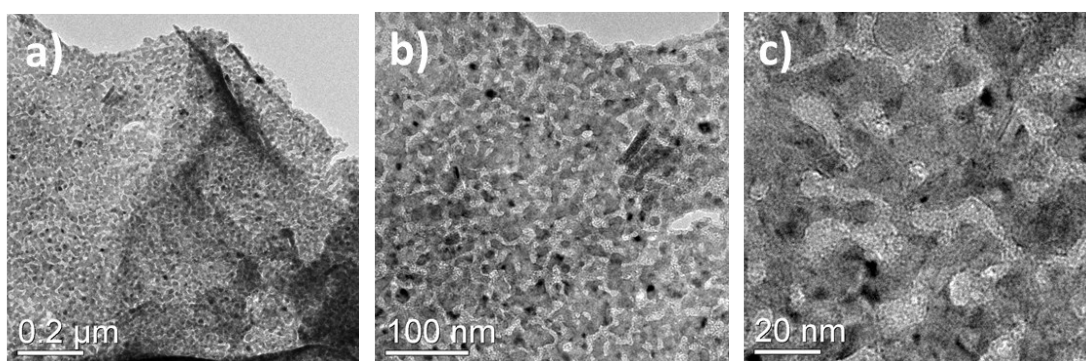
**Figure S6.** Higher resolution SEM image of the porous MoNi<sub>4</sub> networks annealed at 450°C.



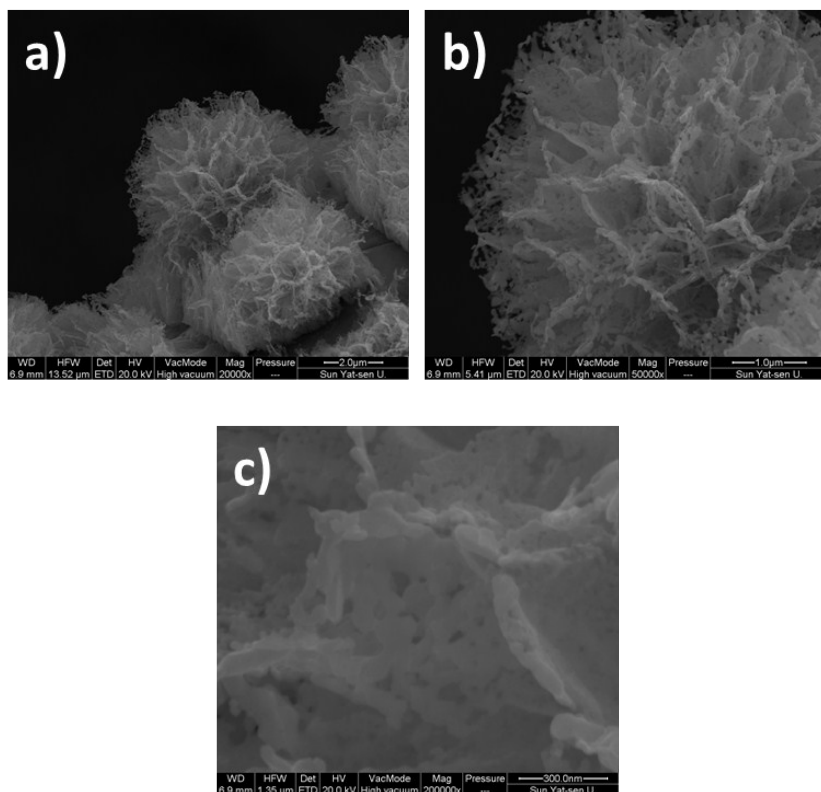
**Figure S7.** The corresponding energy dispersive X-ray (EDX) spectrum of porous MoNi<sub>4</sub> networks annealed at 450°C.



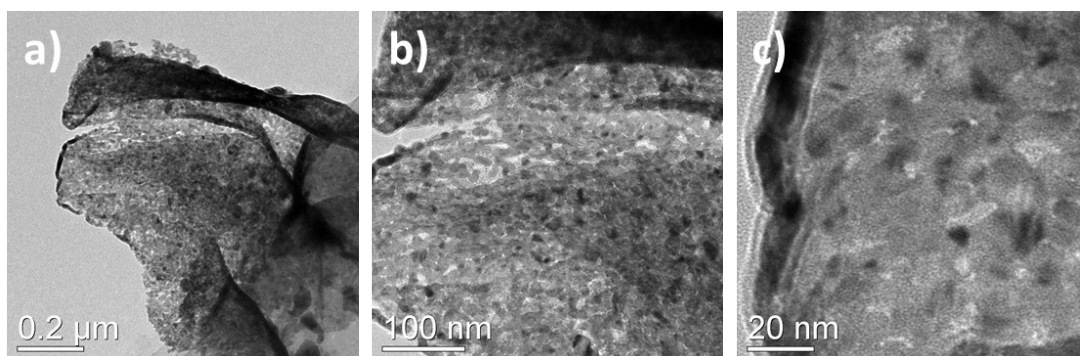
**Figure S8.** SEM images of porous MoNi<sub>4</sub> networks annealed at 300°C at different magnifications.



