Electronic supplementary information for

Engineering electronic structure of FeP with rare earth elements to promote the electrocatalytic hydrogen evolution performance

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Supplementary figures

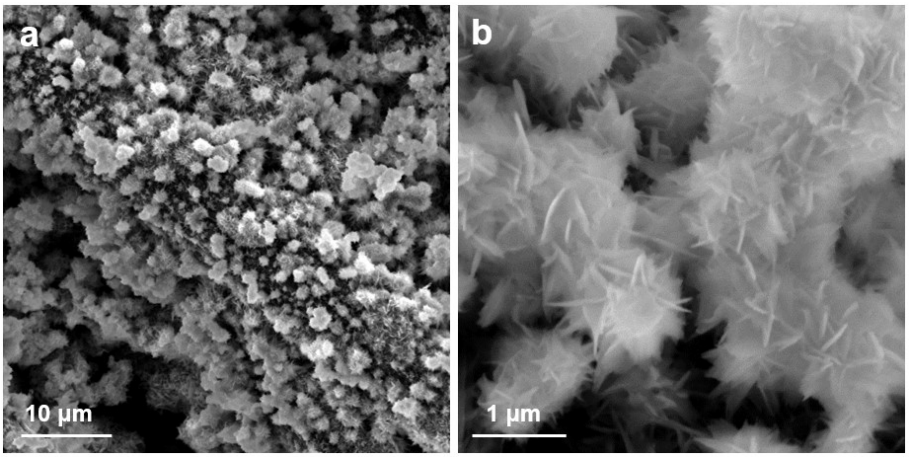


Figure s1. SEM images for FeP/CC sample with different magnifications.

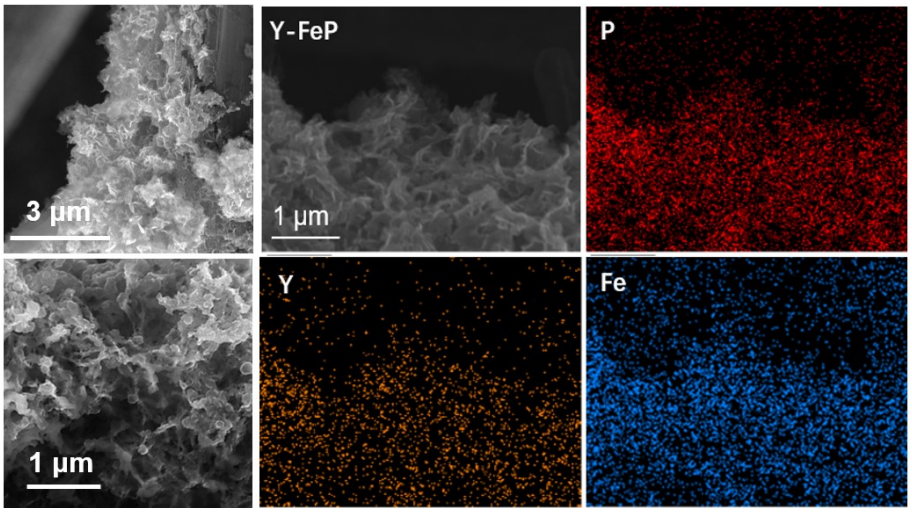


Figure s2. SEM and corresponding element mapping images for Y-FeP/CC.

