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Supporting Information

for *Adv. Sci.*, DOI 10.1002/advs.202303682

Charge Self-Regulation of Metallic Heterostructure $Ni_2P@Co_9S_8$ for Alkaline Water Electrolysis with Ultralow Overpotential at Large Current Density

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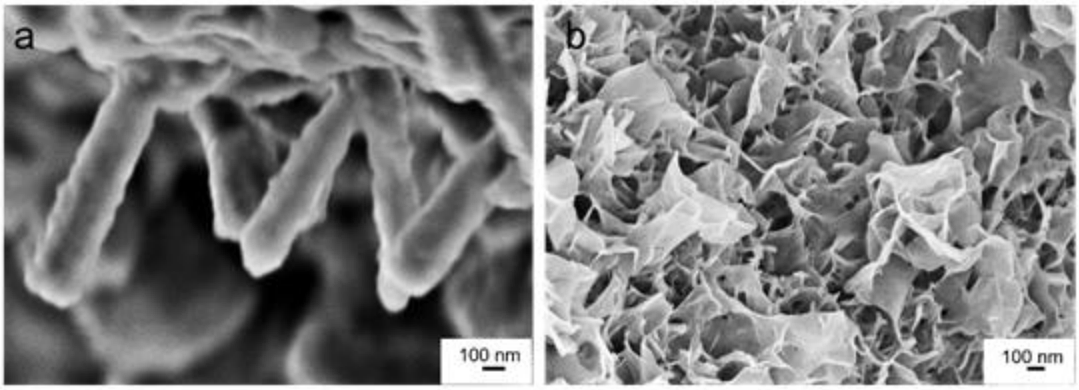

Figure S1 FESEM observation of (a) Ni_2P and (b) Co_9S_8.

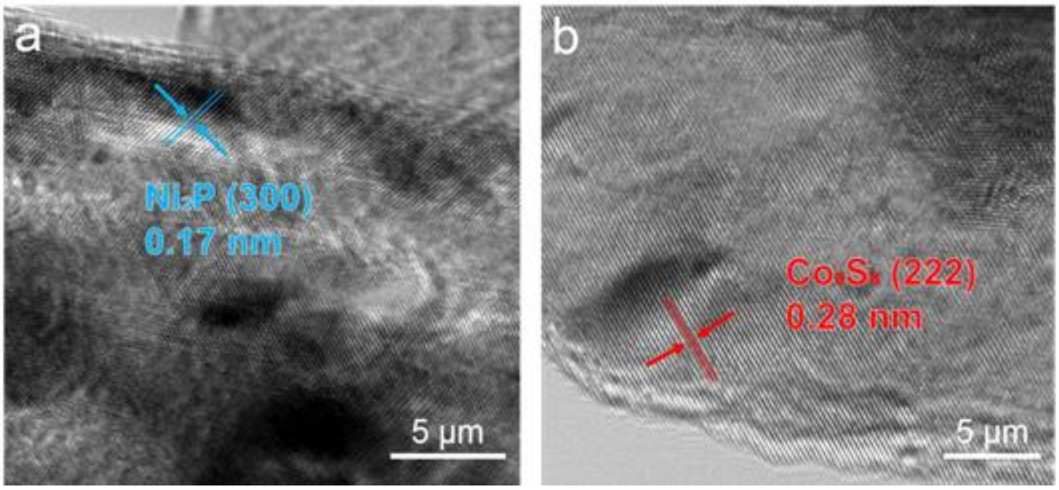

Figure S2 HR-TEM observation of (a) Ni_2P and (b) Co_9S_8.

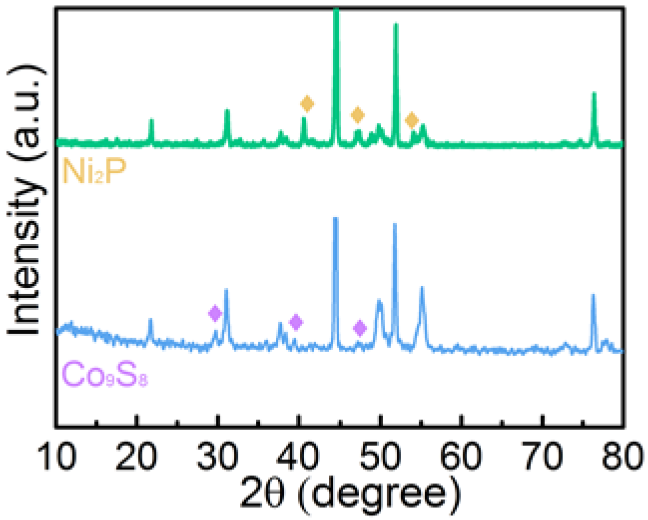

Figure S3 XRD patterns of Ni_2P and Co_9S_8.

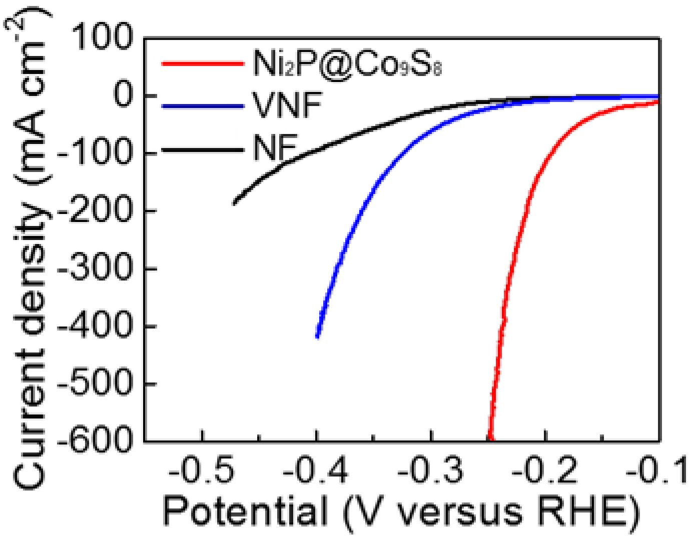

Figure S4 LSV curves of $Ni_2P@Co_9S_8$, VNF and NF for HER.

