Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Hierarchical MoP/NiFeP Hybrid Hollow Spheres as Highly Efficient Bifunctional Electrocatalysts for Overall Water Splitting

*Lifeng Lin, Min Chen and Limin Wu**

Department of Materials Science and State Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, China

Calculation of TOF

The values of turnover frequency (TOF) was calculated assuming that all Mo, Ni and Fe ions in the catalysts were active and contributed to the catalytic reaction, since the exact number of active sites was not known (the lowest TOF values)

$$\mathrm{TOF} = j\mathrm{S}/(\alpha \mathrm{F} n)$$

Here, j (A/cm^2) is the measured current density at certain overpotential; S (GCE area, 0.196 cm^2) is the surface area of GCE; α is the number of electrons transferring in HER or OER; F is Faraday constant (96485.3 C mol^{-1}), and n is the metal ions molar number calculated from ICP results of the as-prepared catalysts (Table S1). Herein, the TOF was undervalued when all metal atoms were used to calculate it.

Calculation of Faradic efficiency

The Faradic efficiency was calculated by the equation as follows

$$\text{Faradic efficiency} = nFm/Q$$

Here, n = 2 and 4 for HER and OER respectively, F is Faraday constant (96485.3 C mol^{-1}), m is moles of gas evolved, Q (C) is the total amount of charge passed through the cell.

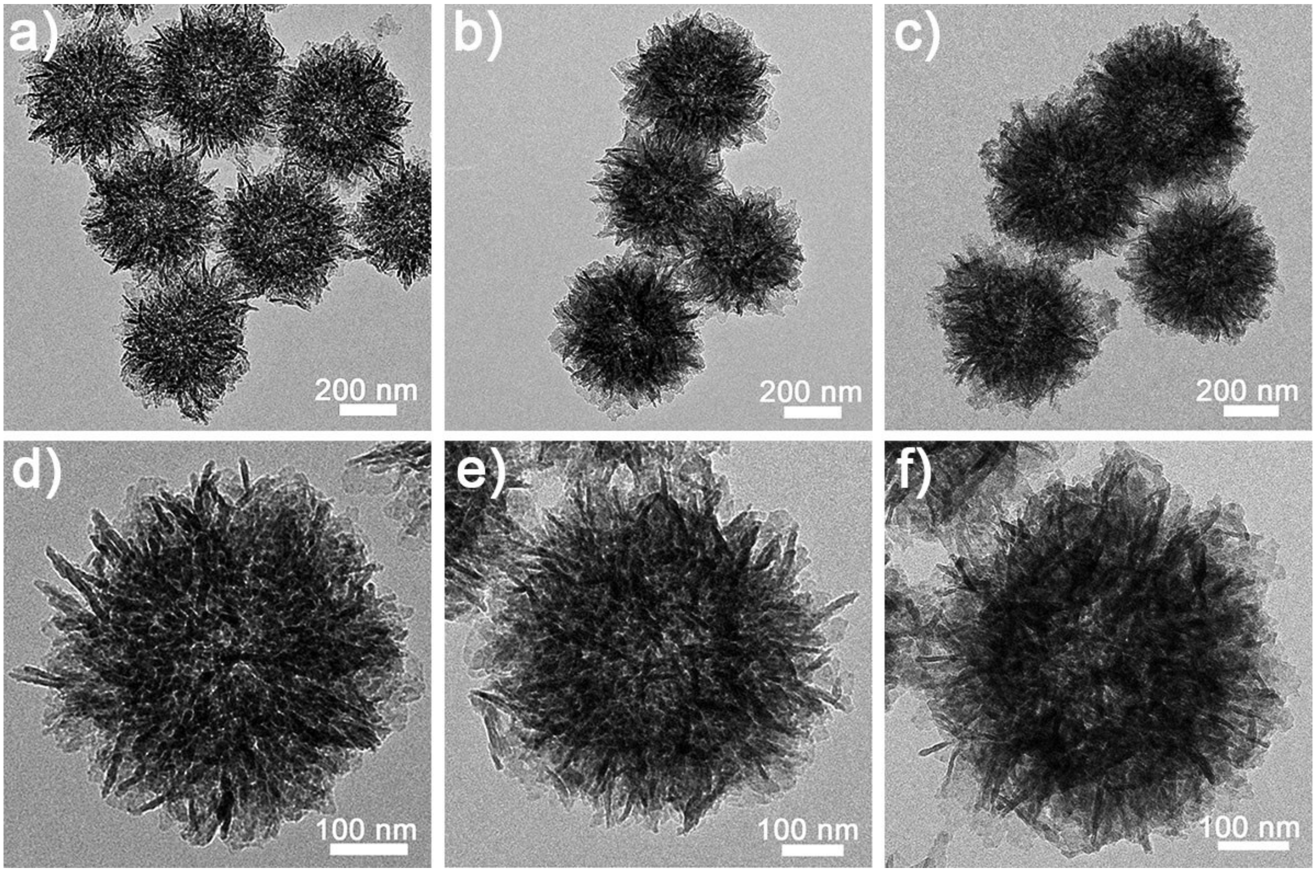

Figure S1. TEM images of (a and d) Mo-PDA HSs, (b and e) Mo-PDA/NiFe-PBA-1 HSs, (c and f) Mo-PDA/NiFe-PBA-2 HSs.