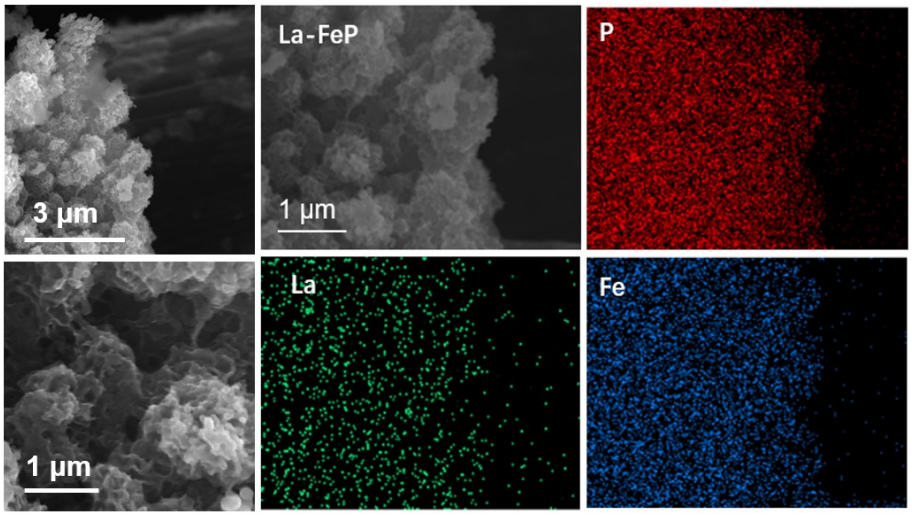


Figure s3. SEM and corresponding element mapping images for La-FeP/CC.

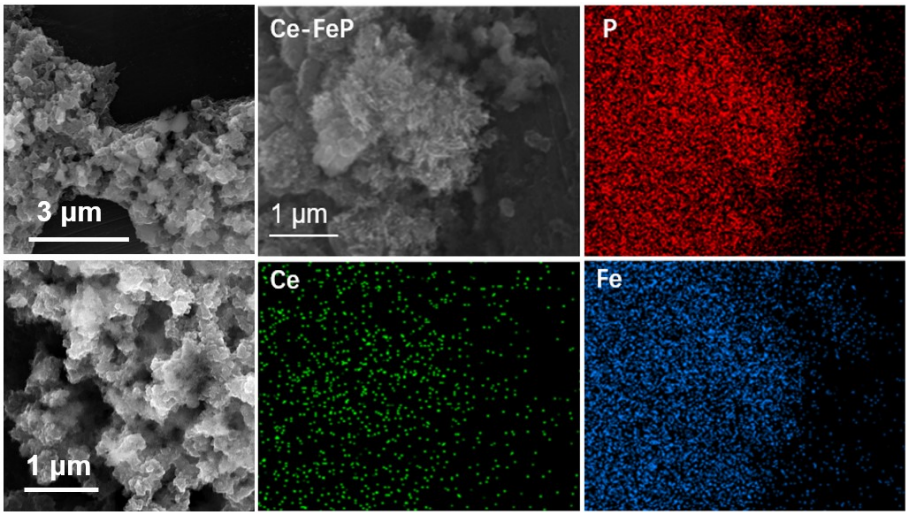


Figure s4. SEM and corresponding element mapping images for Ce-FeP/CC.

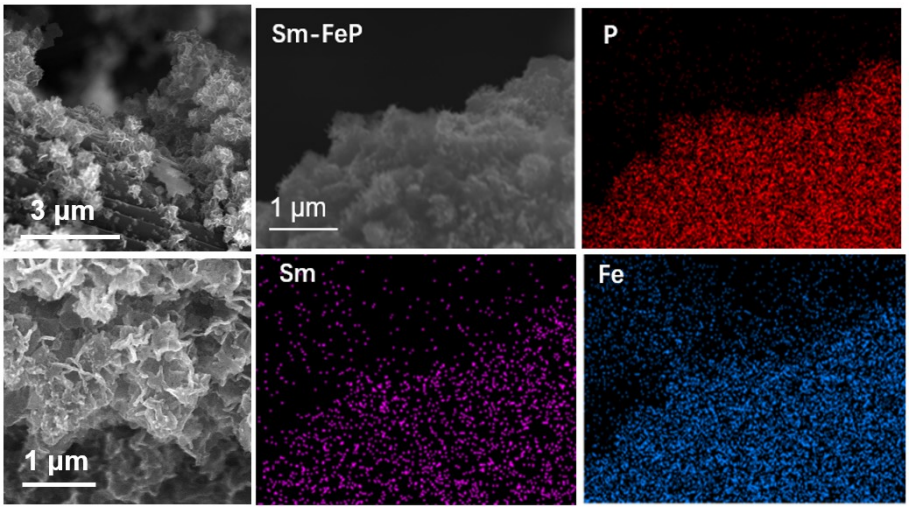


Figure s5. SEM and corresponding element mapping images for Sm-FeP/CC.

