Supporting Information

Hierarchically Heterostructured Metal Hydr(oxy)oxides for Efficient Overall Water Splitting

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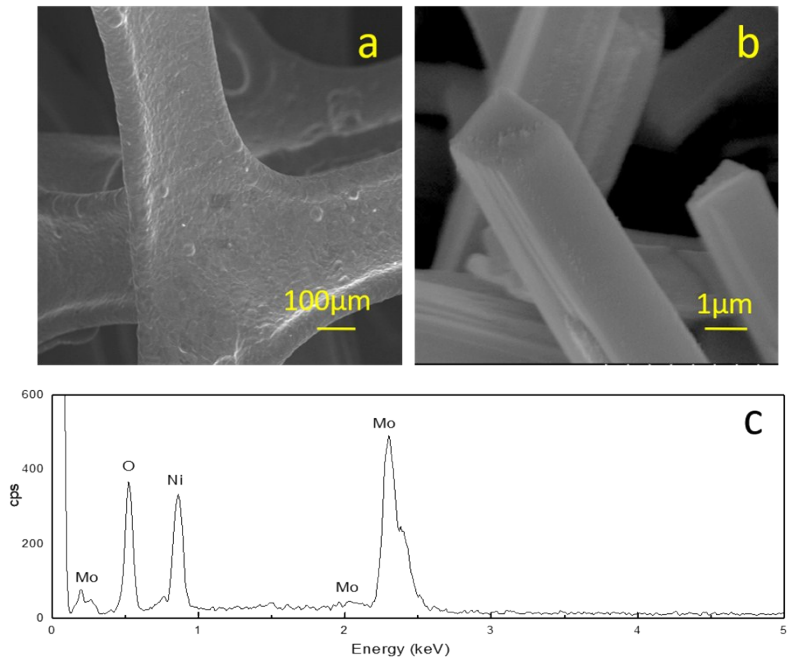

Fig. S1. a-b) SEM image of a) Ni foam, b) $NiMoO_4$ rods. c) EDX spectra of $NiMoO_4$ rods.

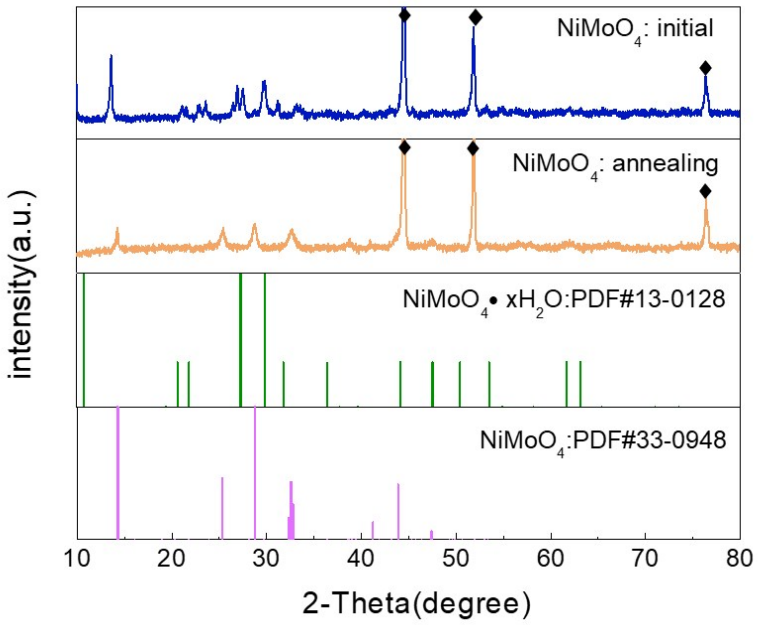

Fig. S2. The XRD patterns of $NiMoO_4$ rods before and after the annealing process at 200 ^oC.