**Figure S9.** TEM images of porous MoNi<sub>4</sub> networks annealed at 300°C at different magnifications.



**Figure S10.** SEM images of porous MoNi<sub>4</sub> networks annealed at 600°C at different magnifications.



**Figure S11.** TEM images of porous MoNi<sub>4</sub> networks annealed at 600°C at different magnifications.



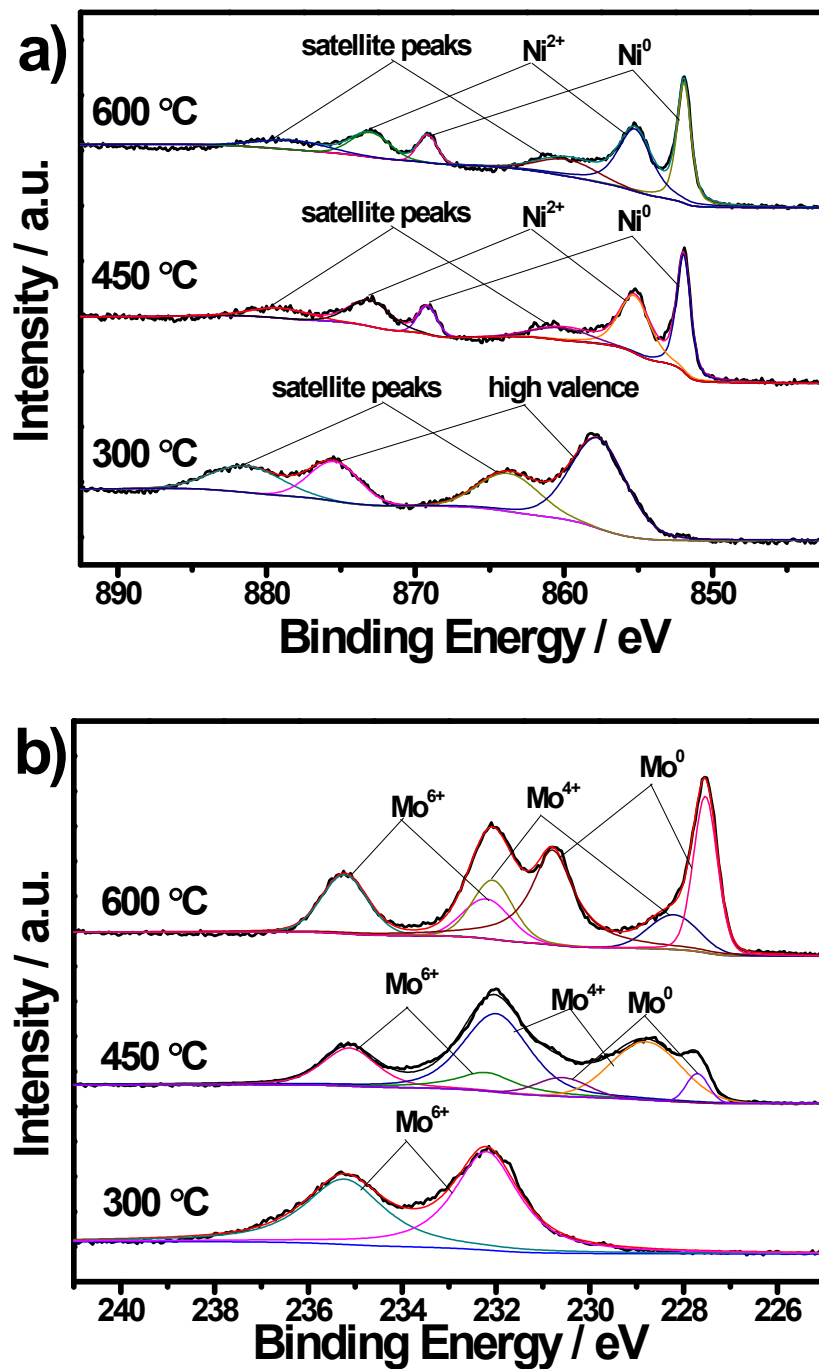
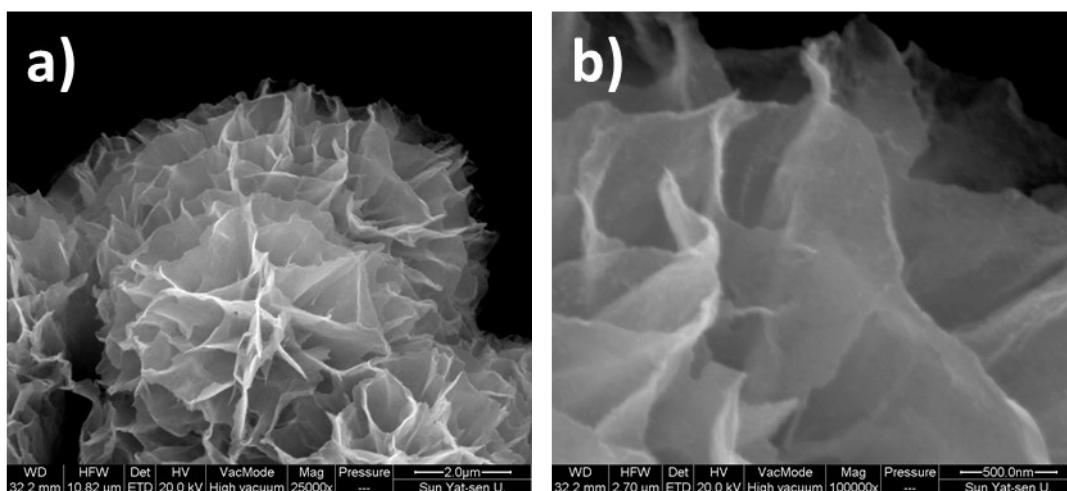
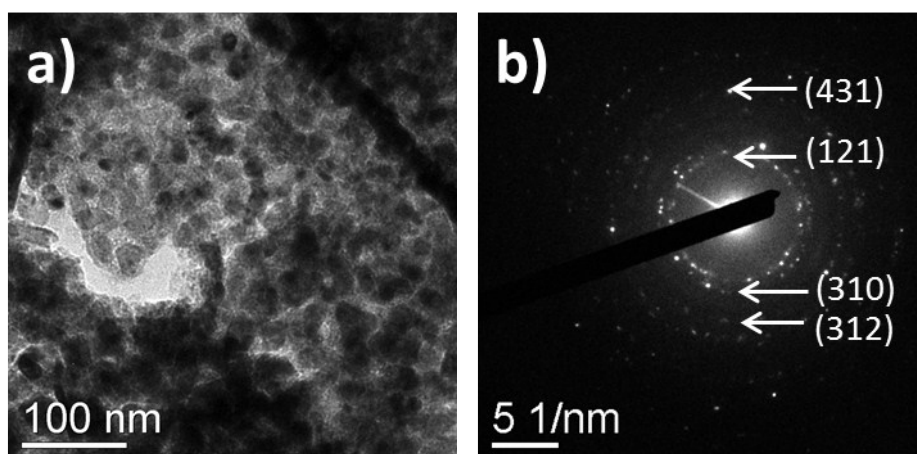