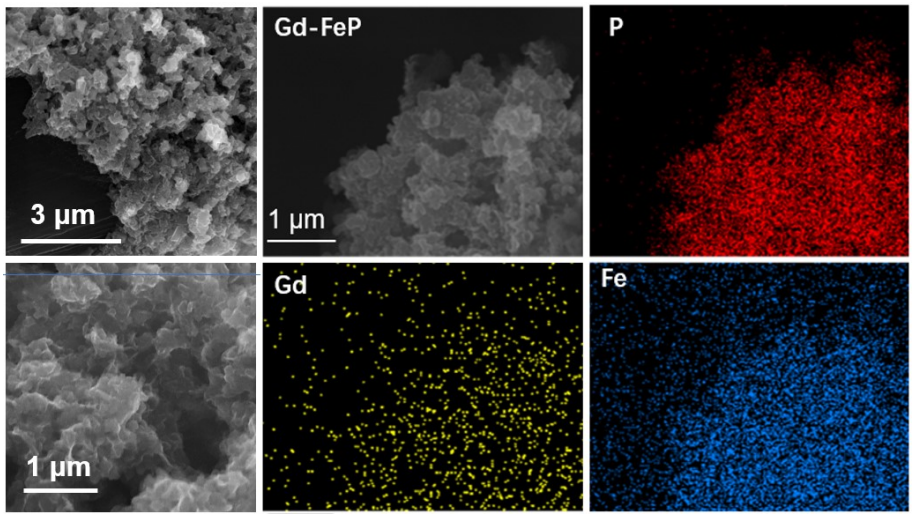


Figure s6. SEM and corresponding element mapping images for Gd-FeP/CC.

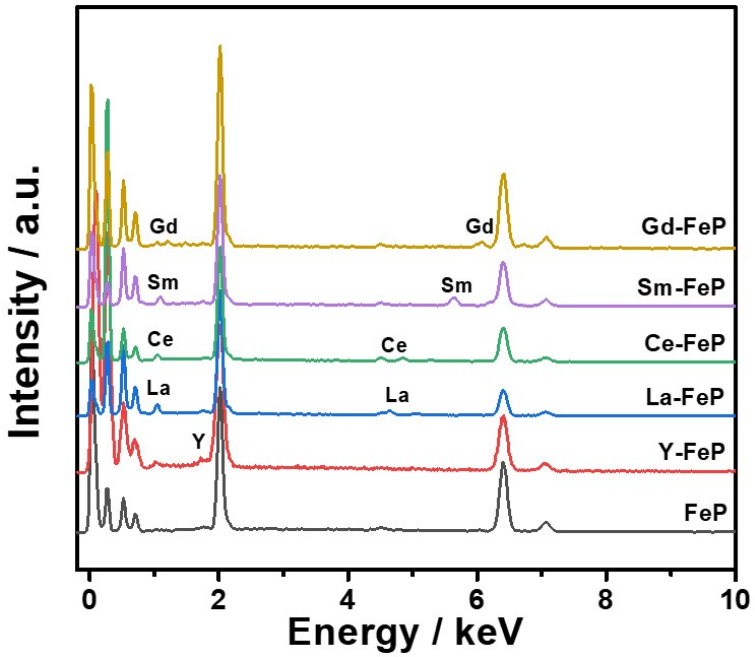


Figure s7. EDS spectra for RE-FeP and FeP samples.