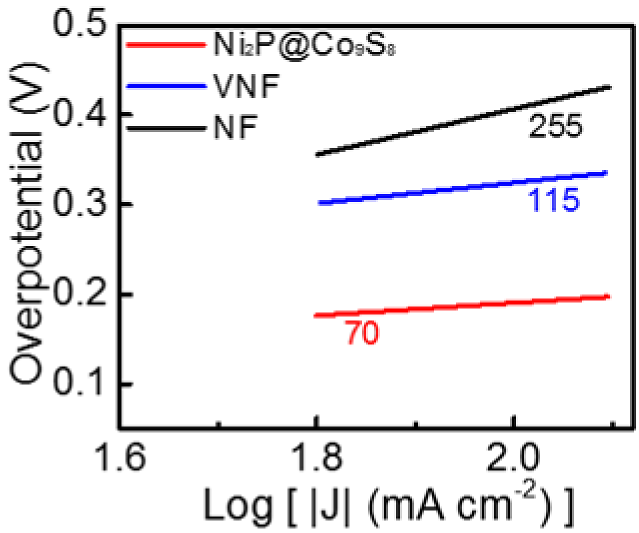

Figure S5 Tafel slopes of $Ni_2P@Co_9S_8$, VNF and NF for HER.

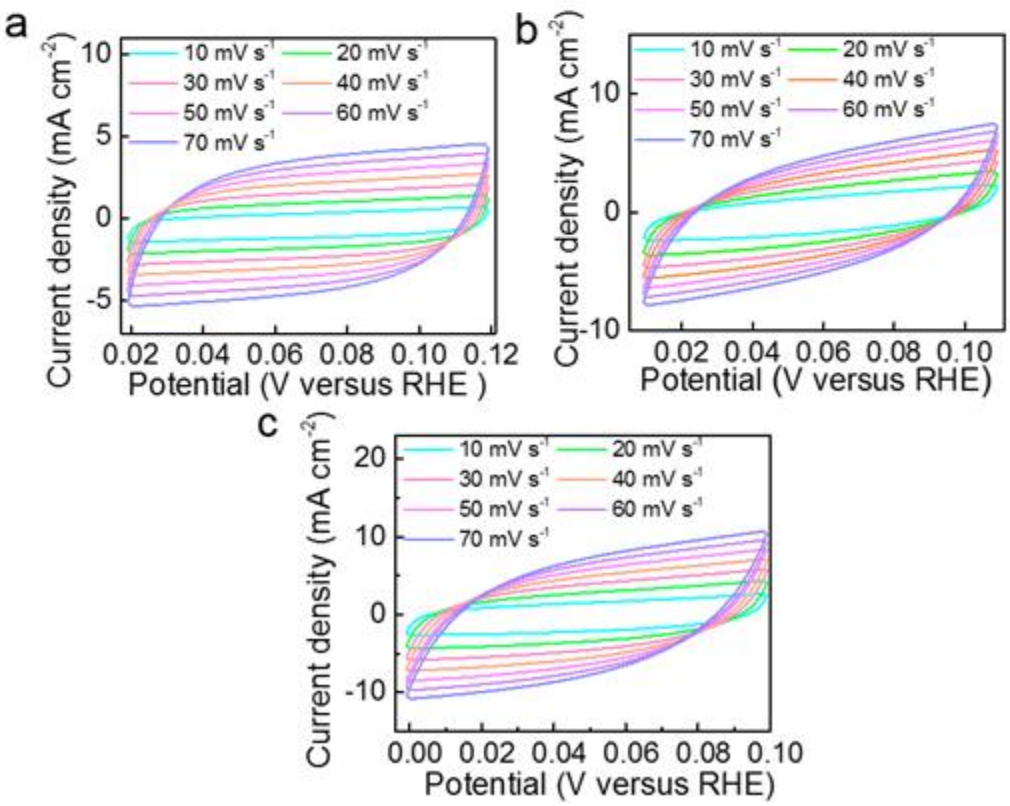

Figure S6 CV curves of (a) Ni_2P, (b) Co_9S_8 and (c) $Ni_2P@Co_9S_8$ for HER.

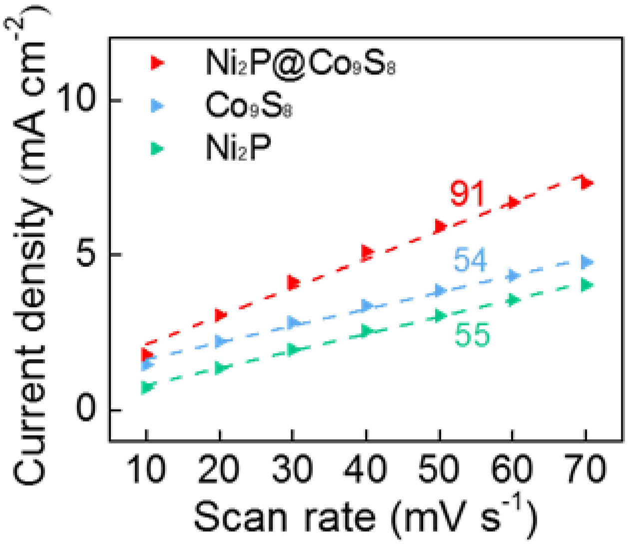

Figure S7 Plots used to evaluate the double-layer capacitances of Ni_2P, Co_9S_8 and $Ni_2P@Co_9S_8$ for HER.

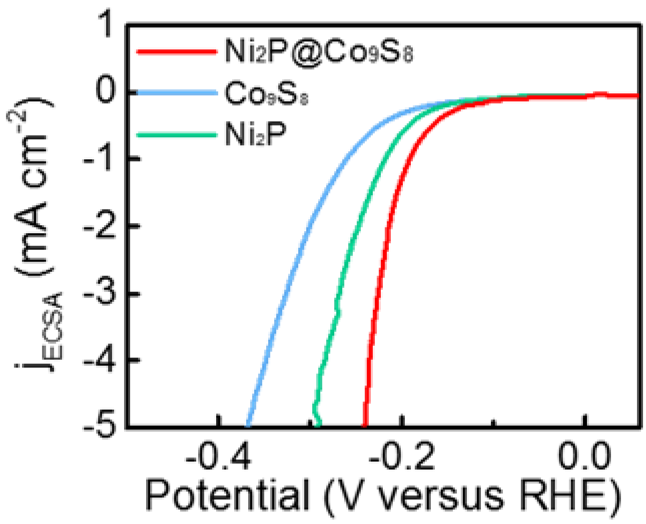

Figure S8 Polarization curves with the current density normalized to ECSA of Ni_2P, Co_9S_8 and $Ni_2P@Co_9S_8$ for HER.