Figure S12. XPS spectra of the MoNi<sub>4</sub> networks annealed at different temperature. (a)

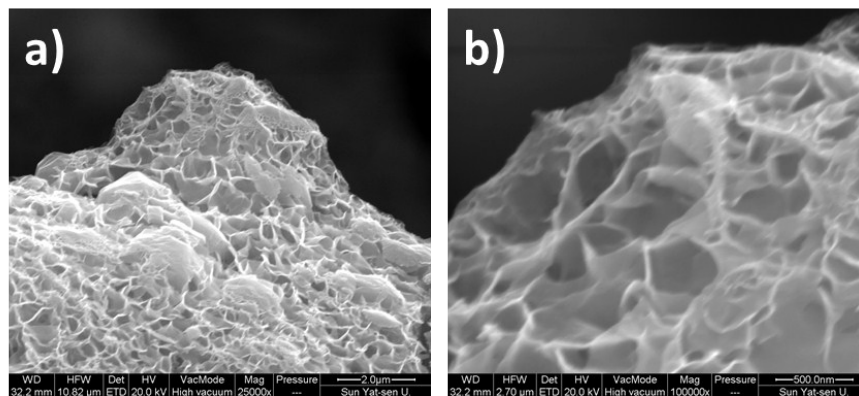
Ni 2p peaks. (b) Mo 3d peaks.