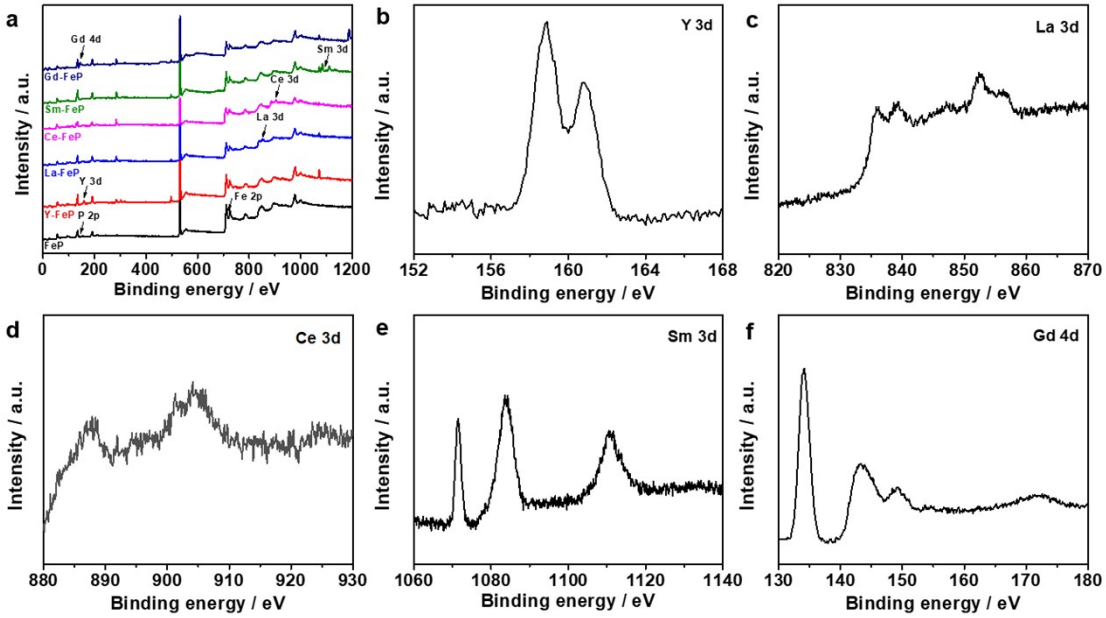


Figure s8. (a) Full spectra and (b-f) high-resolution XPS spectra for various RE-CeP samples.

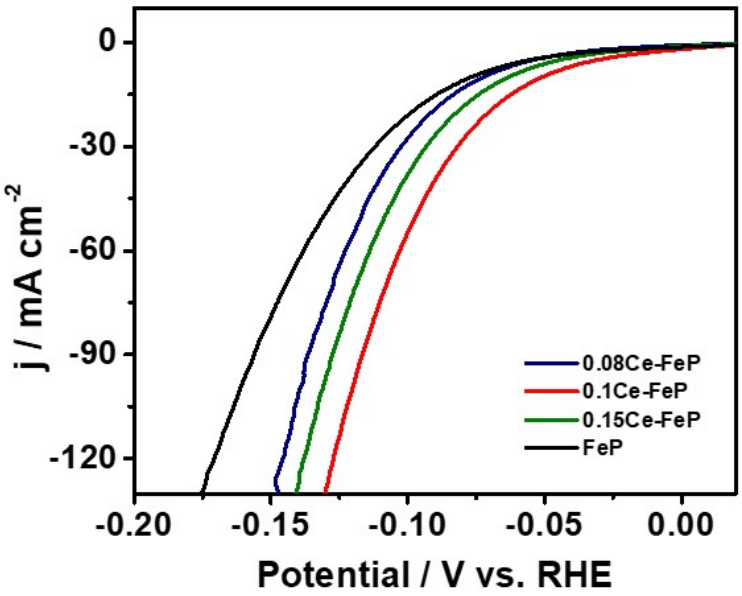


Figure s9. Polarization curves (with iR corrections) of Ce-FeP/CC with different Ce amounts and FeP/CC for HER in acid solution.

