Accelerating Hydrogen Evolution in Ru-doped FeCoP Nanoarray with Lattice Distortion toward Highly Efficient Overall Water Splitting

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The detail calculation process of TOF for OER

The values of TOF are calculated by assuming that all metal ions in the catalysts are active and contribution to the OER.

$TOF_{OER} = j \times A/(4 \times F \times n)$

where j (mA·cm^{-2}) is the measured current density at overpotential η = 220 mV. A is the surface area, F is the Faraday's constant (96,485 C mol^{-1}), the number of 4 means 4 electrons per O_2 molecular, and n (mol) is the number of moles of the metal atom calculated from catalyst loading density. The molecular weights of FeCoP and FeCoRuP are 88.88 and 92.61, respectively.

The detail calculation process of TOF for HER

The values of TOF for FeCoP and FeCoRuP are calculated by assuming that according to the following formula:[1,2]

$$TOF(H_2/s) = \frac{\#\ total\ hydrogen\ turnovers\ per\ geometric\ area}{\#\ active\ sites\ per\ geometric\ area}$$

Note: A 100% Faradic efficiency was assumed during calculation since the NiCoP catalyst exhibited a nearly 100% Faradic efficiency for HER as reported in literature.[3]

The number of the total hydrogen turn overs can be calculated from the current density related to the two electrons from the LSV polarization curve (iR-corrected) according to:

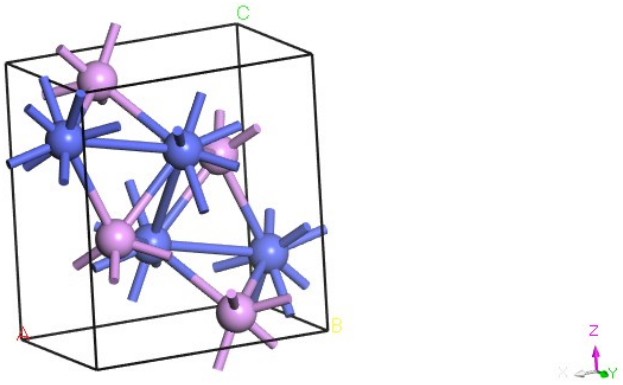
$$\#\text{total hydrogen turnovers} = (j\ \frac{mA}{cm_2})\ (\frac{1C/s}{1000\ mA})\ (\frac{1\ mol\ e^{-1}}{96485.3\ C})\ (\frac{1\ mol}{2\ mol\ e^{-1}})$$

$$= (\frac{6.022\times10^{23} molecules\ H_2}{1\ mol\ H_2}) = 3.12 \times 10^{15}\ \frac{H_2/s}{cm^2}\ \text{per}\ \frac{mA}{cm^2}$$

As for the surface active sites, we estimated that the number of the active sites as the

total number of the surface sites (both the metal and phosphorus atoms serve as active sites) from the roughness factor together with the unit cell of the catalysts, which may underestimate the total TOF. Taking CoP (the crystal structure as shown below) as an example, the surface active sites per real surface area can be calculated as following:

Surface Sites = $\left(\frac{8\ atoms\ per\ unit\ cell}{93.07 Å^3\ per\ unit\ cell}\right)^{2/3}$ = 1.948 × 10^{15} atoms/cm^2 real surface area



a = 5.08 Å b = 3.28 Å c = 5.59 Å Cell Volume = 93.07 $Å^3$

According to the XRD patterns, we performed the XRD refinement for the powders. The cell volumes for FeCoP and FeCoRuP are 93.28 $Å^3$ and 93.81 $Å^3$, respectively, and the numbers of surface sites for FeCoP and FeCoRuP are 1.945 × 10^{15} and 1.937 × 10^{15} atoms/cm^2 real surface area, respectively.

The electrochemically active surface area (ECSA) was estimated from capacitive current associated with the C_{dl} of catalytic surface according to:

ECSA = C_{dl}/C_s

where C_s is the specific capacitance of a flat standard electrode with 1 cm^2 of real surface area, which is generally from 20 to 60 μF cm^{-2}.[4] The value in this work is 40 μF cm^{-2}.

$$ECSA^{FeCoRuP} = \frac{125.2\ mF \cdot cm^{-2}}{40\ \mu F \cdot cm^{-2}\ per\ cm^2_{ECSA}} = 3125.0\ cm^2_{ECSA}$$

$$\text{ECSA}^{\text{FeCoP}} = \frac{75.9\ mF \cdot cm^{-2}}{40\ \mu F \cdot cm^{-2}\ per\ cm^{2}_{ECSA}} = 1897.5\ cm^{2}_{ECSA}$$

Finally, the TOF can be calculated according to:

$$\text{TOF}_{\text{HER}} = \frac{3.12 \times 10^{15}\ \frac{H_2/s}{cm^2}\ per\ \frac{mA}{cm^2} \times |j|}{\#\ surface\ active\ sites \times A_{ECSA}}$$