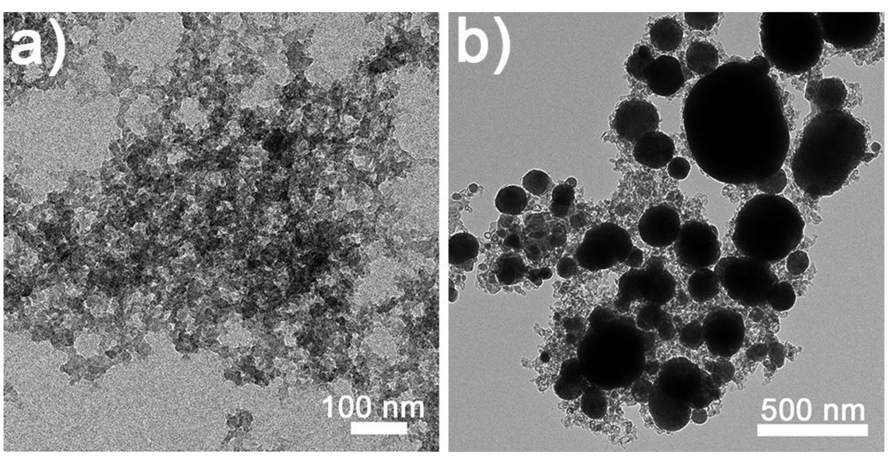

Figure S2. TEM images of (a) NiFe-PBA NPs and (b) NiFeP NPs.

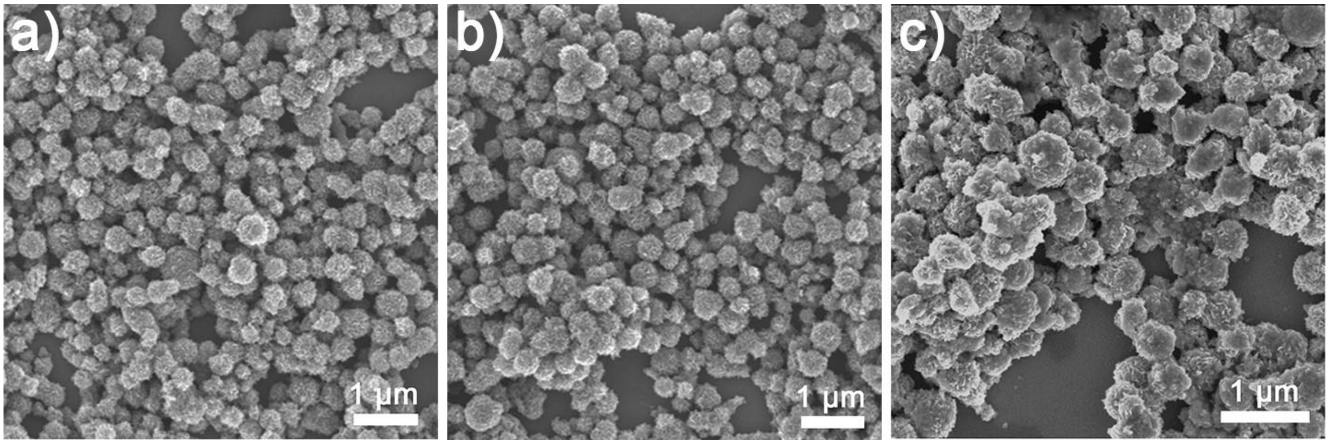

Figure S3. SEM images of (a) MoP HSs, (b) MoP/NiFeP-1 HSs and (c) MoP/NiFeP-2 HSs.

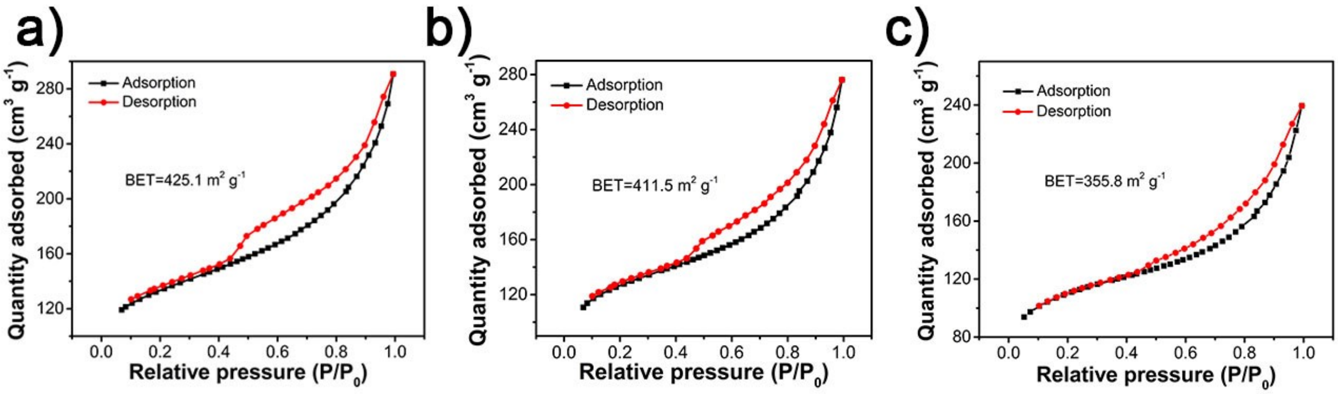

Figure S4. N_2 sorption isotherms of (a) MoP HSs, (b) MoP/NiFeP-1 HSs and (c) MoP/NiFeP-2 HSs.