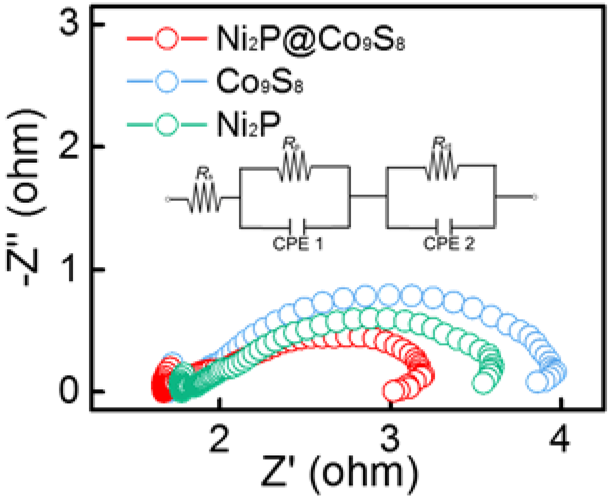

Figure S9 Nyquist plots of Ni_2P, Co_9S_8 and $Ni_2P@Co_9S_8$ for HER.

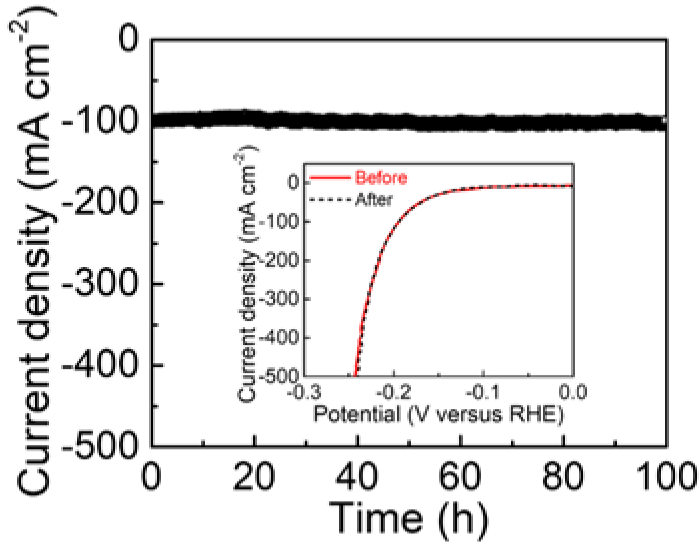

Figure S10 The long-time current density vs time curve (*i-t* curve) of $Ni_2P@Co_9S_8$ at the potential of -0.188 V versus RHE, and the inset shows the polarization data for $Ni_2P@Co_9S_8$ before and after 100 h.

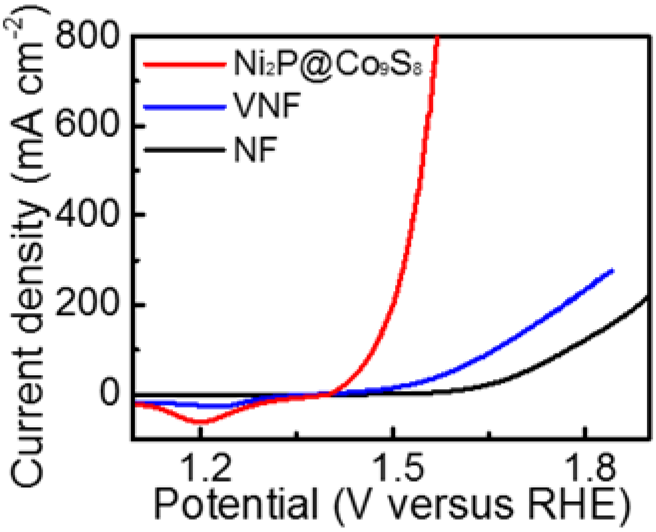

Figure S11 Polarization curves of $Ni_2P@Co_9S_8$, VNF and NF for OER.

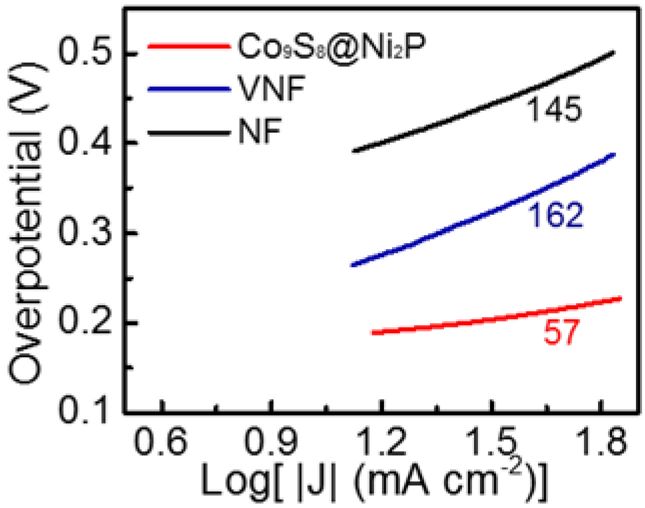

Figure S12 Tafel slopes of $Ni_2P@Co_9S_8$, VNF and NF for OER.