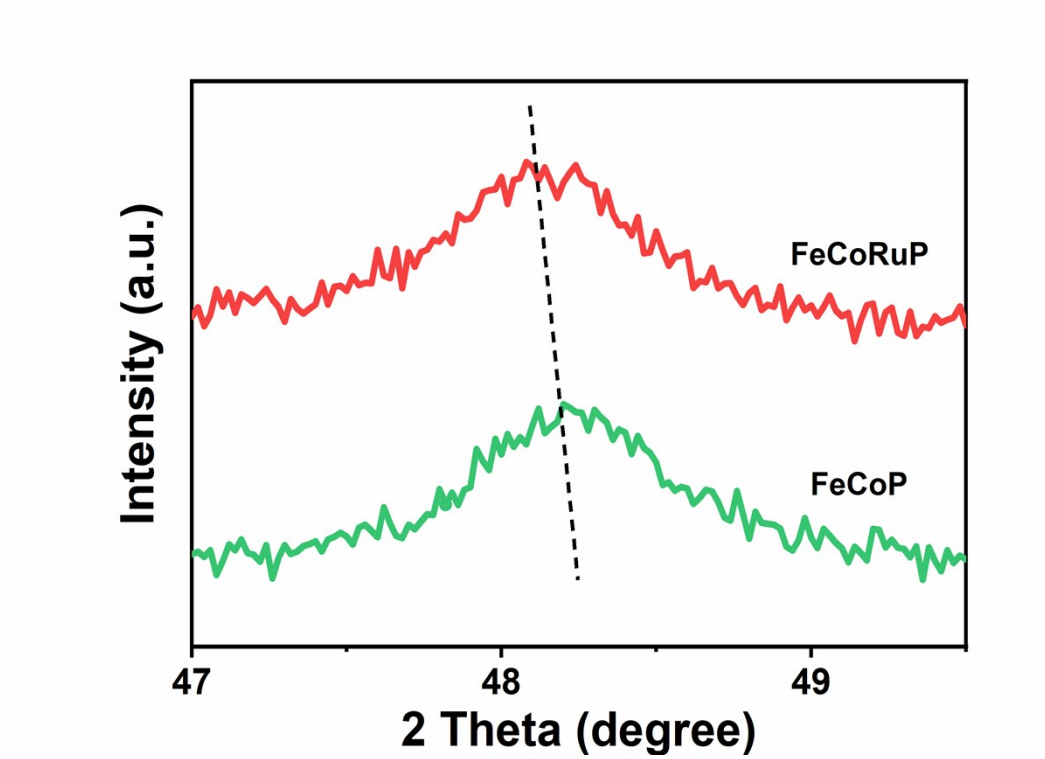


Figure S1. XRD patterns of FeCoP and FeCoRuP.

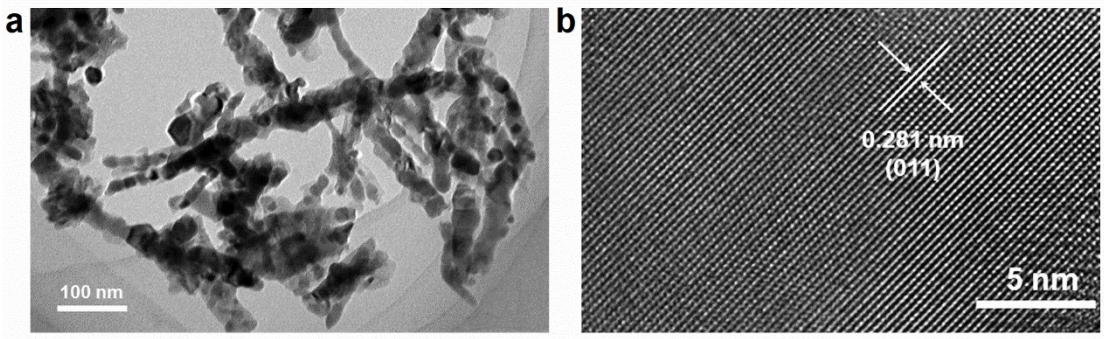


Figure S2. a) TEM image and b) high-resolution TEM image of FeCoP nanoneedle.