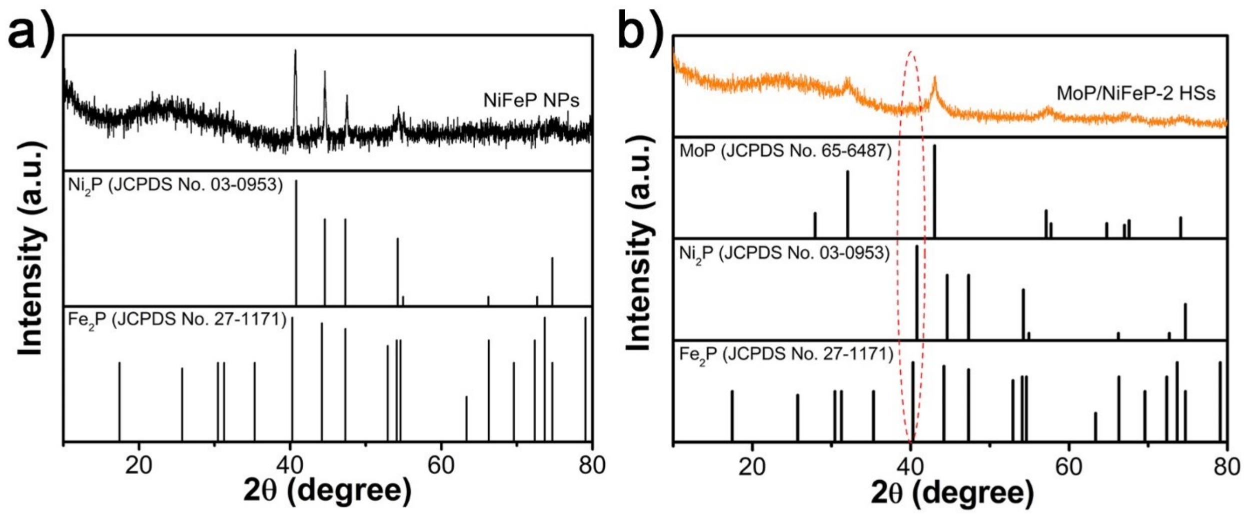

Figure S5. XRD patterns of (a) NiFeP NPs and (b) MoP/NiFeP-2 HSs.

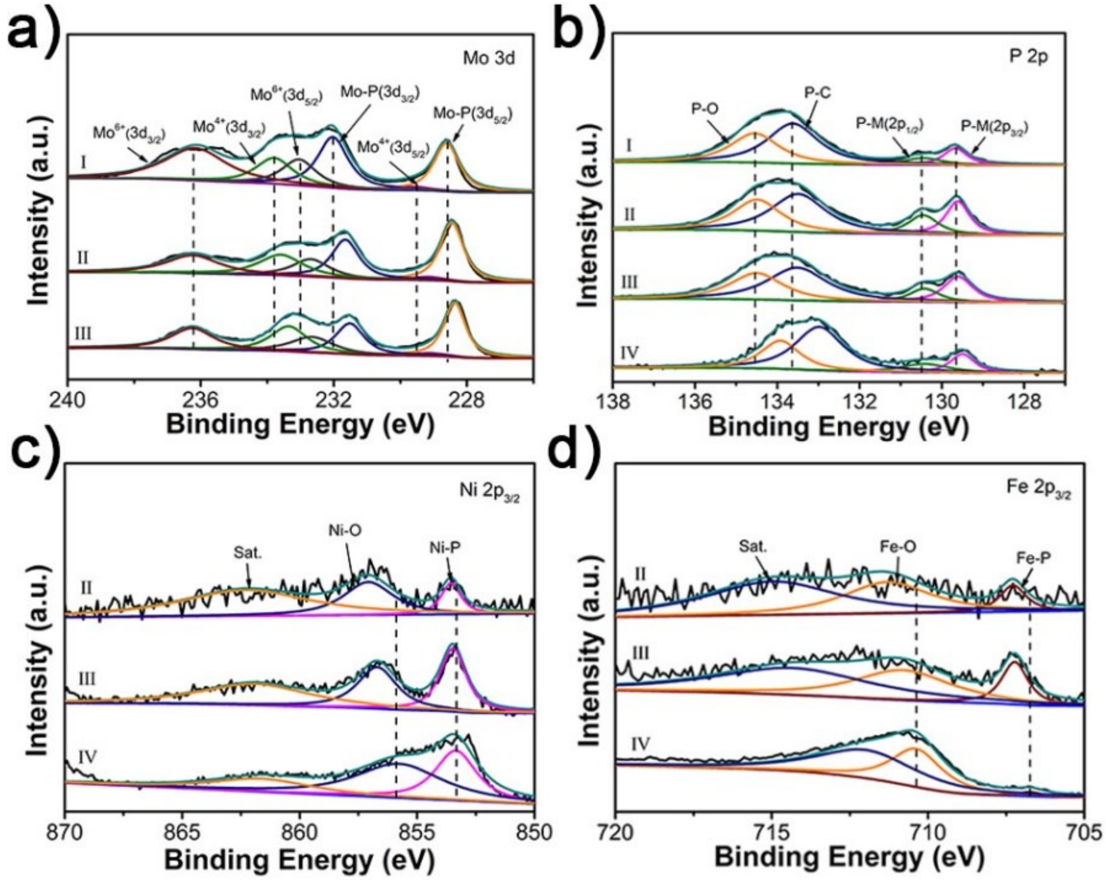

Figure S6. High resolution XPS spectra of (a) Mo 3d, (b) P 2p, (c) Ni $2p_{3/2}$ and (d) Fe $2p_{3/2}$ of (I) MoP HSs, (II) MoP/NiFeP-1 HSs, (III) MoP/NiFeP-2 HSs and (IV) NiFeP NPs.