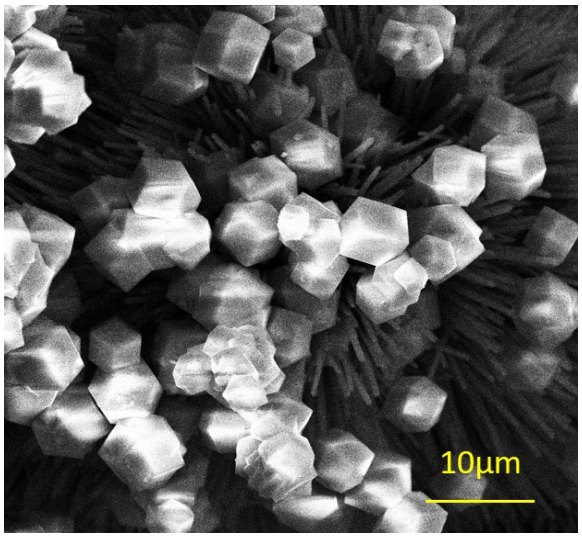

Fig. S3. The morphology of Ni-W-O/$NiMoO_4$-2 heterostructure synthesized with 2 mmol $(NH_4)_{10}W_{12}O_{41}\cdot xH_2O$.

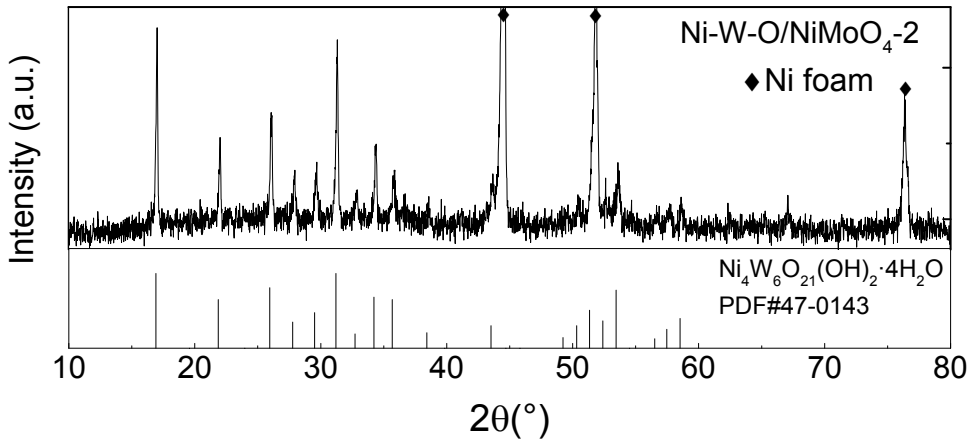

Fig. S4. The XRD patterns of Ni-W-O/$NiMoO_4$-2 rods.