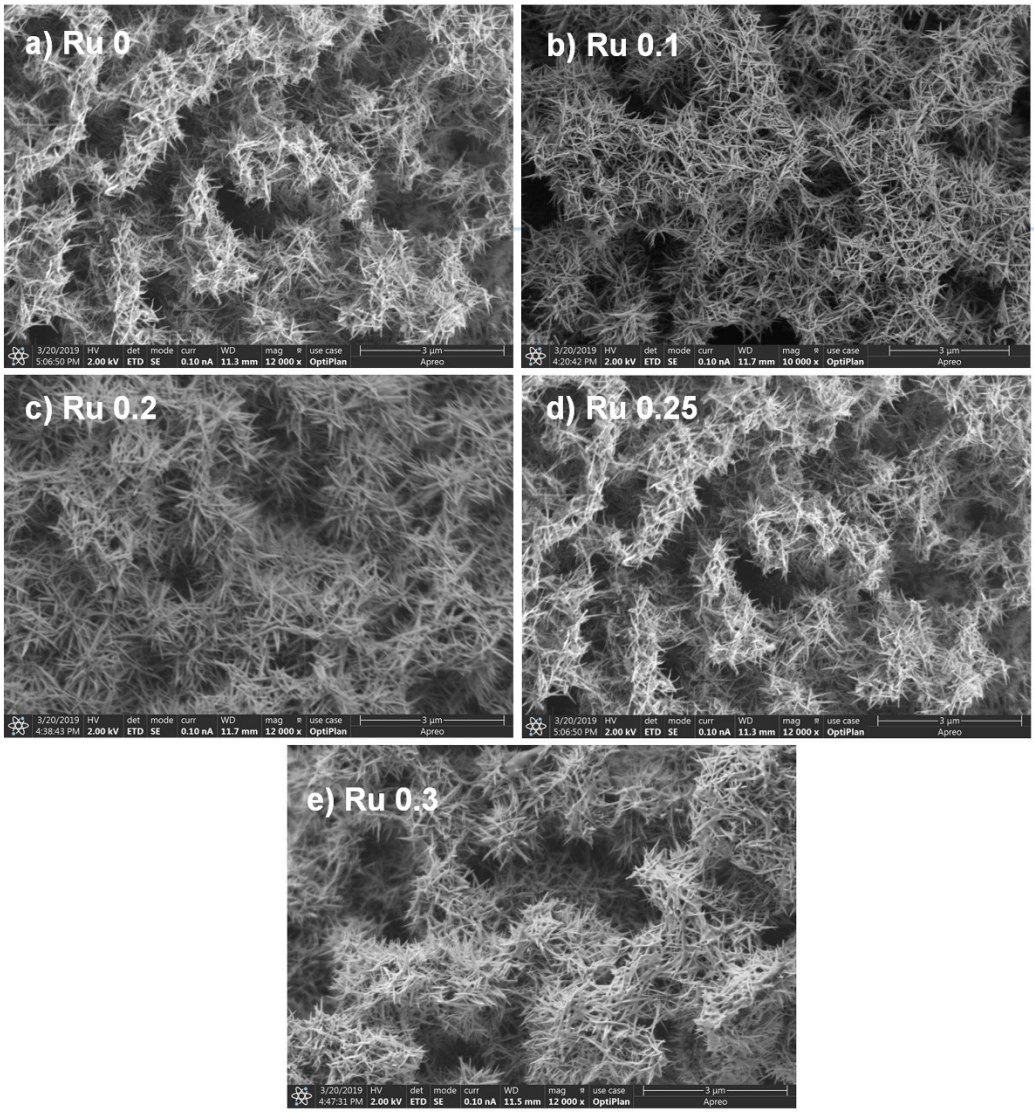


Figure S3. SEM images with different atomic Ru contents (Ru/(Ru+Fe+Ru): 0, 2%, 4.4%, 6.2% and 7.8%, marked Ru0, Ru0.1, Ru0.2, Ru0.25 and Ru0.3, respectively. Among them, Ru0.25 is the FeCoRuP in the manuscript.)

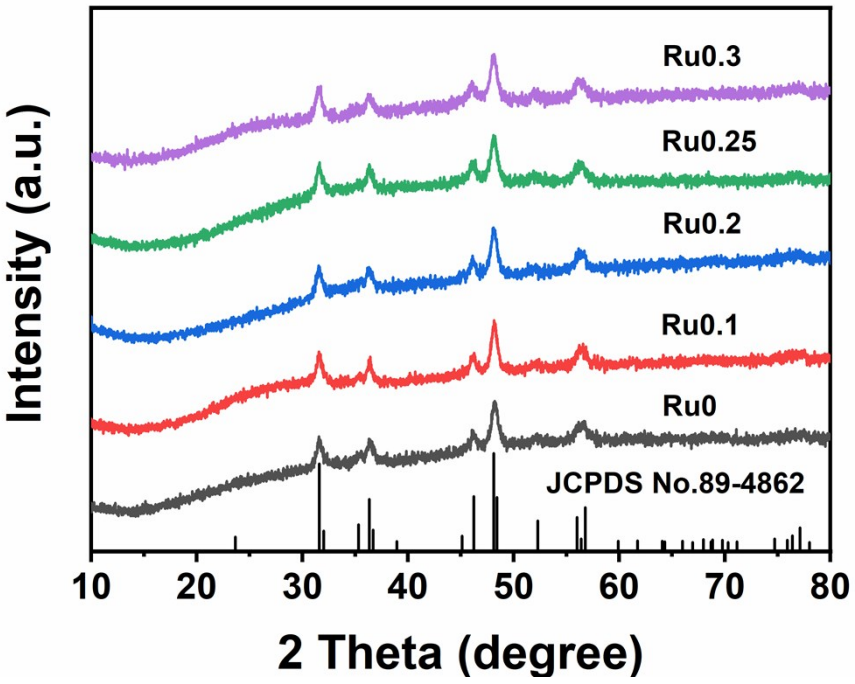


Figure S4. XRD with different atomic Ru contents (Ru/(Ru+Fe+Ru): 0, 2%, 4.4%, 6.2% and 7.8%, marked Ru0, Ru0.1, Ru0.2, Ru0.25 and Ru0.3, respectively.)

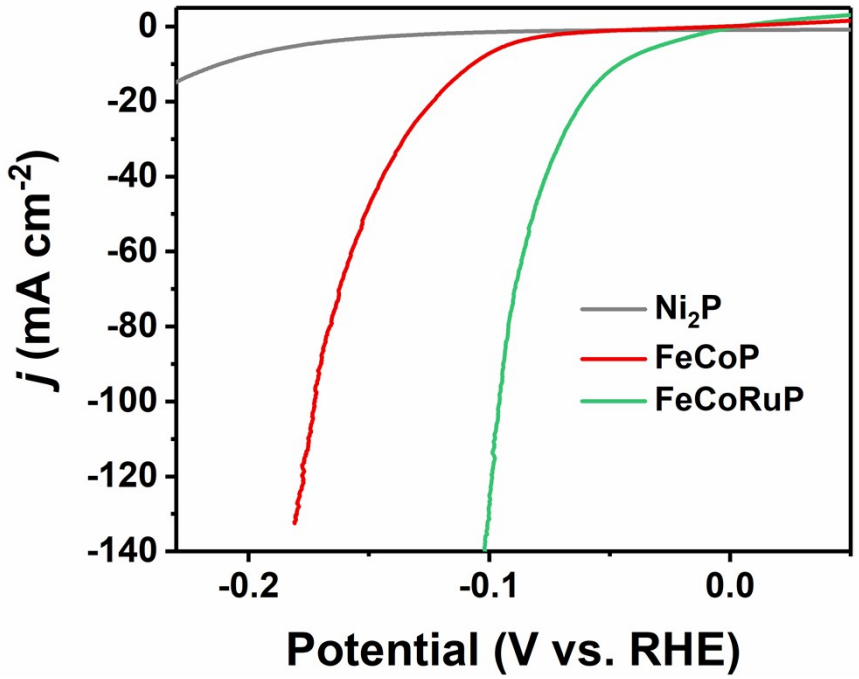


Figure S5. HER polarization curves of FeCoP, FeCoRuP, and phosphatized Ni foam Ni_2P.