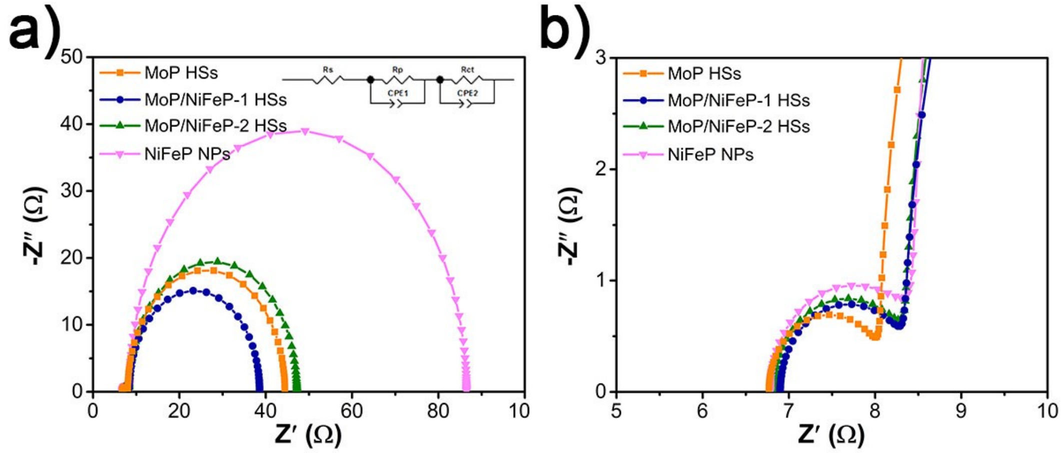

Figure S7. (a) Nyquist plots (at η=150 mV, -0.15 V *vs.* RHE) of MoP HSs, MoP/NiFeP-1 HSs, MoP/NiFeP-2 HSs and NiFeP NPs as HER electrocatalysts obtained in 1 M KOH and (b) the corresponding zoom-in regions. R_s, R_p, R_{ct}, CPE1, and CPE2 represent the solution resistance, electrode texture and charge transfer resistances, and constant phase elements, respectively.

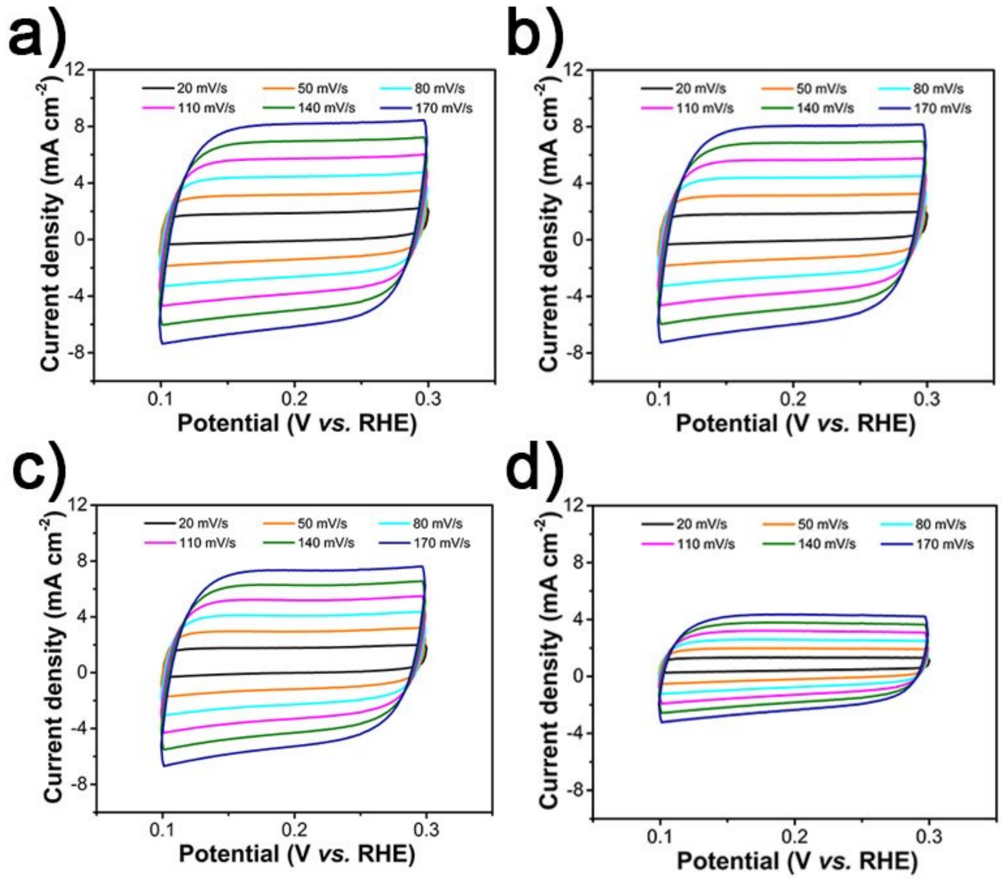

Figure S8. Cyclic voltammograms of (a) MoP HSs, (b) MoP/NiFeP-1 HSs, (c) MoP/NiFeP-2 HSs and (d) NiFeP NPs in 1 M KOH as HER catalysts.

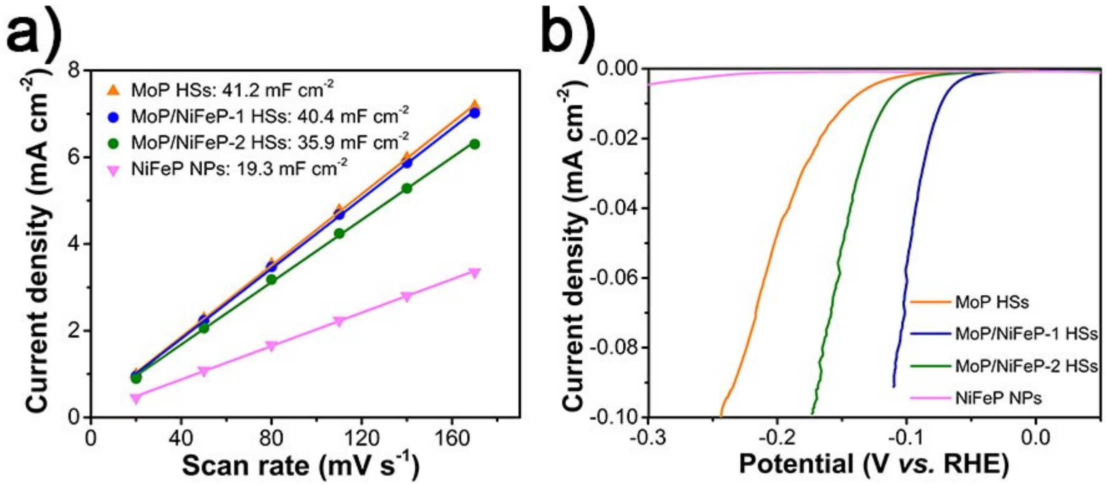

Figure S9. (a) Capacitive current at 0.13 V (*vs.* RHE) as a function of scan rate obtained in 1 M KOH and (b) normalized polarization curves by ECSA of the electrocatalysts.