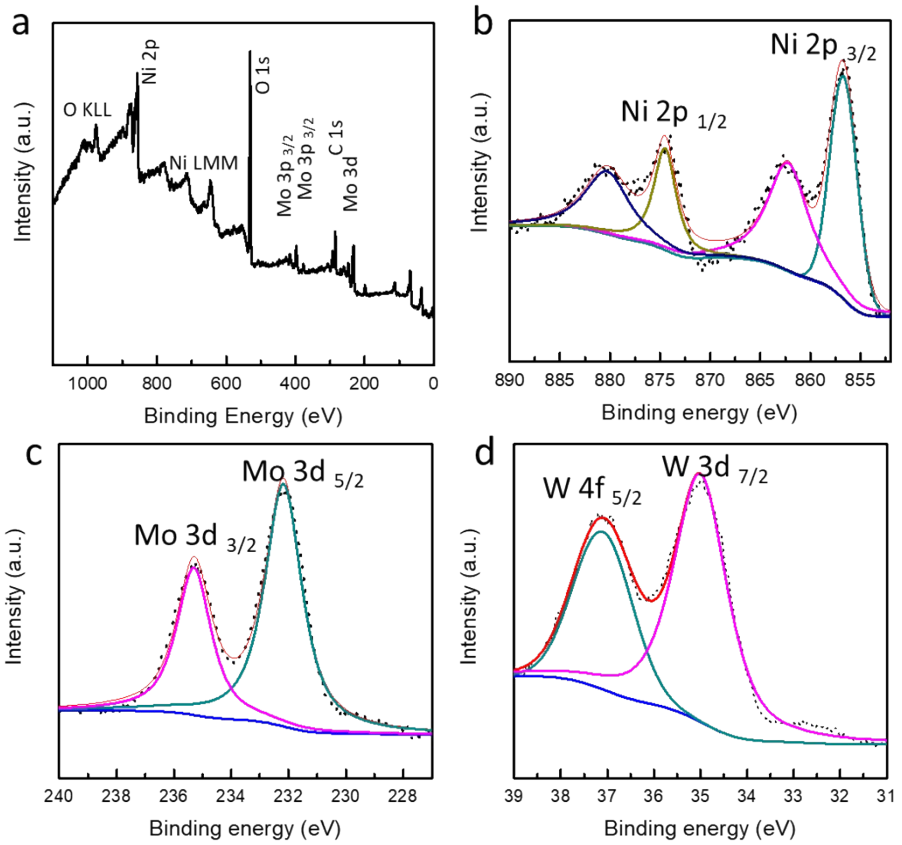

Fig. S5. XPS analysis of survey scan (a), Ni 2p (b), Mo 3d (c) and W 2f (d) spectra in the obtained Ni-W-O/NiMoO4-2 heterostructure.

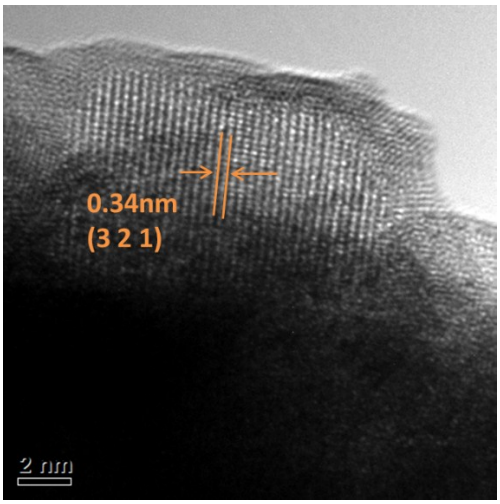

Fig. S6. HRTEM image of the microcubes of Ni-W-O/$NiMoO_4$-2 heterostructures.

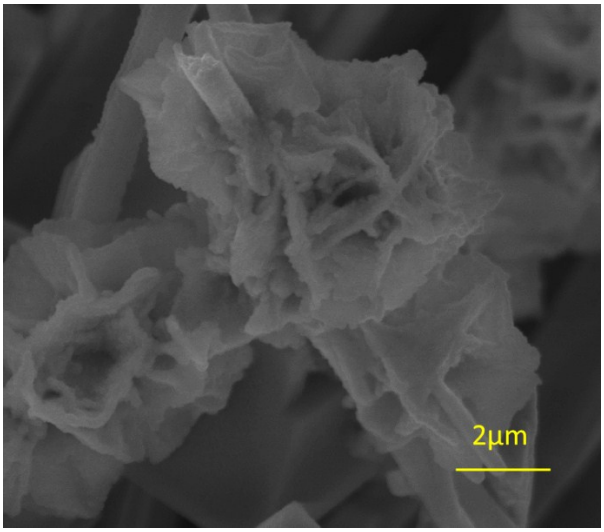

Fig. S7. The morphology of Ni-W-O/$NiMoO_4$-1.5 heterostructure with the moderate concentration (0.05 mol/L) of precursor.