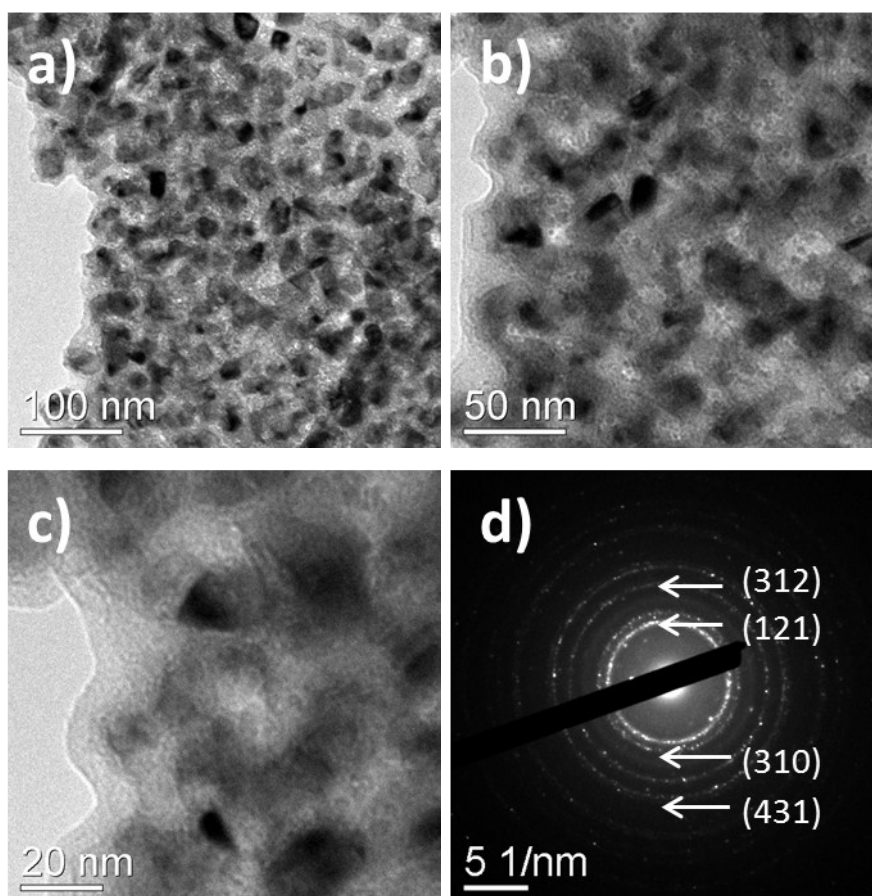
**Figure S13.** SEM images of porous MoNi<sub>4</sub> networks annealed at 450°C after the HER stability test.



**Figure S14.** (a) TEM images and (b) the corresponding selected-area electron diffraction (SAED) pattern of porous MoNi<sub>4</sub> networks annealed at 450°C after the HER stability test.



**Figure S15.** SEM images of porous MoNi<sub>4</sub> networks annealed at 450°C after the OER stability test.



**Figure S16.** (a-c) TEM images and (d) the corresponding selected-area electron diffraction (SAED) pattern of the porous MoNi<sub>4</sub> networks annealed at 450°C after the OER stability test.

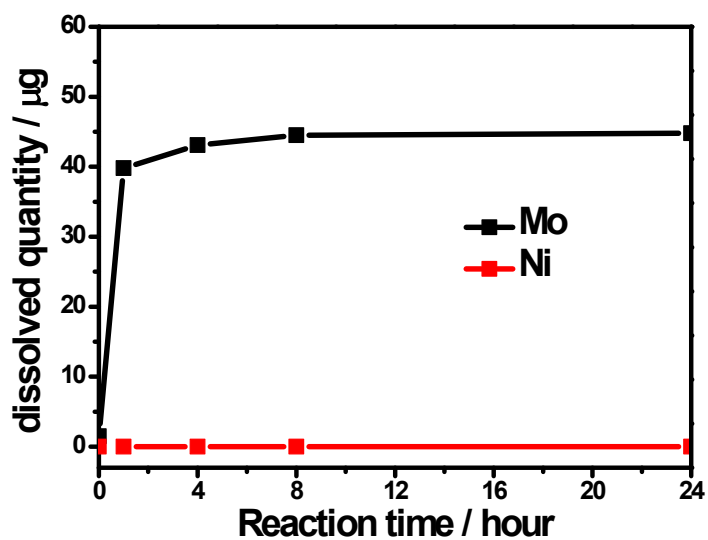


Figure S17. Dissolved quantity - time curves of Mo and Ni during OER.