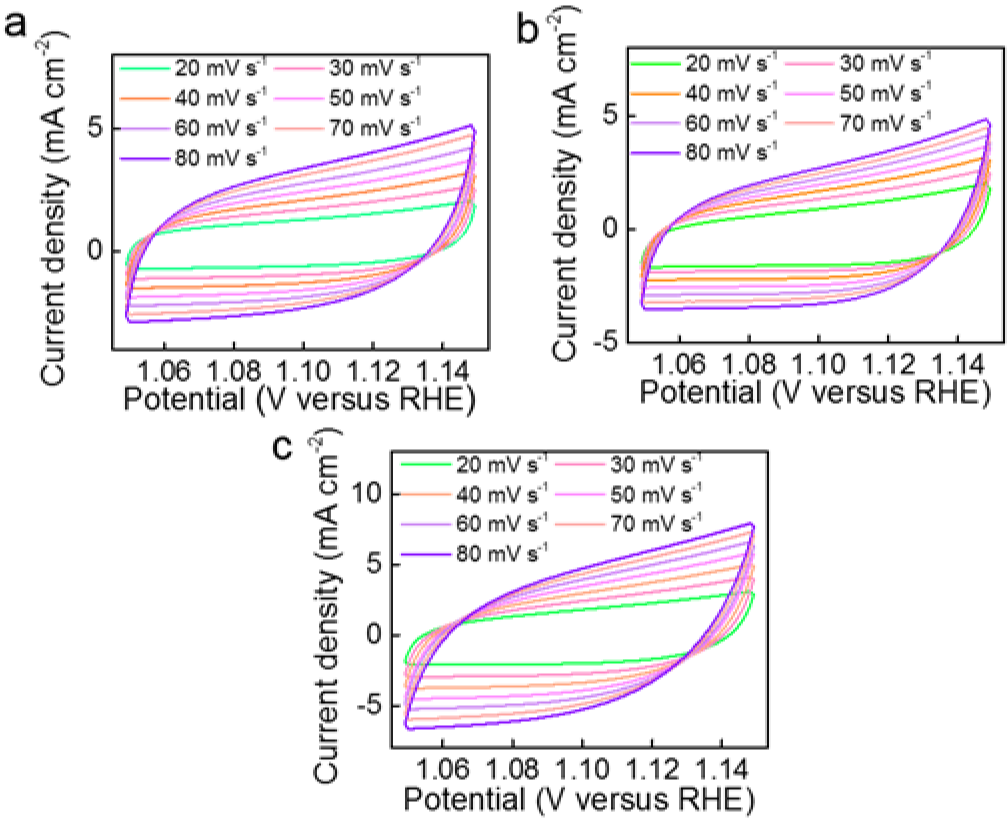

Figure S13 CV curves of (a) Ni_2P, (b) Co_9S_8 and (c) $Ni_2P@Co_9S_8$ for OER.

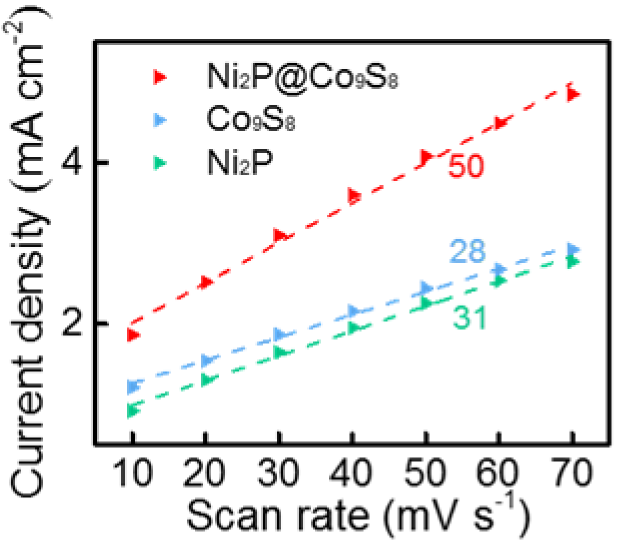

Figure S14 Plots used to evaluate the double-layer capacitances of Ni_2P, Co_9S_8 and $Ni_2P@Co_9S_8$ for OER.

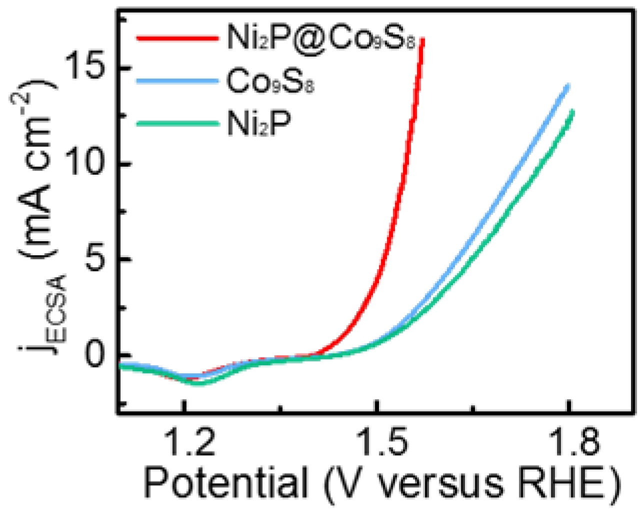

Figure S15 Polarization curves with the current density normalized to ECSA of Ni_2P, Co_9S_8 and $Ni_2P@Co_9S_8$ for OER.

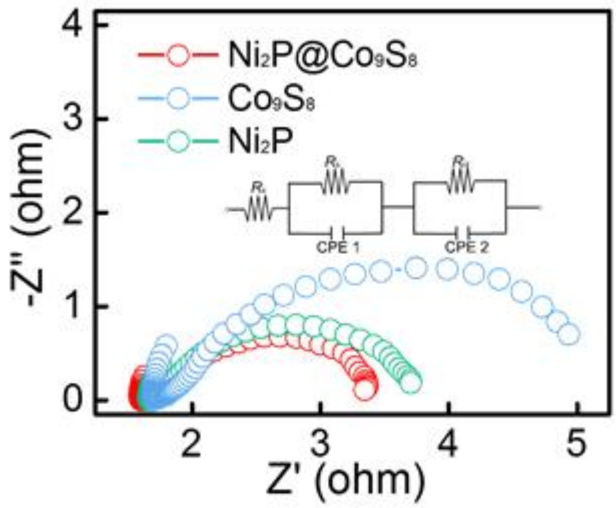

Figure S16 Nyquist plots of Ni_2P, Co_9S_8 and $Ni_2P@Co_9S_8$ for OER.

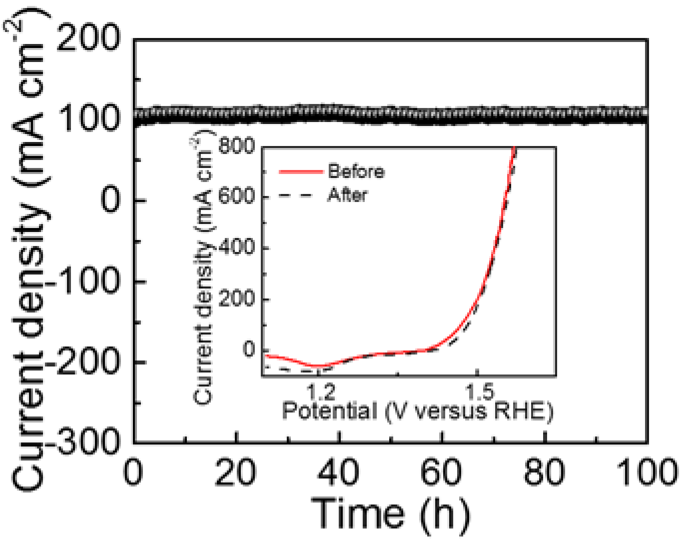

Figure S17 The *i-t* curve of $Ni_2P@Co_9S_8$ at the potential of 1.485 V versus RHE, and the inset shows the polarization data for $Ni_2P@Co_9S_8$ before and after 100 h.