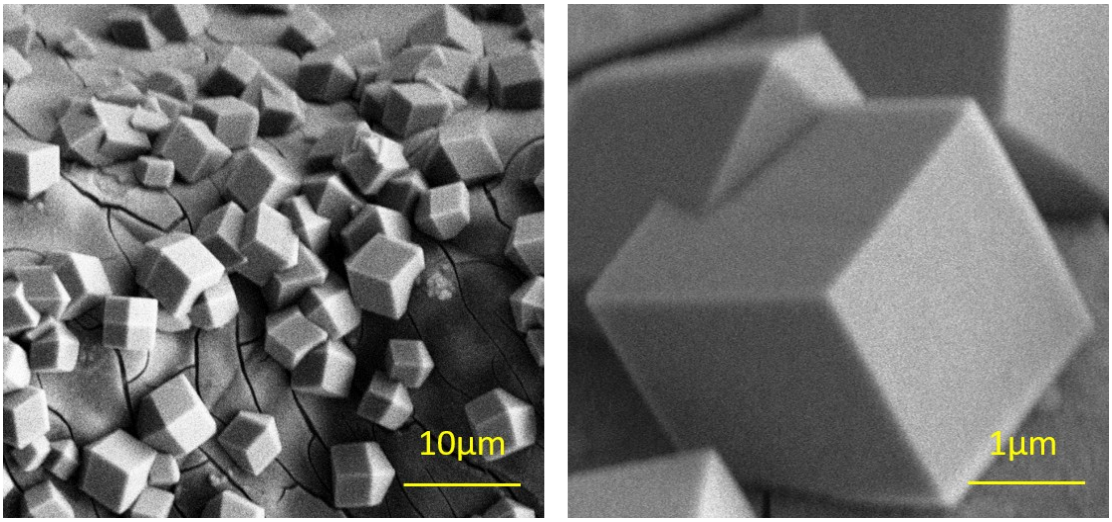

Fig. S8. The morphology of pure Ni-W-O microcubes on Ni foam.

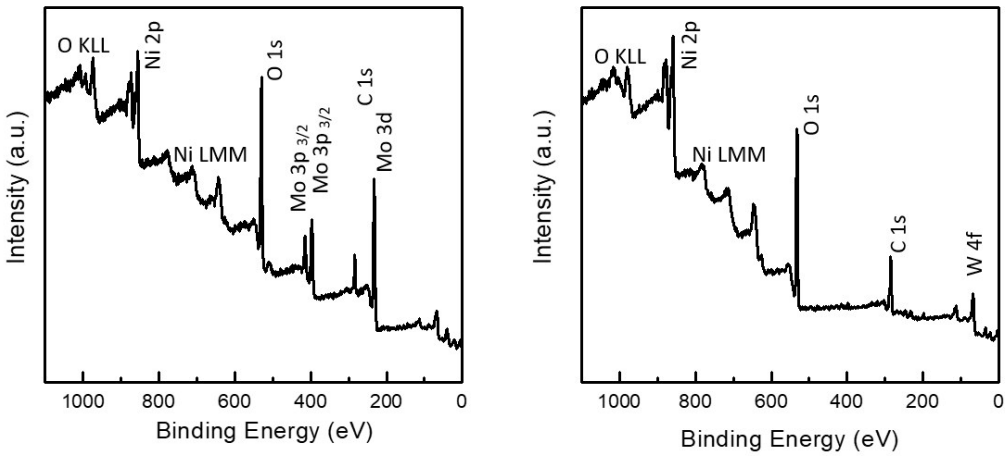

Fig. S9. XPS survey of the pure $NiMoO_4$ rods and the pure Ni-W-O microcubes.

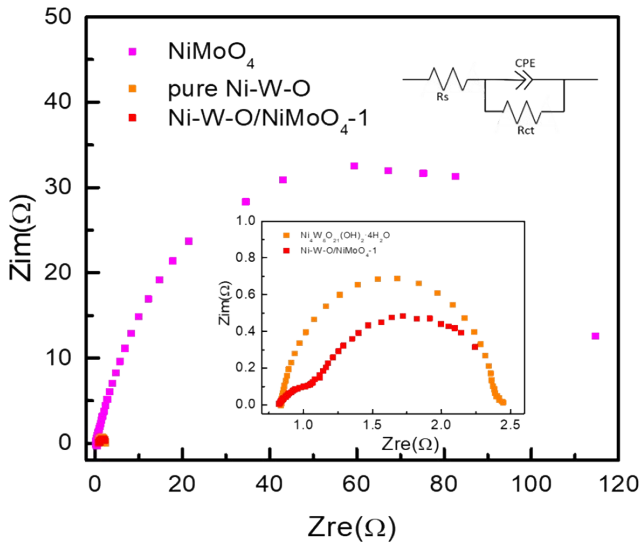

Fig. S10. Nyquist plots of $NiMoO_4$ rods, pure Ni-W-O microcubes and Ni-W-O/$NiMoO_4$-1 electrodes tested in N_2 saturated KOH electrolyte for HER.