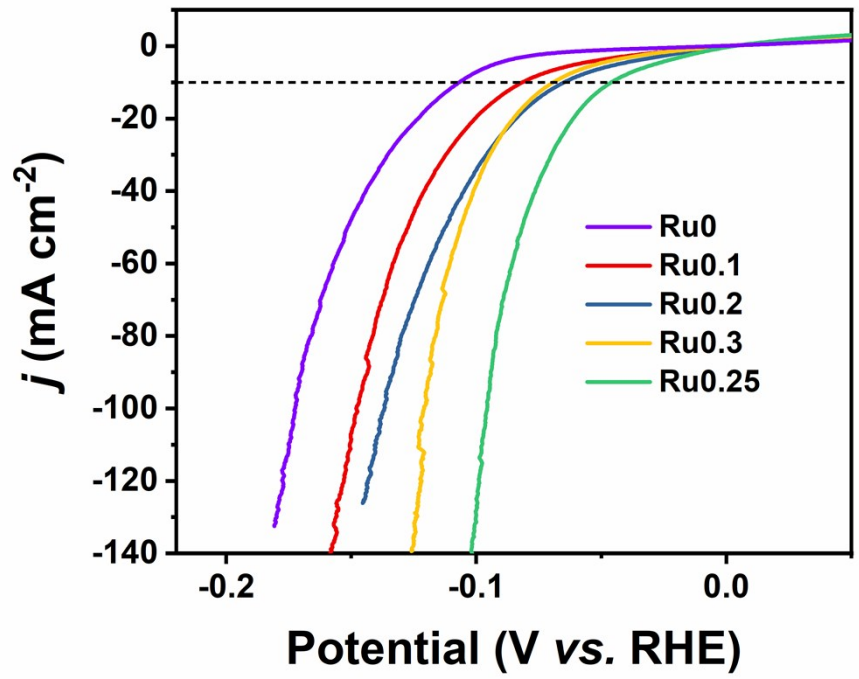


Figure S6. Polarization curves of Ru-doped FeCoP samples with different Ru contents.

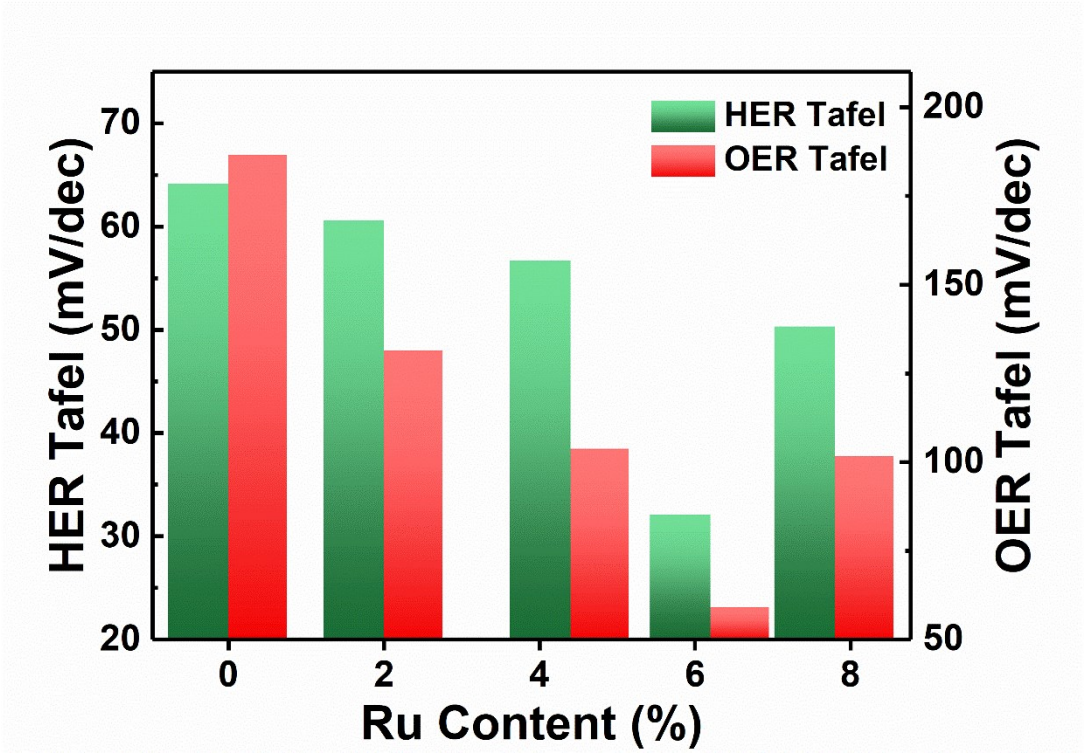


Figure S7. Tafel slope of HER and OER for different Ru-incorporation FeCoP in 1.0

M KOH.

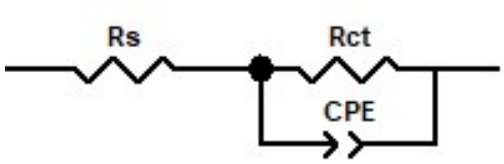


Figure S8. One-time-constant model equivalent circuit used for data fitting of EIS spectra (Rs is the overall series resistance, CPE is the constant-phase element, Rct is the charge-transfer resistance related to OER/HER process).