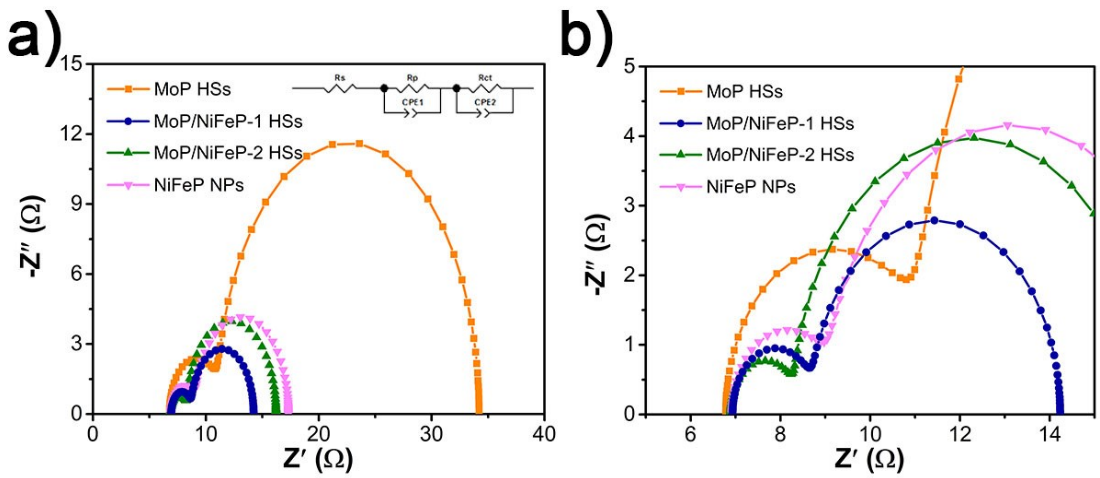

Figure S10. (a) Nyquist plots (at η=300 mV, 1.53 V *vs.* RHE) of MoP HSs, MoP/NiFeP-1 HSs, MoP/NiFeP-2 HSs and NiFeP NPs as OER electrocatalysts obtained in 1 M KOH and (b) the corresponding zoom-in regions. R_s, R_p, R_{ct}, CPE1, and CPE2 represent the solution resistance, electrode texture and charge transfer resistances, and constant phase elements, respectively.

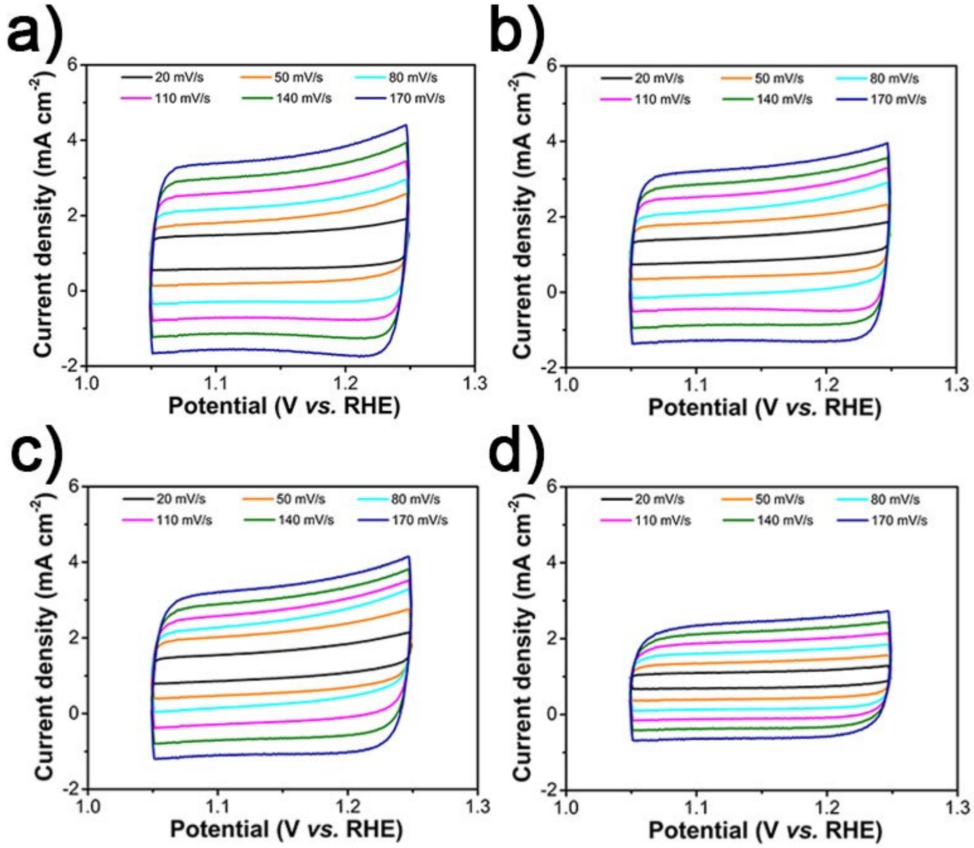

Figure S11. Cyclic voltammograms of (a) MoP HSs, (b) MoP/NiFeP-1 HSs, (c) MoP/NiFeP-2 HSs and (d) NiFeP NPs in 1 M KOH as OER catalysts.