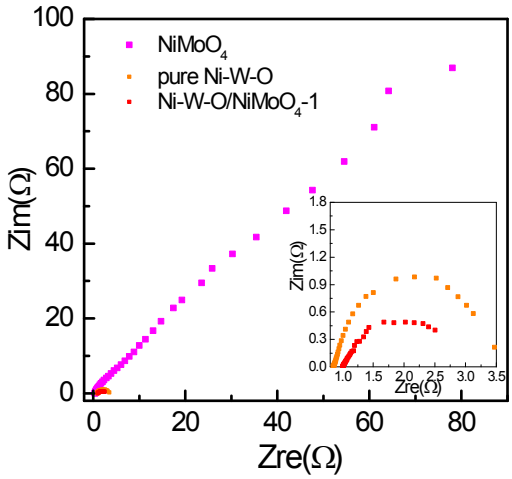

Fig. S11. Nyquist plots of $NiMoO_4$ rods, $Ni_4W_6O_{21}(OH)_2 \cdot 4H_2O$ microcubes and Ni-W-O/$NiMoO_4$-1 electrodes tested in O_2 saturated KOH electrolyte for OER.

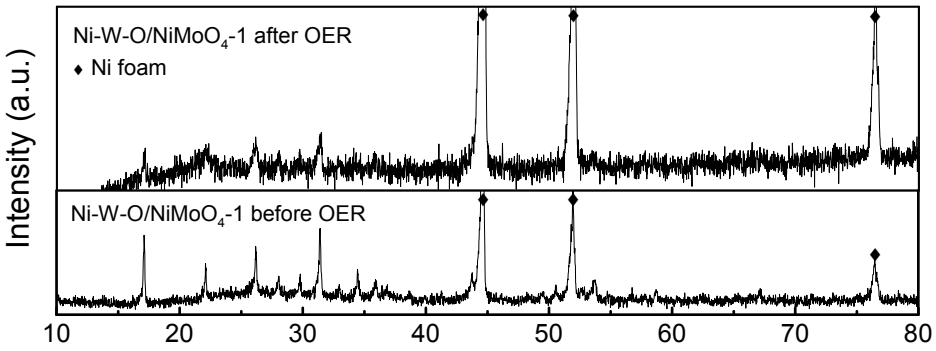

Fig. S12. The XRD patterns of Ni-W-O/$NiMoO_4$-1 heterostructure before and after long-term (3 days) OER test.

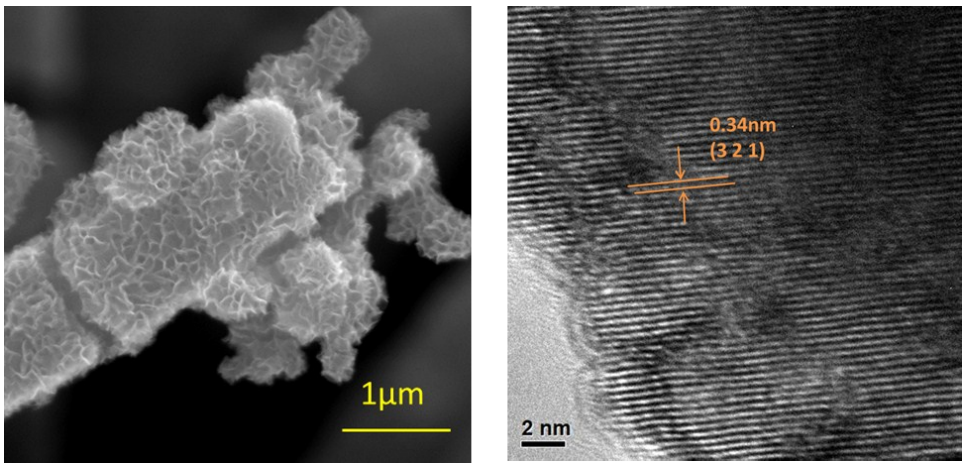

Fig. S13. SEM and HRTEM images of the Ni-W-O/$NiMoO_4$-1 heterostructure after long-term (3 days) OER test.