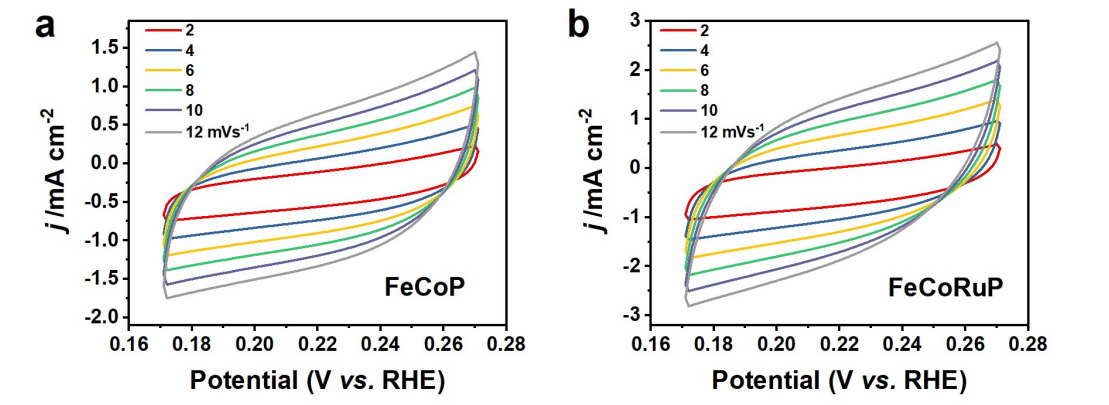


Figure S9. HER CV curves in an overpotential windows of 1.05-1.11 mV vs. RHE in 1 M KOH for a) FeCoP and b) FeCoRuP.

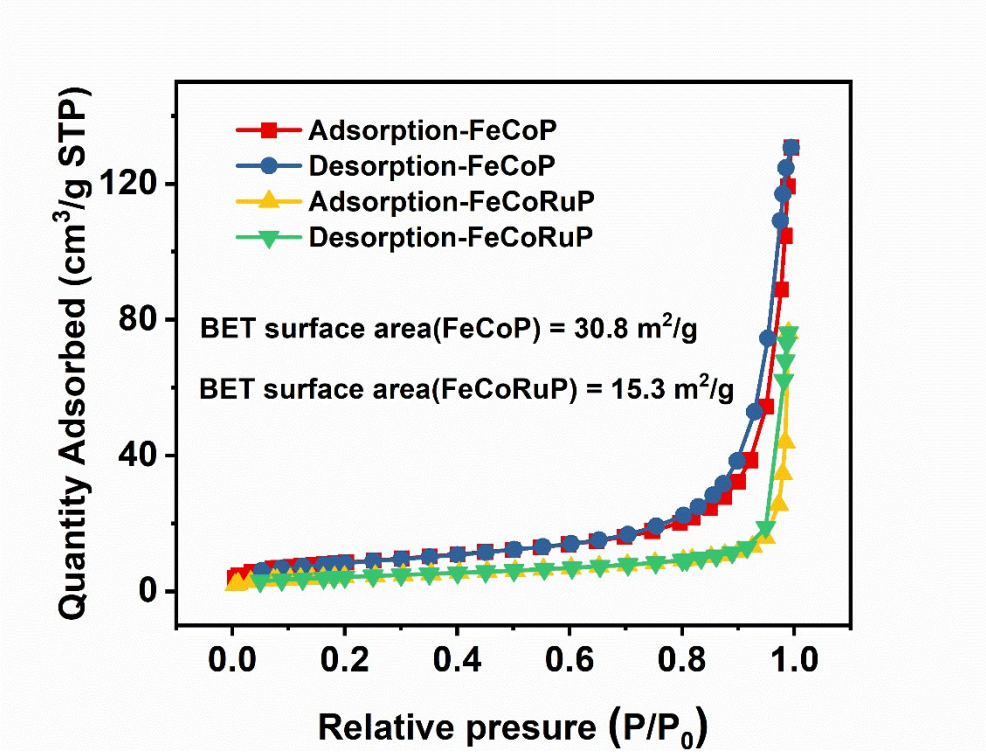


Figure S10. Nitrogen adsorption-desorption isotherms of FeCoP and FeCoRuP.

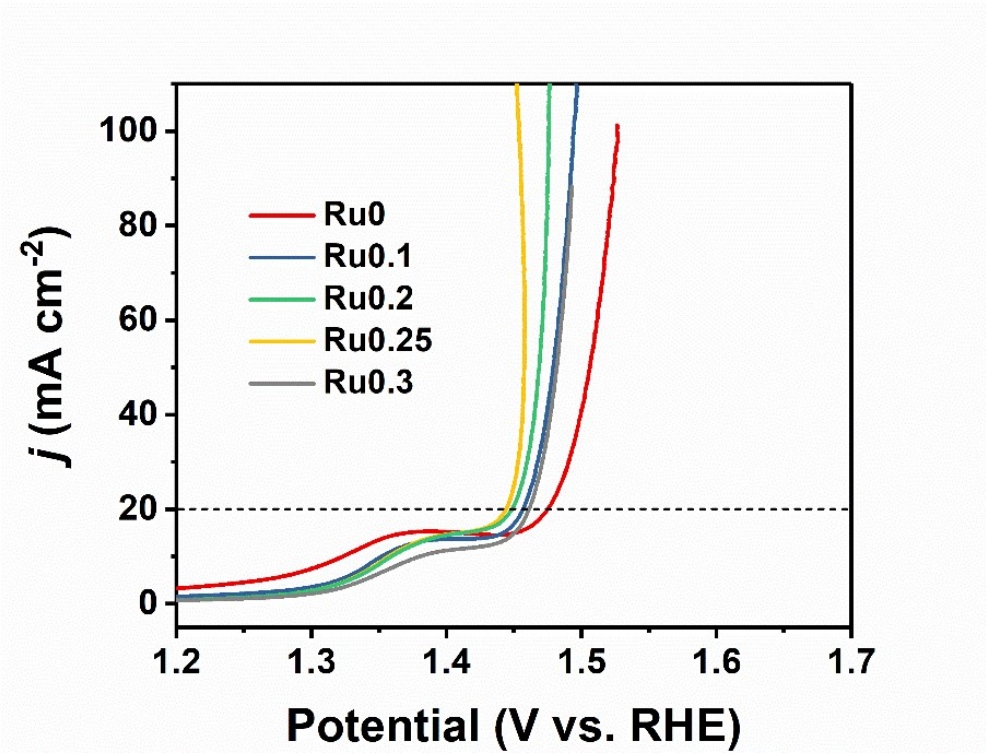


Figure S11. Polarization curves of Ru-doped FeCoP samples with different Ru

contents.