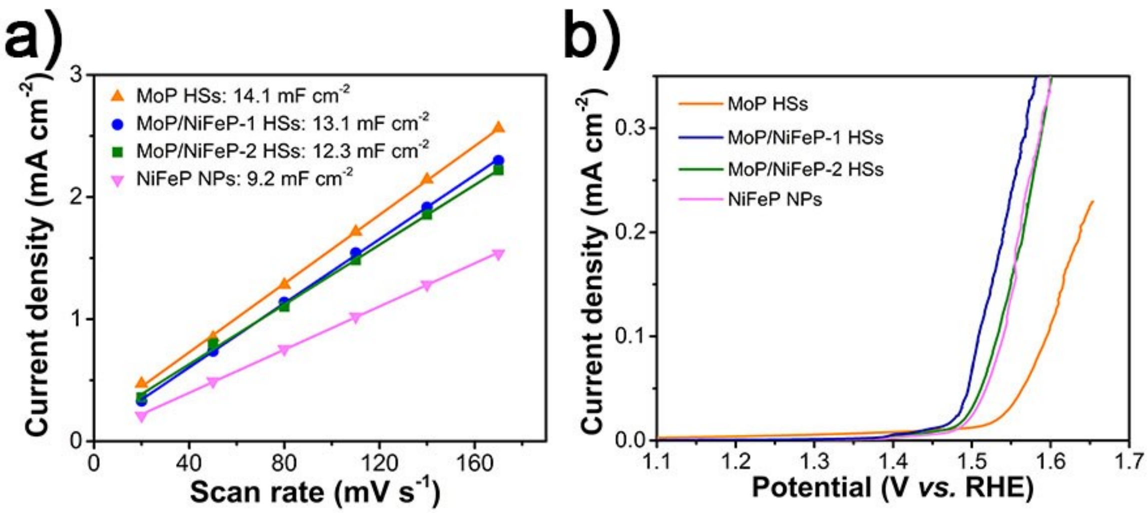

Figure S12. (a) Capacitive current at 1.15 V (*vs.* RHE) as a function of scan rate obtained in 1 M KOH and (b) normalized polarization curves by ECSA of the electrocatalysts.

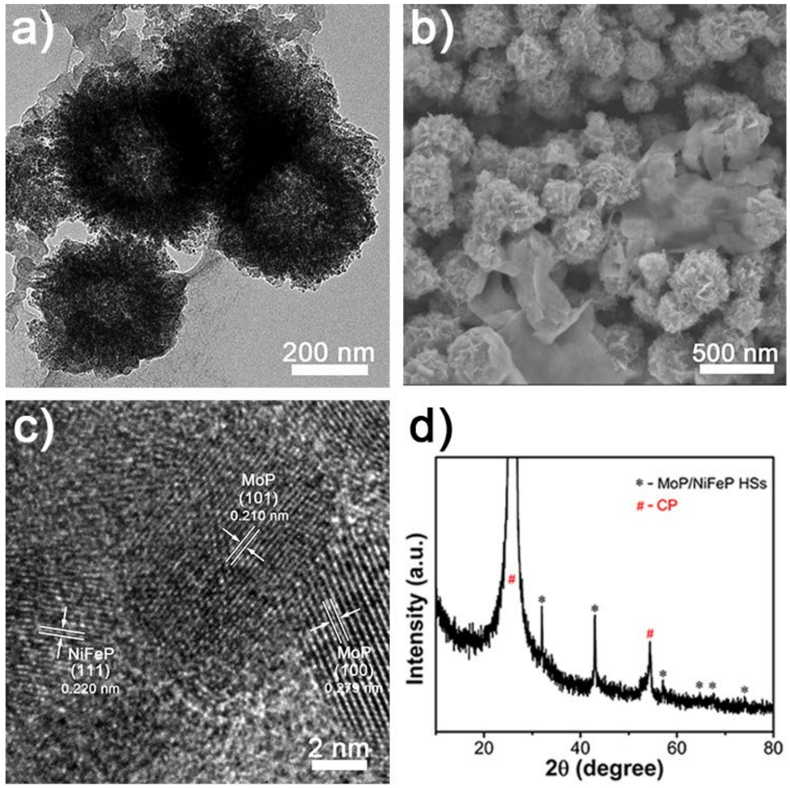

Figure S13. (a) TEM image, (b)FESEM image, (c) HRTEM image and (d) XRD of MoP/NiFeP-1 HSs after long term overall water splitting on the cathode.