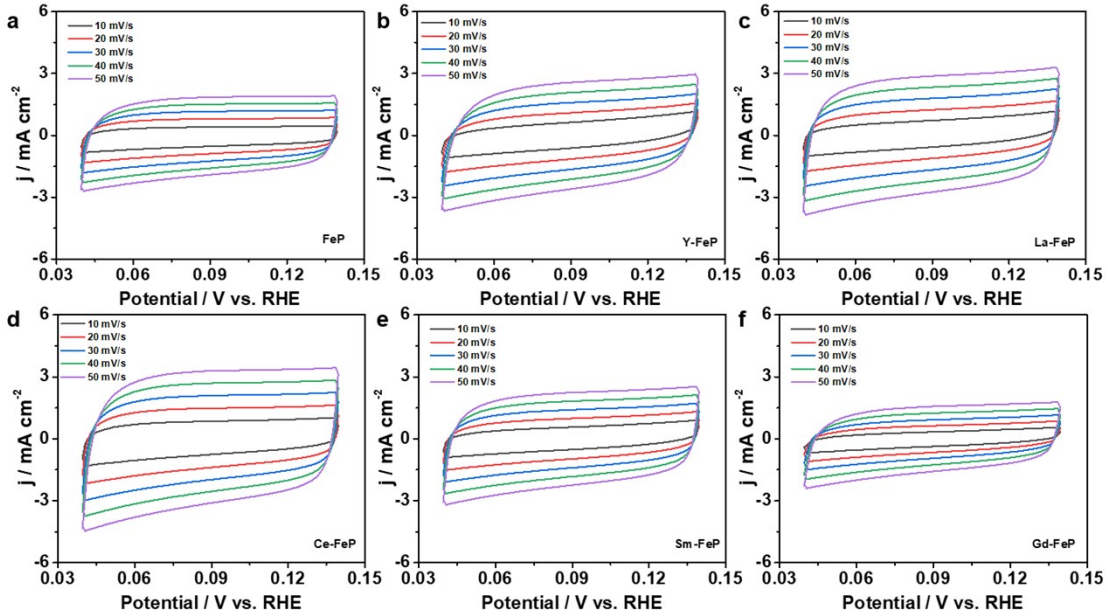


Figure s10. CV curves in 0.5 M H_2SO_4 for (a) FeP, (b) Y-FeP, (c) La-FeP, (d) Ce-FeP, (e) Sm-FeP, and (f) Gd-FeP with different scan rates.

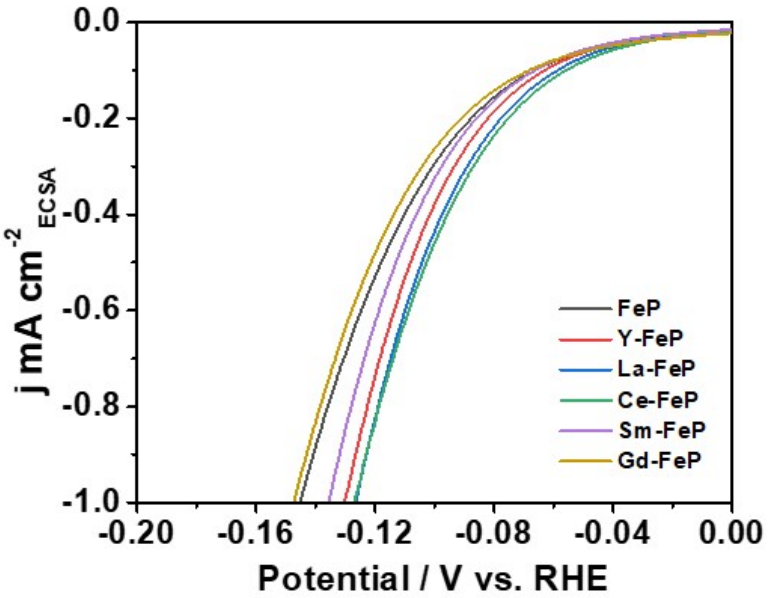


Figure s11. Normalized polarization curves based on ECSA results for FeP and RE-FeP samples in acidic solution.