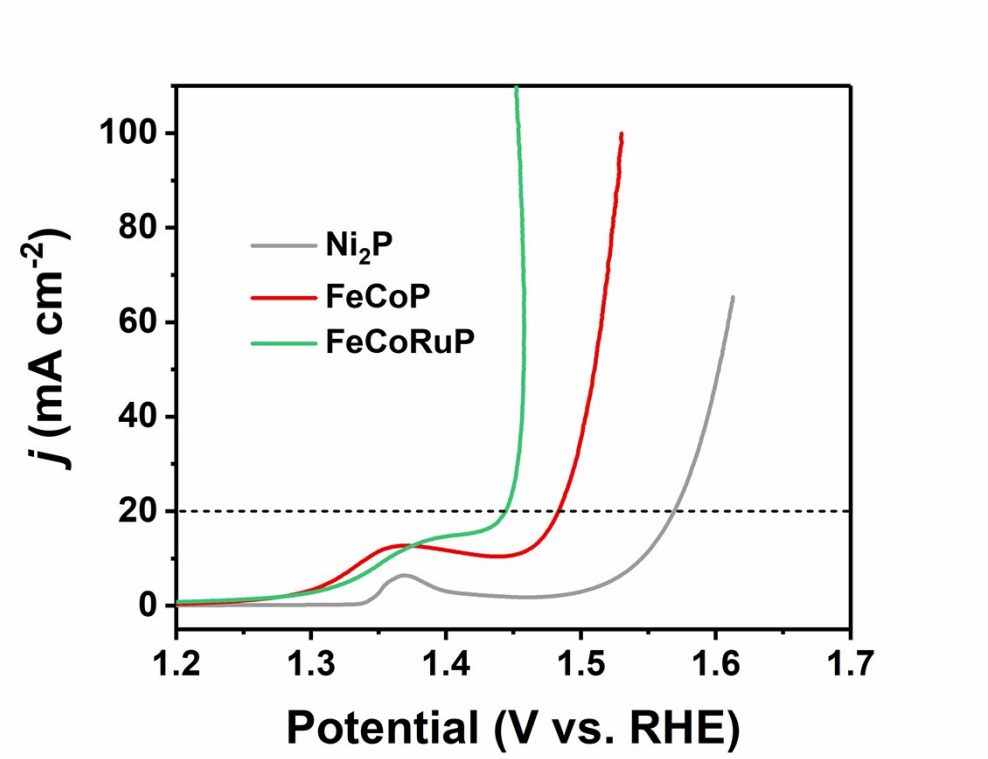


Figure S12. OER polarization curves of FeCoP, FeCoRuP, and phosphatized Ni foam Ni_2P.

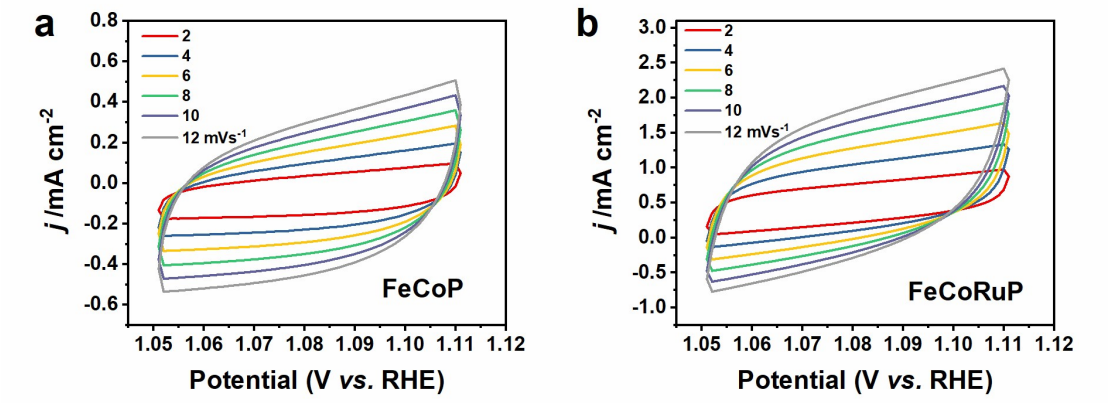


Figure S13. OER CV curves in an overpotential windows of 1.05-1.11 mV vs. RHE in 1 M KOH for (a) FeCoP and (b) FeCoRuP.

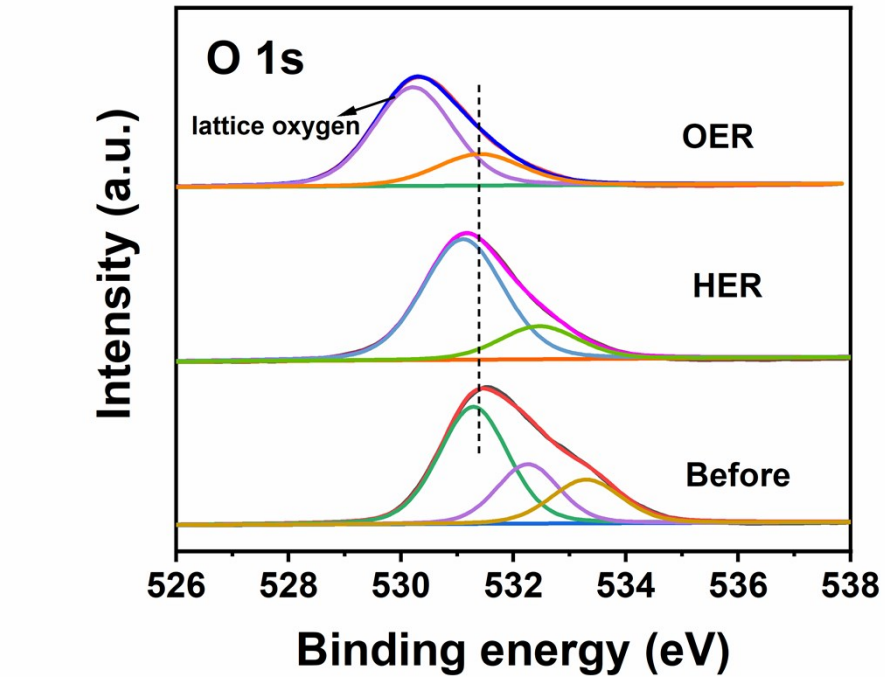


Figure S14. The O 1*s* of FeCoRuP before and after OER/HER long-term test.