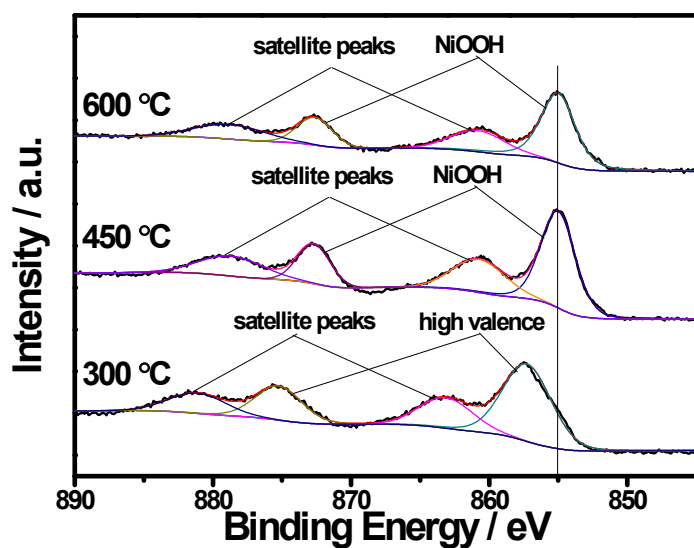
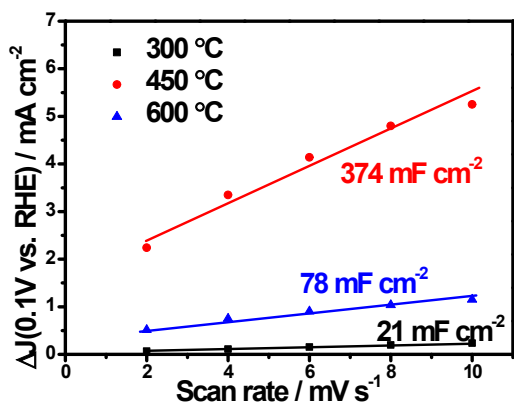
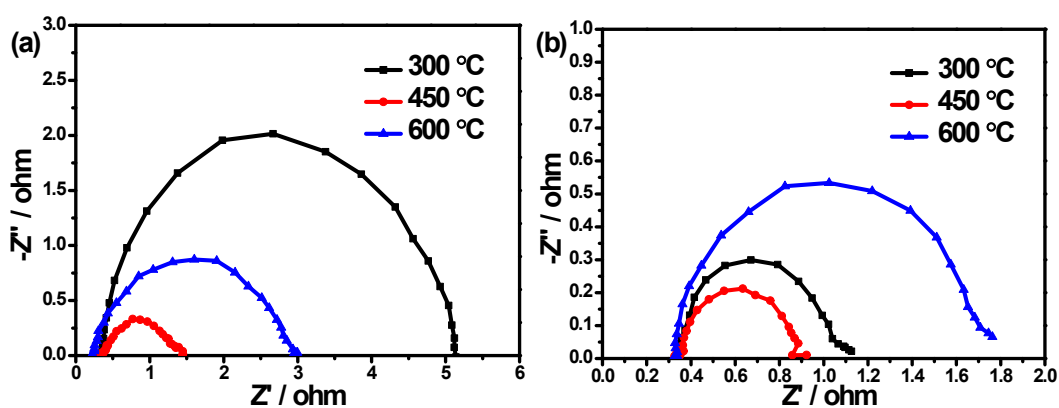


Figure S18. XPS spectra (Ni 2p peaks) of the MoNi<sub>4</sub> networks annealed at different temperature after OER.



**Figure S19.** Electrochemically surface area measurements. The corresponding  $j_{\text{geo}}$  vs scan rates plots of the porous  $\text{MoNi}_4$  networks annealed at  $450^\circ\text{C}$ .



**Figure S20.** The Nyquist plots of the porous  $\text{MoNi}_4$  networks annealed at  $450^\circ\text{C}$  at (a)  $-100\text{ mV vs. RHE}$  and (b)  $1.6\text{ V vs. RHE}$ . All of the potentials and voltages are without  $iR$  corrected.

## **References**

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