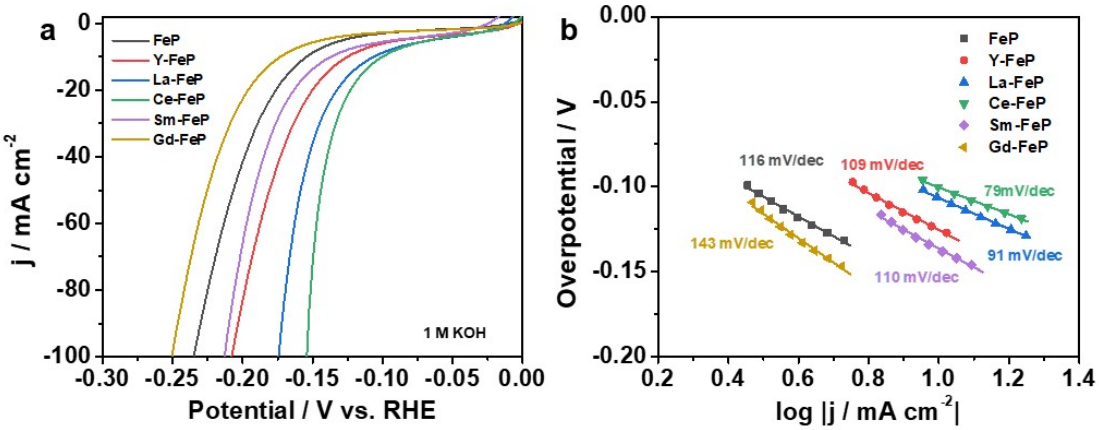


Figure s12. (a) Polarization curves, and corresponding (b) Tafel slopes for various RE-FeP in 1 M KOH solution.

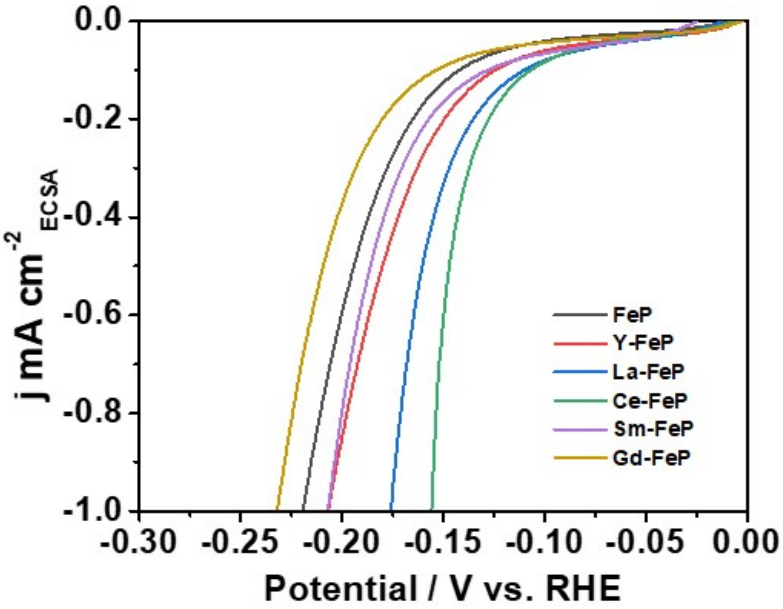


Figure s13. Normalized polarization curves based on ECSA results for FeP and RE-FeP samples in alkaline solution.

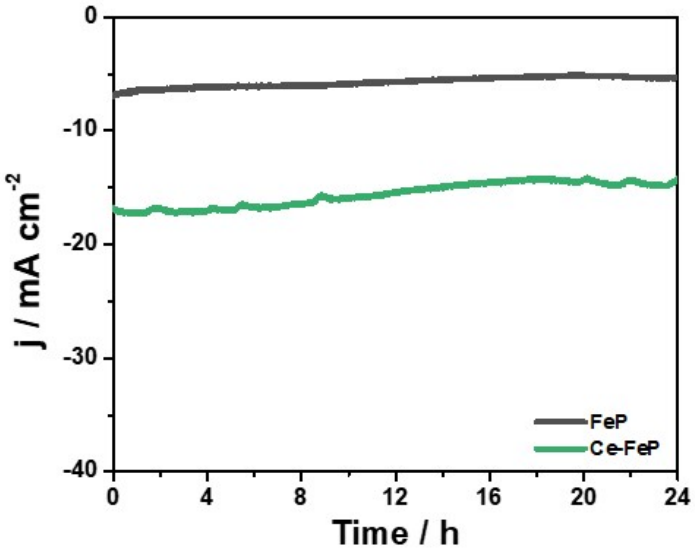


Figure s14. Stability test of Ce-FeP/CC and FeP/CC under the overpotential of 204 mV without iR corrections in 1 M KOH solution.