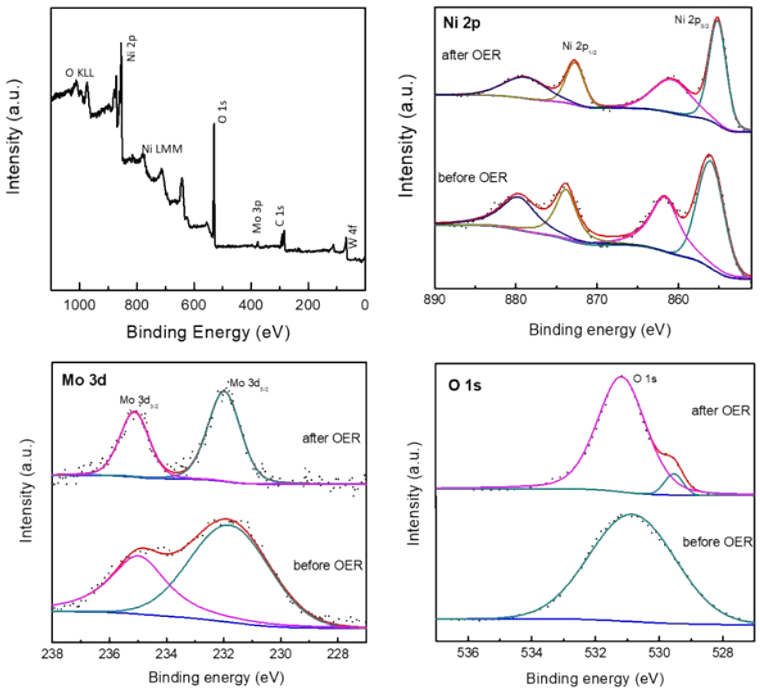

Fig. S14. XPS analysis of survey scan (a), Ni 2p (b), Mo 3d (c) and O 1s (d) spectra in the Ni-W-O/NiMoO4-1 after long-term (3 days) OER test.

Table S1. Comparison of HER performances for various electrocatalysts in 1.0 M KOH.

Catalyst	Electrolyte	η_{10} (mV) (V *vs* RHE)	Tafel slope (mA dec^{-1})	Ref.
Ni-W-O/$NiMoO_4$-1	**1 M KOH**	**52**	**80**	**This work**
$NiCo_2O_4$	1 M KOH	110	49.7	1
Ni-Co-P-300	1 M KOH	150	60.1	2
Ni_2P/Ni/NF	1 M KOH	98	72	3
Ni/NiP	1 M KOH	130	58.5	4
$NiCo_2S_4$ NW/NF	1 M KOH	210	58.9	5
MoP/Ni_2P/NF	1 M KOH	75	100.2	6
Co_4Ni_1P NTs	1 M KOH	129	52	7
S-$NiFe_2O_4$/NF	1 M KOH	138	61.3	8
NiCoP	1 M KOH	62	68.2	9
Co_4Mo_2@NC	1 M KOH	218	73.5	10
NiFe-LDH /$NiCo_2O_4$/NF	1 M KOH	192	59	11
nickel sulfides	1 M KOH	148	79	12
Cu@NiFe LDH	1 M KOH	116	58.9	13
Ni/Mo_2C-PC	1 M KOH	179	101	14
NiFe LDH-NS@DG10	1 M KOH	300	110	15

Table S2. Comparison of OER performances for various electrocatalysts in 1.0 M KOH.

Catalyst	Electrolyte	η (mV) (V *vs* RHE)	Tafel slope (mA dec^{-1})	Ref.
Ni-W-O/$NiMoO_4$-1	**1 $_M$ KOH**	**253(η_{30})**	**92**	**This work**
Ni_3Se_2-Au@Glass	1 $_M$ KOH	320(η_{10})	97.1	16
Ni_3Se_2-Ni foam	1 $_M$ KOH	270(η_{10})	142.8	16
$NiCo_2O_4$	1 $_M$ KOH	340(η_{10})	75	17
porous MoS_2	1 $_M$ KOH	260(η_{10})	54	18
Ni/NiP	1 $_M$ KOH	270(η_{30})	73.2	4
$NiCo_2S_4$ NW/NF	1 $_M$ KOH	260(η_{10})	40.1	5
MoP/Ni_2P/NF	1 $_M$ KOH	300(η_{20})	77.6	6
S-$NiFe_2O_4$/NF	1 $_M$ KOH	267(η_{10})	36.7	8
Co_4Mo_2@NC	1 $_M$ KOH	330(η_{10})	48.7	10
NiFe-LDH /$NiCo_2O_4$/NF	1 $_M$ KOH	290(η_{50})	53	11
nickel sulfides	1 $_M$ KOH	320(η_{10})	59	12
Ni/Mo_2C-PC	1 $_M$ KOH	368(η_{10})	-	19

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