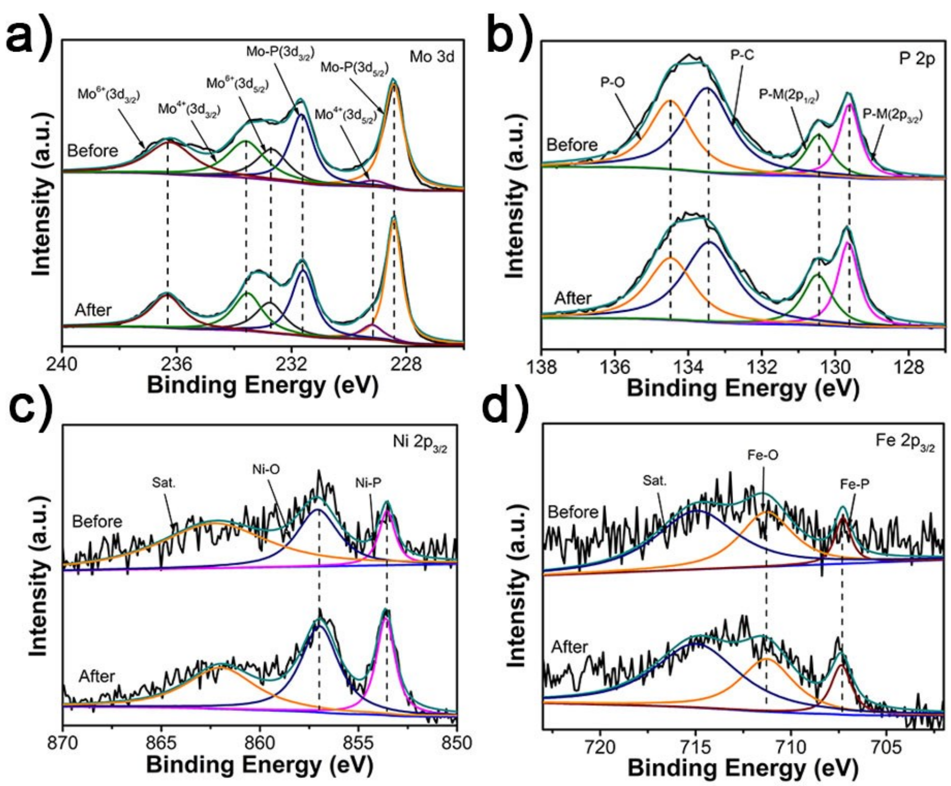

Figure S14. High resolution XPS spectra of (a) Mo 3d, (b) P 2p, (c) Ni $2p_{3/2}$ and (d) Fe $2p_{3/2}$ of MoP/NiFeP-1 HSs after long term overall water splitting on the cathode.

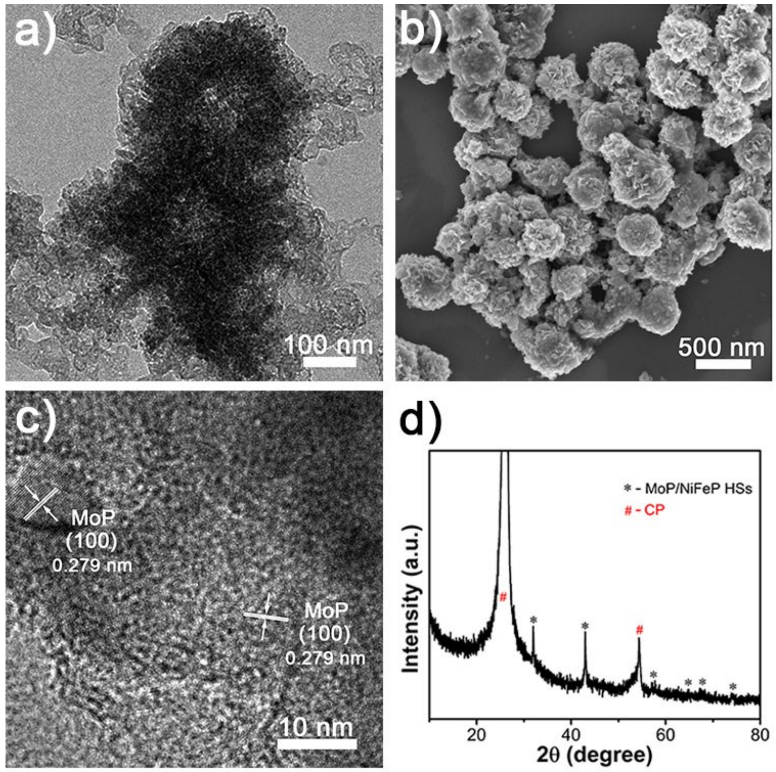

Figure S15. (a) TEM image, (b)FESEM image, (c) HRTEM image and (d) XRD of MoP/NiFeP-1 HSs after long term overall water splitting on the anode.