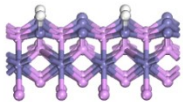
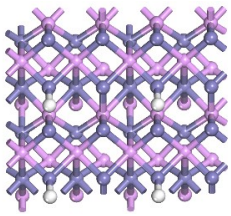
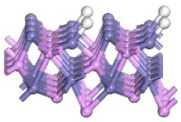
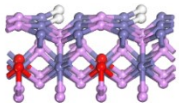
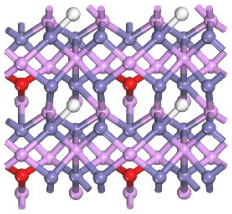
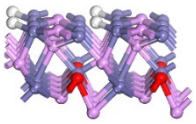
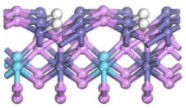
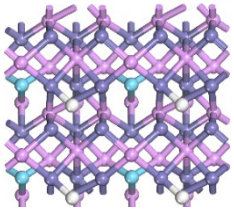
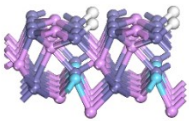
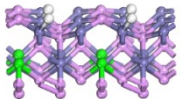
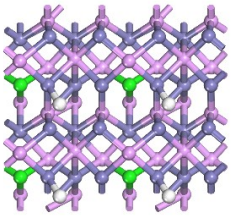
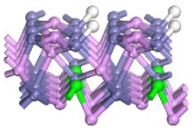
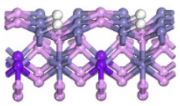
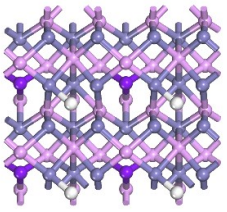
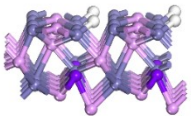
Table s1. ICP-AES result for RE-FeP to calculate the molar ratio of RE to Fe.

Sample	Concentration of Fe / umol/mL	Concentration of RE / umol/mL	Molar ratio of RE/(Fe+ RE)
Y-FeP	1.38	0.09	6.1%
La-FeP	1.0	0.076	7.1%
Ce-FeP	1.78	0.165	8.5%
Sm-FeP	1.24	0.125	9.2%
Gd-FeP	1.27	0.125	8.6%

Table s2. Comparison in HER activity for various Fe-based electrocatalysts.

Catalysts	Electrolyte	Overpotential @10mA cm^{-2}/mV	Reference
Ce-FeP/CC	0.5 M H_2SO_4	51	this work
Ce-FeP/CC	1 M KOH	100	this work
FeP	0.5 M H_2SO_4	79	Appl. Catal. B-Environ., 2020, 260, 118156
FeP	1 M KOH	95	Appl. Catal. B-Environ., 2020, 260, 118156
FeP@NPC	0.5 M H_2SO_4	75	Appl. Surf. Sci., 2022, 597, 153662
FeP@NPC	1 M KOH	109	Appl. Surf. Sci., 2022, 597, 153662
Carbon-shell-coated FeP	0.5 M H_2SO_4	71	J. Am. Chem. Soc., 2017, 139, 6669
FeP/C nanosheets	0.5 M H_2SO_4	51.1	Adv. Sci., 2019, 6, 1801490
FeP@PPy/CTs	0.5 M H_2SO_4	103.1	Chem. Eng. J., 2022, 433, 133643
Ni-doped FeP/C	0.5 M H_2SO_4	72	Sci. Adv., 2019, 5, eaav6009
Ni-doped FeP/C	1 M KOH	95	Sci. Adv., 2019, 5, eaav6009
MoO_2-FeP@C	1 M KOH	103	Adv. Mater., 2020, 32, 2000455
NF@NiFe LDH/CeO_x	1 M KOH	154	ACS Appl. Mater. Interfaces, 2018, 10, 35145
CeFeCoP/NF	1 M KOH	97	J. Solid State Chem., 2022, 314, 123434
Fe_xNi_y/CeO_2/NC	1 M KOH	240	Inorg. Chem. Front., 2020, 7, 470
Er-doped CoP/CC	0.5 M H_2SO_4	52	J. Mater. Chem. A, 2019, 7, 5769
Ce-doped NiFe-LDH	1 M KOH	147	Sustainable Energy Fuels, 2020, 4, 312

Table s3. Front view, overlook view, and side view for optimized structures of FeP-H and RE-FeP-H structure.

Sample	Front view	Overlook view	Side view
FeP			
Y-FeP			
La-FeP			
Ce-FeP			
Sm-FeP			
Gd-FeP