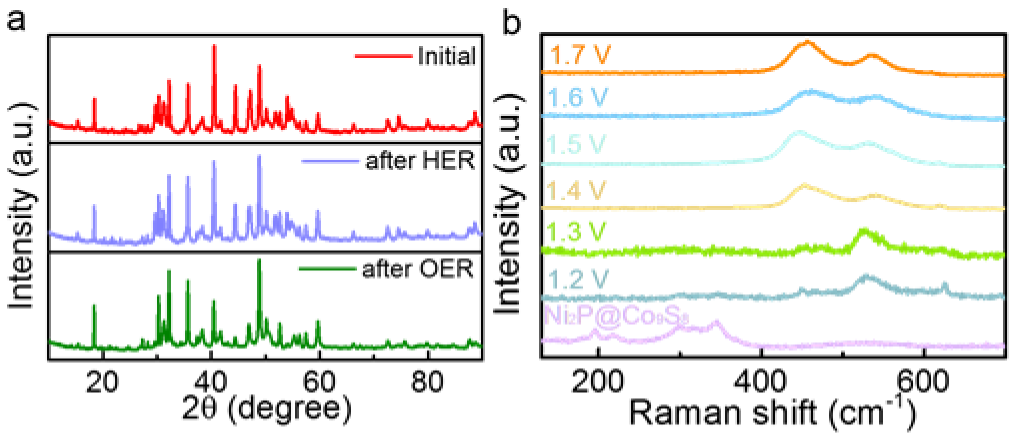

Figure S18 (a) XRD patterns of $Ni_2P@Co_9S_8$ before and after HER and OER reactions; (b) In situ Raman spectra of OER on $Ni_2P@Co_9S_8$ in 1 M KOH.

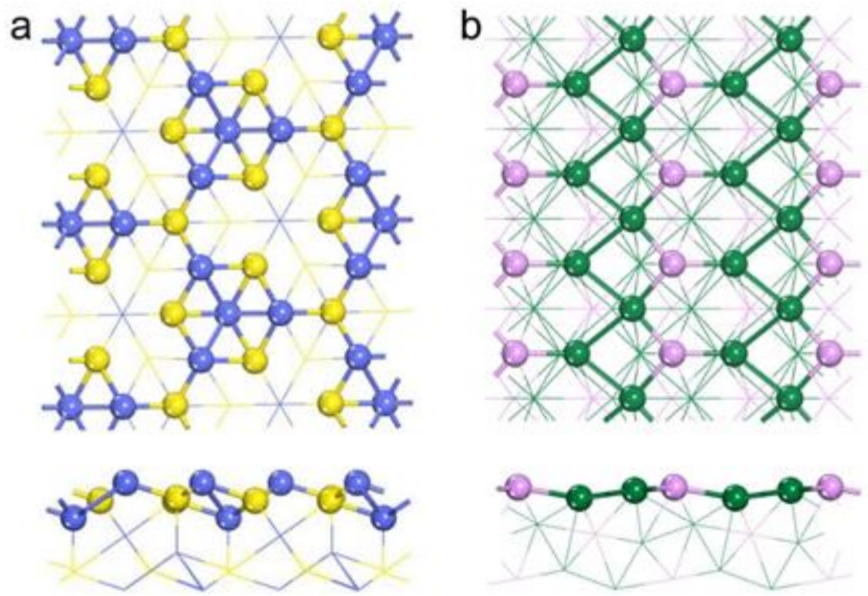

Figure S19 Optimized structures of (a) Co_9S_8(111) and (b) Ni_2P(100). The top layers are displayed in the ball-stick style while others are in the line style.

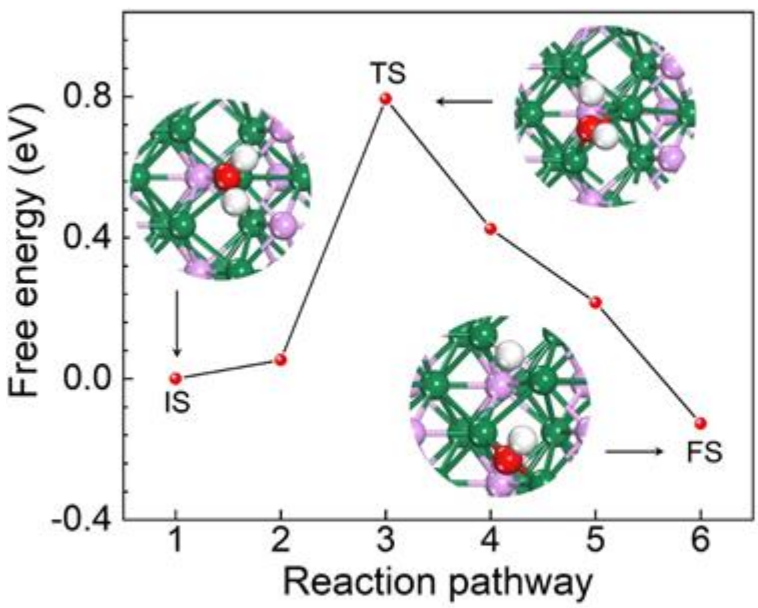

Figure S20 The energy barrier and reaction pathway of water dissociation on Ni_2P, including the corresponding configurations of IS, TS and FS.

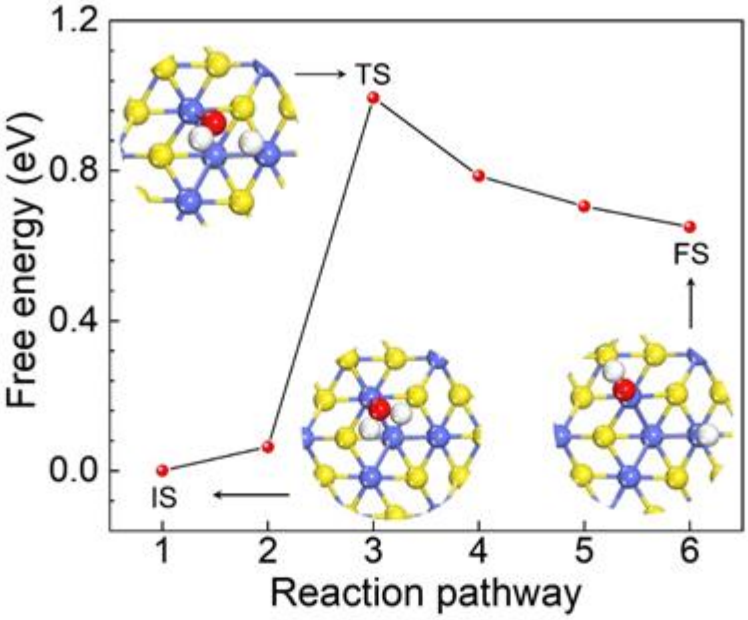

Figure S21 The energy barrier and reaction pathway of water dissociation on Co_9S_8, including the corresponding configurations of IS, TS and FS.