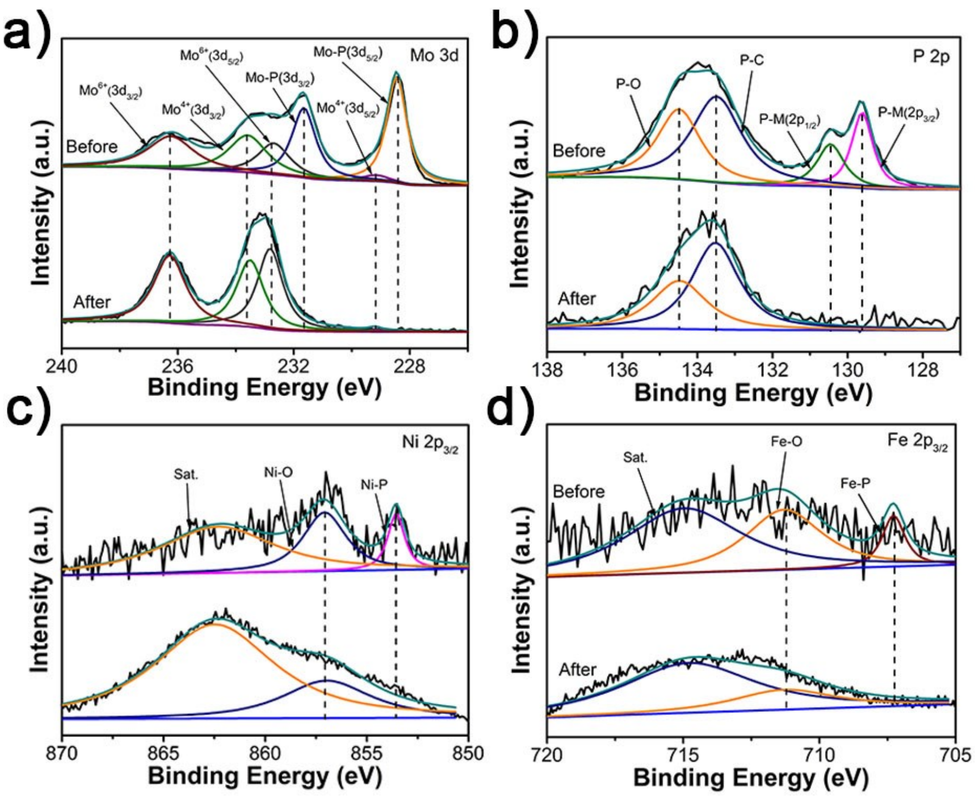

Figure S16. High resolution XPS spectra of (a) Mo 3d, (b) P 2p, (c) Ni $2p_{3/2}$ and (d) Fe $2p_{3/2}$ of MoP/NiFeP-1 HSs after long term overall water splitting on the anode.

Table S1. Summary of the actual metal molar ratios of the as-prepared catalysts analyzed by ICP-OES.

Sample	Mo (%)	Ni (%)	Fe (%)
MoP HSs	100	0	0
MoP/NiFeP-1 HSs	90.6	4.9	4.5
MoP/NiFeP-2 HSs	71.2	15.1	13.7
NiFeP NPs	0	51.2	48.8

Table S2. HER performances of MoP/NiFeP-1 HSs and the recently reported electrocatalysts in 1 M KOH.

Catalyst	η_{10} (mV)	Loading (mg cm^{-2})	Substrate	References
MoP/NiFeP-1 HSs	**73**	**0.2**	**GCE**	**This work**
$Co_{0.31}Mo_{1.69}C$/MXene/NC	75	0.2	GCE	*Adv. Energy Mater.* **2019**, 9, 1901333
CoP/NiCoP	75	0.318	GCE	*Adv. Funct. Mater.* **2019**, 29, 1807976
S-MoP NPL	104	-	Mo foil	*ACS Catal.* **2019**, 9, 651
Co-O-1T-MoS_2/SWNT	113	-	GCE	*ACS Nano* **2019**, 13, 11733
NiFeP/SG	115	-	GCE	*Nano Energy* **2019**, 58, 870
MoC-Mo_2C/PNCDs	121	0.4	CFP	*Adv. Mater.* **2019**, 31, 1900699
Ni/Mo_2C-NCNFs	143	1.40	GCE	*Adv. Energy Mater.* **2019**, 9, 1803185
MoP@NC	149	0.28	GCE	*Appl. Catal. B-Environ.* **2020**, 263, 118358
MoP/NC	170	0.56	GCE	*Appl. Catal. B-Environ.* **2019**, 245, 656

Table S3. OER performances of MoP/NiFeP-1 HSs and the recently reported electrocatalysts in 1 M KOH.

Catalyst	η_{10} (mV)	Loading (mg cm^{-2})	Substrate	References
MoP/NiFeP-1 HSs	**256**	**0.2**	**GCE**	**This work**
Co_4N-$VN_{1-x}O_x$	263	~2	Carbon cloth	*Appl. Catal. B-Environ.* **2019**, 241, 521
Ni-MOF@Fe-MOF	265	0.2	GCE	*Adv. Funct. Mater.* **2018**, 28, 1801554
(Ni, Fe)S_2@MoS_2	270	-	Carbon paper	*Appl. Catal. B-Environ.* **2019**, 247, 107
Ni/Mo_2C-NCNFs	288	1.40	GCE	*Adv. Energy Mater.* **2019**, 9, 1803185
$NiCo_2O_4$@MoS_2	305	-	Carbon paper	*Chem. Mater.* **2019**, 31, 7590
NG-NiFe@MoC_2	320	0.2	GCE	*Nano Energy* **2018**, 50, 212
Co-NC@Mo_2C	347	0.83	GCE	*Nano Energy*, **2019**, 57, 746
Co/β-Mo_2C@N-CNTs	356	-	GCE	*Angew. Chem. Int. Ed.* **2019**, 58, 4923
MoS_2-NiS_2/NGF	370	-	Graphene foam	*Appl. Catal. B-Environ.* **2019**, 254, 15

Table S4. Overall water splitting performances of MoP/NiFeP-1 HSs and the recently reported electrocatalysts.

Catalyst	Cell Voltage (V)	Loading (mg cm^{-2})	Substrate	References
MoP/NiFeP-1 HSs	**1.51**	**1.5**	**Carbon paper**	**This work**
Mo-Co_9S_8@C	1.56	-	Nickel foam	*Adv. Energy Mater.* **2020**, 10, 1903137
(Ni, Fe)S_2@MoS_2	1.56	-	Carbon paper	*Appl. Catal. B-Environ.* **2019**, 247, 107
Co_3S_4@MoS_2	1.58	0.6	Carbon paper	*Nano Energy* **2018**, 47, 494
$NiCo_2S_4$	1.58	-	Nickel foam	*Adv. Funct. Mater.* **2019**, 29, 1807031
Ni/Mo_2C-NCNFs	1.64	2	Nickel foam	*Adv. Energy Mater.* **2019**, 9, 1803185
Co_4N-$VN_{1-x}O_x$	1.64	~2	Carbon cloth	*Appl. Catal. B-Environ.* **2019**, 241, 521
$Ni_{0.9}Fe_{0.1}PS_3$@MXene	1.65	2	Nickel foam	*Adv. Energy Mater.* **2018**, 8, 1801127
Co-NC@Mo_2C	1.685	0.83	GCE	*Nano Energy* **2019**, 57, 746

PO-Ni/Ni-N-CNFs	1.69	2.0	Carbon paper	*Nano Energy* **2018**, 51, 286