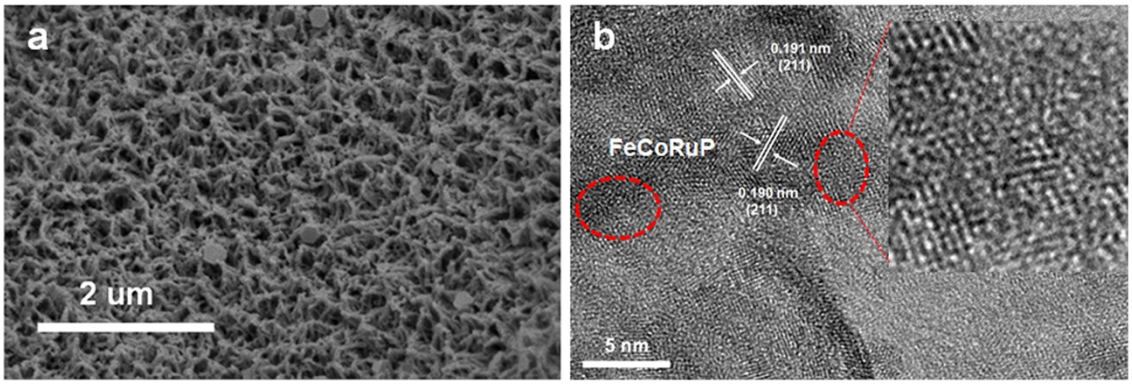


Figure S15. (a) SEM image and (b) HRTEM image of FeCoRuP after HER test.

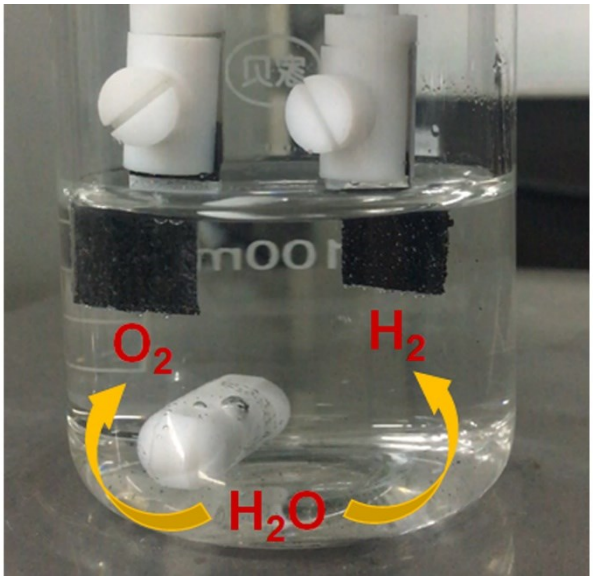


Figure S16. Digital photograph of the production of H_2 and O_2 bubbles on the FeCoRuP/NF electrodes.

Table S1. Average mass loading of catalysts on NF substrates.

Samples	**Mass loading (mg cm^{-2})**
$Fe_{0.67-x}Co_{1.33}Ru_x$-P ($x = 0$)	0.73
$Fe_{0.67-x}Co_{1.33}Ru_x$-P ($x = 0.1$)	0.81
$Fe_{0.67-x}Co_{1.33}Ru_x$-P ($x = 0.2$)	0.78
$Fe_{0.67-x}Co_{1.33}Ru_x$-P ($x = 0.25$)	0.74
$Fe_{0.67-x}Co_{1.33}Ru_x$-P ($x = 0.3$)	0.78
20% Pt/C	0.73
IrO_2/RuO_2	0.73

Table S2. Mole ration of Fe, Ru and Co in $Fe_{0.67-x}Co_{1.33}Ru_x$-P nanosheets calculated from ICP-AES.

$Fe_{0.67-x}Co_{1.33}Ru_x$**-P**	**Fe:Ru:Co**	**Ru/(Fe+Ru)**	**Ru/(Fe+Ru+Co)**
$x = 0$	0.30:0:0.44	0	0
$x = 0.1$	3.44:0.23:7.62	6.2%	2.0%
$x = 0.2$	1.29:0.20:3.08	13.6%	4.4%
$x = 0.25$	0.48:0.12:1.36	20.1%	6.2%
$x = 0.3$	0.42:0.14:1.21	24.9%	7.8%

Table S3. Comparison of some representative recently reported HER electrocatalysts in alkaline electrolyte (1.0 M KOH).