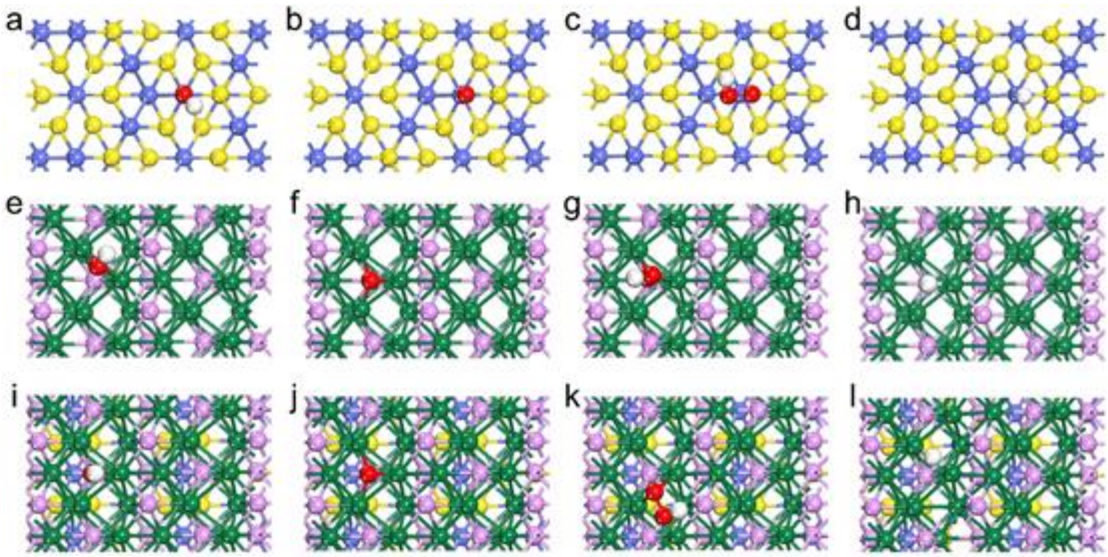

Figure S22 Top views of *OH, *O, *OOH and *H on (a-d) Co_9S_8, (e-h) Ni_2P and (i-l) $Ni_2P@Co_9S_8$.

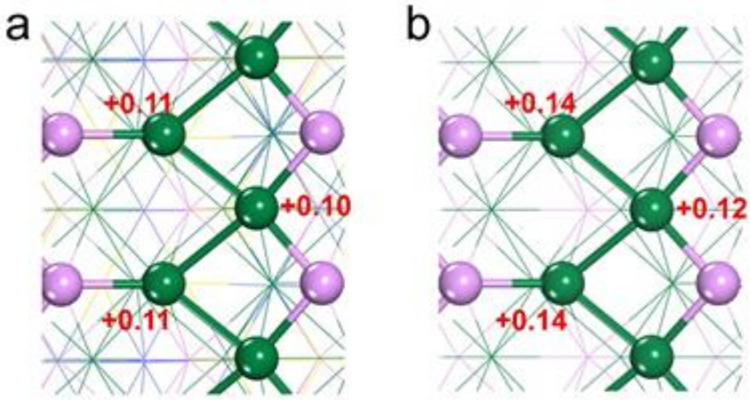

Figure S23 Bader charge analyses of (a) $Ni_2P@Co_9S_8$ and (b) Ni_2P including the Bader charge values of surface active Ni sites.

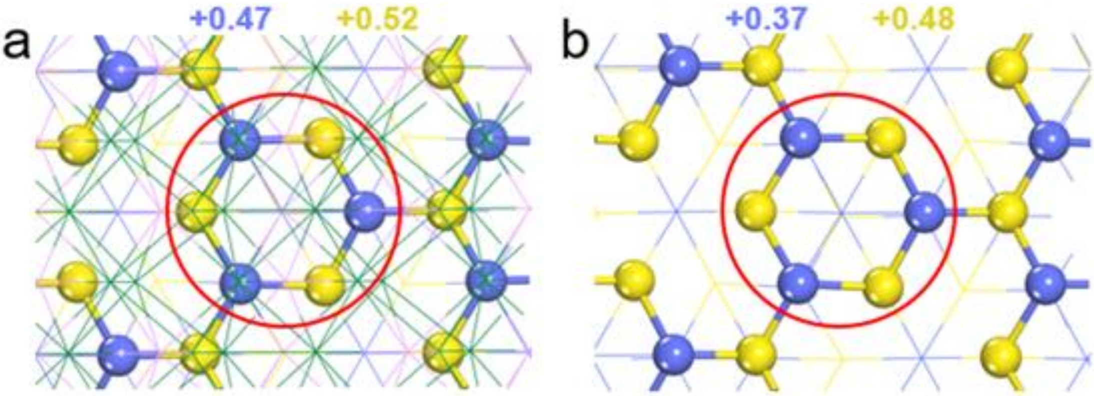

Figure S24 Bader charge analysis of topmost Co and S atoms in (a) $Ni_2P@Co_9S_8$ and (b) Co_9S_8. Target Co and S atoms are shown by red circles, and blue and yellow numbers are the average Bader charge values of three target Co and S atoms, respectively.

Table S1 Calculated double layer capacitance and corresponding RF values (HER).

Catalyst	C_{dl} (mF cm^{-2})	RF
$Ni_2P@Co_9S_8$	91	2275
Co_9S_8	54	1350
Ni_2P	55	1375

Table S2 R_{ct} values of $Ni_2P@Co_9S_8$, Co_9S_8 and Ni_2P for HER.

Catalyst	R_{ct} (Ω)
$Ni_2P@Co_9S_8$	2.79
Co_9S_8	3.52
Ni_2P	3.85

Table S3 Calculated double layer capacitance and corresponding RF values (OER).