Catalysts	Support	η (mV) at 10 $mAcm^{-2}$	Tafel slope ($mV\ dec^{-1}$)	Reference
Ru-doped FeCoP/NF	**Ni foam**	**45**	**32.1**	**This work.**
$Fe_{0.29}Co_{0.71}P$/NF	Ni foam	74	53.6	*Nano Energy,* 2020, 67, 104147.
Ru-MoS_2/CNT	Carbon paper	50	62	*Adv. Sci.* 2019, **6**, 1900090.
NiCoP@Ru	Ni foam	52	50	*Chem. Commun.,* 2017, **53**, 13153.
CoP nanowires (0.35)	Ni foam	110	54	*J. Mater. Chem. A* 2014, **2**, 14634.
CoP/Tia (2.0)		90	43	*Chem. Mater.* 2014, **26**, 4326.
Ni_2P hollow nanoparticles (1.0)		116	46	*J. Am. Chem. Soc.* 2013, **135**, 9267.
FeP nanosheets (0.28)		~ 240	67	*Chem. Commun.* 2013, **49**, 6656.
Fe-O-P NRs		96	47	*J. Mater. Chem. A.* 2018,**6**, 9467-9472.
FeP/Ti foil	Ti foil	170		*ACS Nano.* 2014, **8**, 11101-11107.
FeP NP	Carbon cloth	115	70	*ACS Appl. Mater. Interfaces* 2014, **6**, 20579−20584.
FeP NAs		202	71	*ACS Catal.* 2014, **4**, 4065−4069
Co/CoP		253	73.8	*Adv. Energy Mater.*, 2017, **7**, 1602355.
NiFe-P film		87	48	*J. Mater. Chem. A*, 2016, **4**, 13866.
Mn-doped NiS_2	Ni foam	71	57	*J. mater. Chem. A* 2019, **7**,25628
Fe-doped CoP	Ti foil	78	48	*Adv. Mater.* 2017, **29**, 1602441
Cr-doped FeNiP	Glassy carbon	109	106.5	*Adv. Mater.,* 2019, **31**, e1900178.

Amorphous NiFeP	Ni foam	158	122	*ACS Energy Lett.*, 2016, **2**, 1035.
Co-Ni_3N	Carbon cloth	195	156	*Adv. Mater.*, 2018, **30**, e1705516.
N,P-MoS_2	Carbon cloth	78	113	*Nano Energy,* 2019, **58**, 862.
Ni-CoP	Glassy carbon	90	71	*Nano Energy,* 2019, **56**, 411.
CoSe/Ti	Ti foil	121	65	*Chem. Commun.* 2018, **51**, 16683.
NiCoP nanotubes/NF	Ni foam	150	80	*Adv. Funct. Mater.* 2016, **26**, 6785
MoS_2-Ni_3S_2 nanoparticles/NF	Ni foam	145	62	*ACS Catal.* 2017, **7**, 2357.
$Fe_{0.29}Co_{0.71}P$/NF	Ni foam	74	53.6	*Nano Energy,* 2020, 67, 104147.
$MoS_2/Co_9S_8/Ni_3S_2$/NF	Ni foam	113	85	*J. Am. Chem. Soc.* 2019, **141**, 710417.

Table S4. The TOF values of FeCoRuP/NF and FeCoP for OER (at η = 220 mV) and HER (at η = 100 mV).

TOF values	**FeCoRuP**	**FeCoP**
TOF_{HER} (s^{-1})	0.0660	0.0061
TOF_{OER} (s^{-1})	0.0408	0.0035

Table S5. Performance comparison of overall water splitting activities with recently reported robust bifunctional catalysts on different substrates in 1.0 M KOH.

Electrode architecture (Electrocatalyst)	**Support**	**Voltage at 10 $mAcm^{-2}$ (V)**	**Stability test (h)**	**Reference**
Ru-doped FeCoP/NF	**Ni foam**	**1.47**	**110**	**This work.**
Pt/C ‖ IrO_2 couple	Ni foam	1.68		This work

$Fe_{0.29}Co_{0.71}P$/NF	Ni foam	1.59	100	*Nano Energy,* 2020, 67, 104147.
Fe doped CoP	Ti foil	1.6	54	*Adv. Mater.* 2017, **29**, 1700017
Cr-doped FeNiP/NCN	Ni foam	1.50	20	*Adv. Mater.* 2019, **31**, 1900178.
CoP film	Copper foil	1.64	43	*Angew. Chem., Int., Ed.* 2015, 54, 6251.
FeP		1.63	180	Chem. Sci., 2018, **9**, 8590.
NiFeRu-LDH	Ni foam	1.52	10	*Adv. Mater.* 2018, **30**, 1706279
NiCoP/rGO	Carbon	1.59	75	*Adv. Funct. Mater*. 2016, **26**, 6785.
np-$(Co_{0.52}Fe_{0.48})_2P$		1.53		*Energy. Environ. Sci*. 2016, **9**, 2257.
FeP_x/Fe-N-C/NPC	Ni foam	1.58	24	*Adv. Energy Mater*. 2018, 1803312
NiFeLDH@NiCoP/NF	Ni foam	1.57		*Adv. Funct. Mater.* 2018, **28**, 1706847.
NiFeP/SG	Sponge-like graphenes	1.54		*Nano Energy* 2019, **58**, 870-876.
Ni-Fe-P-350		1.68		*ACS Appl. Mater. Interfaces* 2017, **9**, 26134.
$Co_5Mo_{1.0}P$ NSs@NF	Ni foam	1.68		*Nano Energy* 2018, **45**,448-455.
$NiCo_2P_x$/CNTs	Ni foam	1.61		*J. Mater. Chem. A* 2018, **6**, 7420.
NiCoP/CC	Carbon cloth	1.52		*ACS Catal.* 2017, **7**, 4131.
$Co_{0.6}Fe_{0.4}P$	Ni foam	1.58		*Chem. Sci.*, 2019, **10**, 464.
NiS/Ni_2S/CC	Carbon cloth	1.62		*J. Mater. Chem. A* 2018, **6**, 8233.
Ni/Mo_2C(1:2)-NCNFs	Ni foam	1.64	100	*Adv. Energy Mater.* 2019, **9**, 1803185.
Fe, Co-doped NiSe2	Carbon cloth	1.52	30	*Adv. Mater.* 2018, **30**, 1802121.
$MoS_2/Co_9S_8/Ni_3S_2$/NF	Ni foam	1.54	24	*J. Am. Chem. Soc.* 2019, **141**, 710417.

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4 J. Kibsgaard and T. F. Jaramillo, *Angew. Chem. Int. Ed.*, 2014, **53**, 14433–14437.