Catalyst	C_{dl} (mF cm^{-2})	RF
$Ni_2P@Co_9S_8$	50	1250
Co_9S_8	28	700
Ni_2P	31	775

Table S4 R_{ct} values of $Ni_2P@Co_9S_8$, Co_9S_8 and Ni_2P for OER.

Catalyst	R_{ct} (Ω)
$Ni_2P@Co_9S_8$	2.51
Co_9S_8	3.06
Ni_2P	2.76

Table S5 Comparison of overpotentials at 100 mA cm^{-2} and Tafel slopes of different heterogeneous electrocatalysts recently reported for HER in 1.0 M KOH solution

Catalyst	Tafel (mV dec^{-1})	η (mV) @ 100 mA cm^{-2}	Reference
$Ni_2P@Co_9S_8$	70	188	This work
c-NiP_2/m-NiP_2	67	200	*Angew. Chem. Int. Ed.* ***2021****, 60, 259*
Ni_2P/MoS_2	60.2	260	*Adv. Funct. Mater*. ***2019****, 29, 1809151*
$ZnP@Ni_2P$-$NiSe_2$	82	214	*Adv. Funct. Mater.* ***2022****, 32, 2113224*
Ni_5P_4-Ni_2P NS	79.1	200	*Angew. Chem. Int. Ed.* ***2015****, 54*, 8188-8192
$1T_{0.81}$-$MoS_2@Ni_2P$	79	292	*Nat. Commun*. ***2021****, 12, 5260*
NiCu@C	95	247	*J. Am. Chem. Soc*. ***2018****, 140, 610-617*
Ni_5Co_3Mo-OH	59	250	*ACS Energy Lett*. ***2019****, 4, 952-959*
Ni -ZIF/NiB	101	280	*Adv. Energy Mater*. ***2020****, 10, 1902714*
Mo-Co_9S_8@C	68	320	*Adv. Energy Mater.* ***2020****, 10, 1903137*
PBA@$Co(OH)_2$	100	260	*Adv. Energy Mater.* ***2019****, 9, 1802939*
NiFeSe	49	230	*Adv. Energy Mater.* ***2019****, 9, 1802983*
Ni-Mo-N/CFC	70	250	*Nat. Commun.* ***2019****,* 10, *5335*
Co-Ni_3N/CC	185	~256	*Adv. Mater.* ***2018****,* 30, *e1705516*
FeNiP-NPHC	102	182	*Adv. Funct. Mater.* ***2022****, 32, 2205767*
$Co_{0.42}Fe_{0.58}P@C$	66.6	181(10)	*Adv. Energy Mater.* ***2022****, 12, 2202394*

Table S6 Comparison of overpotentials at 100 mA cm^{-2} and Tafel slopes of different heterogeneous electrocatalysts recently reported for OER in 1.0 M KOH solution

Catalyst	Tafel (mV dec^{-1})	η (mV) @ 100 mA cm^{-2}	Reference
$Ni_2P@Co_9S_8$	57	253	This work
$MoS_2/Co_9S_8/Ni_3S_2/Ni$	58	420	*J. Am. Chem. Soc.* ***2019****, 141, 10417-10430*
Co_3O_4-NP/N-rGO	62	380	*Adv. Energy Mater.* ***2018*** *8, 1702222*
$CoFe_2O_4$@N-CNFs	80	349	*Adv. Sci.* ***2017****, 4, 1700226*
CF/VGSs/MoS	113	450	*Nat. Commun.* ***2021****, 12, 1380*
Co-MoS_2/BCCF-21	85	370	*Adv. Mater.* ***2018****, 30, 1801450*
Ni_2P-$NiSe_2$	71	326	*Adv. Funct. Mater.* ***2022****, 32, 2113224*
Fe-$Ni_2P@Cu_xS$	59	390	*ACS Energy Lett.* **2019***, 4, 952-959*
S-(Ni,Fe)OOH	48.9	281	*Energy Environ. Sci.* ***2020****, 13, 3439-3446*
$W_{0.5}Co_{0.4}Fe_{0.1}$/NF	310	42	*Angew. Chem. Int. Ed.* ***2017****, 56, 4502-4506*
2D/1D FeNi LDH/MOF	37.1	272	*Adv. Funct. Mater.* ***2021****, 31, 2103318*
Fe_2Ni-BPTC/CC	42	365	*Angew. Chem. Int. Ed.* ***2018****, 57, 9660*
(CrMnFeCoNi)S_x	66	295	*Adv. Energy Mater.* ***2021****, 11, 2002887*
CoMoNiS-NF-31	53	260	*J. Am. Chem. Soc.* ***2019****, 141, 10417-10430.*
MoOx/Ni_3S_2	72	310	*Adv. Funct. Mater.* ***2016****, 26, 4839.*
(Fe,Co)OOH/MI	73	290	*Adv. Mater.* ***2022****, 34, 2200270*
CoNiFeCu	43.5	292	*Adv. Mater.* ***2022****, 34, 2109108*
MoS_2/NiFe LDH‖MoNiFe	23	290	*Nat. Commun.* ***2022****, 13, 2191*

CoNiRu-NT	67	335	*Adv. Mater.* ***2022***, *34, 2107488*
FeCoNiMnRu/CNF	61.3	308	*Nat. Commun.* ***2022***, *13, 2662*
Mn-NG	55	337(10)	*Nat. Catal.* ***2018***, *1, 870-877*
Ni–NHGF	61	331(10)	*Nat. Catal.* ***2018***, *1, 63-72*

Table S7 Comparison of cell voltages at 10 and 100 mA cm^{-2} and stabilities of different bifunctional non−noble metal electrocatalysts recently reported for overall water splitting in 1.0 M KOH solution

Catalyst	Cell voltage at 10 mA cm^{-2} (V)	Cell voltage at 100 mA cm^{-2} (V)	Reference
$Ni_2P@Co_9S_8$	1.46	1.66	This work
FeCoNi/CC	1.55	2.00	*Adv. Energy Mater.* ***2019****, 9, 1901312*
Co_3S_4/MOF	1.55	1.90	*Adv. Mater.* ***2019****, 31, 1806672*
Ni/γ-Fe_2O_3	1.47	1.77	*Nat. Commun.* ***2019****, 10, 5599*
$CoFeZrO_x$	1.63	1.78	*Adv. Mater.* ***2019****, 31, 1901439*
Ni-ZIF/NiB	1.54	1.77	*Adv. Energy Mater.* ***2020****, 10, 1902714*
PBA@$Co(OH)_2$	1.65	1.99	*Adv. Energy Mater.* ***2019****, 9, 1802939*
Cr/FeNi-P	1.54	1.70	*Adv. Mater.* ***2019****, 31, 1900178*
CoMoNiS	1.54	2.09	*J. Am. Chem. Soc.* ***2019****, 141, 10417-10430*
Au/Ni_3S_2/NF	1.52	1.82*	*Appl. Catal. B: Environ.* ***2022****, 304, 120935*
MH-TMO	1.49	1.72	*Adv. Energy Mater.* ***2022,*** *12, 2200067*
BPIr-be	1.57	1.78	*Adv. Mater.* ***2021****, 33, 2104638*
O-CMMOFs-NF	1.47	1.85	*Appl. Catal. B: Environ.* ***2022****, 307, 121151*
Ni-MoO_2/NF-IH	1.50	1.72	*Adv. Funct. Mater.* ***2021****, 31, 2009580.*
CoFeO@BP	1.58	1.78	*Angew. Chem. Int. Ed.* ***2020****, 59, 21106.*
MoS_2/NiFe LDH‖MoNiFe	1.61	1.73	*Nat. Commun.* ***2022****, 13, 2191*

CoFeP@C	1.55	1.78	*Adv. Energy Mater.* ***2022***, *12*, *2202394*
FeCoNi MOF	1.60	1.90	*J. Am. Chem. Soc.* ***2022***, *144*, *3411*

Table S8 Comparison of the overpotentials at 200 mA cm^{-2} toward the HER in 1 M KOH of the $Ni_2P@Co_9S_8$ with other reported high-performance bifunctional catalysts.

Catalyst	η (mV) @ 200 mA cm^{-2}	Reference
$Ni_2P@Co_9S_8$	204	This work
$CoNC@Co_2N/CPs$	330	*Adv. Energy Mater.* ***2020***, *10*, *2002214*
$Ni\text{-}N_3$	345	*Adv. Mater.* ***2020***, *33*, *2003846*
$Cu1Ni_2\text{-}N$	255	*Adv. Energy Mater.* ***2019***, *9*, *1900390*
$Ni_5Co_3Mo\text{-}OH$	290	*ACS Energy Lett.* ***2019***, *4*, *952-959*
Cu_3N	335	*ACS Energy Lett.* ***2019***, *4*, *747-754*
NiMoN/CFC	400	*Nat. Commun.* ***2019***, *10*, *5335*
FeNiS/Ni	300	*Adv. Energy Mater.* ***2020***, *2001963*
NiFeP/graphene	290	*Adv. Mater.* ***2020***, *32*, *1908201*
NiFeSe	325	*Adv. Energy Mater.* ***2019***, *9*, *1802983*

Table S9 Comparison of the overpotentials at 200 mA cm^{-2} toward the OER in 1 M KOH of the $Ni_2P@Co_9S_8$ with other reported high-performance bifunctional catalysts.

Catalyst	η (mV) @ 200 mA cm^{-2}	Reference
$Ni_2P@Co_9S_8$	276	This work
NiCo LDH/NiCoS	378	*Nano Res.* ***2022***, *15, 4986-4995*
CoOOH	340	*J. Mater. Chem. A* ***2019***, *7, 7777-7783*
Co_2P-Co_3O_4	405	*Adv. Energy Mater.* ***2018***, *8, 1802445*
Ni/MoN/rNS)	533	*Adv. Sci.* ***2022***, *9, 2105869*
$NixCo_{3-x}S_4/Ni_3S_2$	318	*Nano Energy* ***2017***, *35, 161-170*
MoO_x/Ni_3S_2	312	*Adv. Funct. Mater.* ***2016***, *26, 4839-4847*
EG/$Co_{0.85}$Se/NiFe-LDH	290*	*Energy Environ. Sci.* ***2016***, *9, 478-483*
FeCoNiCuMn HEA/CNF	386	*Energy Environ. Sci.* ***2023***, *16, 619-628*
MX@MOF-Co_2P	407	*J. Mater. Sci. Technol.* ***2023***, *145, 74-82*
Ni/MoN/rNS	533	*Adv. Sci.* ***2022***, *9, 2105869*
Co/CoO/$Co(OH)_2$	360*	*Appl. Catal. B* ***2021***, *292, 120063*
Ir-1/$Ni_{1.6}Mn_{1.4}O_4$	350	*Adv. Sci.* ***2022***, *9, 2200529*

*The data were calculated according to the curves given in the literature

Table S10 Comparison of the overpotentials at 200 mA cm^{-2} toward the overall water splitting in 1 M KOH of the $Ni_2P@Co_9S_8$ with other reported high-performance bifunctional catalysts

Catalyst	Cell voltage at 200 mA cm^{-2} (V)	Reference
$Ni_2P@Co_9S_8$	1.76	This work
Co_3Se_4/CF	2.11	*Adv. Energy Mater.,* ***2017****, 7, 1602579*
CoP/NCNHP	1.97	*J. Am. Chem. Soc.* ***2018****, 140, 2610-2618*
NiCoP@NF-100	1.87	*J. Energy Chem.* ***2020****, 50, 395-401*
CoPO/NF	1.98	*Adv. Funct. Mater.* ***2018****, 28, 1706120*
NC@$CuCo_2N_x$/CF	1.93	*Adv. Funct. Mater.* ***2017****, 27, 1704169*
Ni-P/NF	2.17*	*J. Mater. Chem. A.* ***2016****, 4, 5639-5646*
Ni-P/CP	3.3*	*Adv. Funct. Mater.* ***2016****, 26, 4067-4077*
Cu_3N	1.8	*ACS Energy Lett.* ***2019****, 4, 747-754*
FeNiS/Ni	1.95	*Adv. Energy Mater.* ***2020****, 2001963.*
FeCoNi/CC	2.13	*Adv. Energy Mater.* ***2019****, 9, 1901312.*
NiFeP/graphene	1.90	*Adv. Mater.* ***2020****, 32, 1908201*

CoNC	1.91	*Energy Environ. Sci.* ***2020****, 13, 545-553*
FeCo/Co_2P@C	2.1	*Adv. Energy Mater.* ***2020****, 10, 1903854.*
CoNSC	1.78	*Adv. Energy Mater.* ***2020****, 10, 2002896*
NiCoP/NF	1.98	*Nano Lett.* ***2016****, 16, 7718-7725*

*The data were calculated according to the curves given in the literature