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Supplementary information

Constructing Ultrathin CoP nanomeshes by Er-doping for Highly Efficient Bifunctional Electrocatalyst for Overall Water Splitting

Gengwei Zhang,[a] Bin Wang,[a] Jinglei Bi,[a] Dangqi Fang,[,a] and Shengchun Yang[a,b]**

[a] *School of Science, Key Laboratory of Shaanxi for Advanced Materials and Mesoscopic Physics, State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an, 710049, People's Republic of China*

[b] *Collaborative Innovation Center of Suzhou Nano Science and Technology, Suzhou Academy of Xi'an Jiaotong University, 215000, Suzhou, People's Republic of China*

**Corresponding authors: ysch1209@mail.xjtu.edu.cn (S. Yang)*

Reagents and material

Cobalt nitrate and potassium hydroxide were obtained from Aladdin Industrial Corporation. Anhydrous ethanol and ethylene glycol (EG) were obtained from Sinopharm Chemical Reagent Co., Ltd. The water used throughout all experiments was purified through a Millipore system, and all chemical regents were analytical grade and without any further purification.

Characterizations

The morphology of the as-produced samples was characterized by scanning electron microscope (SEM, FEI Quanta, FEG 250, energy spectrum: EDAX, Apollo XL-SDD) at an acceleration voltage of 20 kV. The structural characterization further investigated by X-ray diffraction (XRD), which was performed on a Bruker-AXS D8 Advance diffractometer operated at 40 kV voltage and 30 mA current using Cu Kα radiation (λ = 1.5418 Å) in the range of 20-80°. Atomic force microscope (AFM) image was obtained on a Digital Instrument Nanoscope IIIA AFM. The surface structure of the samples was investigated through the X-ray photoelectron spectroscopy (XPS, Kratos Axis UL equipped with monochromatic Al Ka radiation, 150 W, 5 kV at 1486.6 eV, chamber pressure of 10-9 Torr) by referencing the spectra to the C 1s peak for the C-C bond at a binding energy of 284.8 eV. TEM image of the products was recorded on a JEOL JEM-2100 transmission electron microscope. The operation was performed at an accelerating voltage of 200 kV. The energy-dispersive X-ray spectroscopic (EDX) elemental mapping results were characterized by scanning transmission electron microscopy (STEM, JEOL ARM200F). Nitrogen adsorption/desorption isotherms were carried out at 77.3 K using a Micromeritics ASAP 2020M volumetric adsorption analyzer.

TOF calculation

TOF was calculated according to previous method.[1, 2] The turnover frequency (s^{-1}) can be estimated according to this equation:

TOF (s^{-1}) = $I/2nF$ (HER); TOF (s^{-1}) = $I/4nF$ (OER)

where I represents the current density for different samples during the LSV measurement in 1 M KOH, F is the Faraday constant (C/mol), and n is the number of the active sites (mol) for different samples. The number of active sites (n) was measured from CV curves within the potential range of -0.2 to 0.6 V (vs. RHE) at a scan rate of 50 mV/s in 1.0 M PBS (pH=7). n (mol) could be determined with the following equation

n (mol) = $Q/2F$ (HER); n (mol) = $Q/4F$ (OER)

Computational method

The calculations were carried out with the density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP)[3] The exchange-correlation functional was described within the generalized gradient approximation (GGA) parameterized by the Perdew-Burke-Ernzerhof (PBE)[4]. The cut-off energy for the plane wave basis was set to 400 eV. To better describe the electrocatalytic oxygen evolution reaction (OER) of β-CoOOH, we used Hubbard U correction to the 3d states of Co with U=3 eV[5, 6]. A vacuum region of 12 Å perpendicular to the surface was applied to avoid interaction between neighboring surfaces. Atoms were relaxed until the Hellmann-Feynman forces acting on them were less than 0.02 eV/Å.

The calculated lattice parameters for bulk CoP with Pnma space group were a=3.27 Å, b=5.06 Å and c=5.54 Å. The built 1×1 CoP (211) surface was shown in Fig. S17a. The calculated lattice parameters for β-CoOOH with RM space group were a=2.88 Å and c=13.02 Å. Oxygen-terminated β-CoOOH surface with 3×3 lateral cell was built as seen in Fig. S17b.

The adsorption free energy for adsorbates (ΔG_{ads}) in HER and OER can be calculated by the following equation:

$$\Delta G_{ads} = \Delta E_{ads} + \Delta E_{ZPE} - T\Delta S$$

where ΔE_{ads} is the adsorption energy of adsorbates, and T is temperature. ΔE_{ZPE} and ΔS are the energy difference in zero point energy and entropy, respectively. The hydrogen adsorption free energy (ΔG_{H*}) is expressed as $\Delta G_{H*} = \Delta E_{H*} + \Delta E_{ZPE} - T\Delta S$. the ΔE_{H*} can be calculated from $\Delta E_{H*} = E(H*) - E(*) - 1/2E_{H2}$, where E(H*) and E(*) are the DFT energies of the given surface with and without H adsorption respectively and $E(H_2)$ is the DFT energy of a molecular H_2 in gas phase. OER activity is evaluated by the following four elementary steps.

(1) $H_2O + * \rightarrow HO* + H^+ + e^-$

$\Delta G_1 = \Delta G_{OH*}$

(2) $HO* \rightarrow O* + H^+ + e^-$

$\Delta G_2 = \Delta G_{O*} - \Delta G_{OH*}$

(3) $O* + H_2O \rightarrow HOO* + H^+ + e^-$

$\Delta G_3 = \Delta G_{OOH*} - \Delta G_{O*}$

(4) $HOO^* \rightarrow * + O_2 + H^+ + e^-$

$\Delta G_4 = 4.92 - \Delta G_{OOH^*}$

The theoretical overpotentials (η) for OER can be calculated by the following equations:

$G_{OER} = \max \{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\}$

$\eta = G_{OER} /e - 1.23\ V$

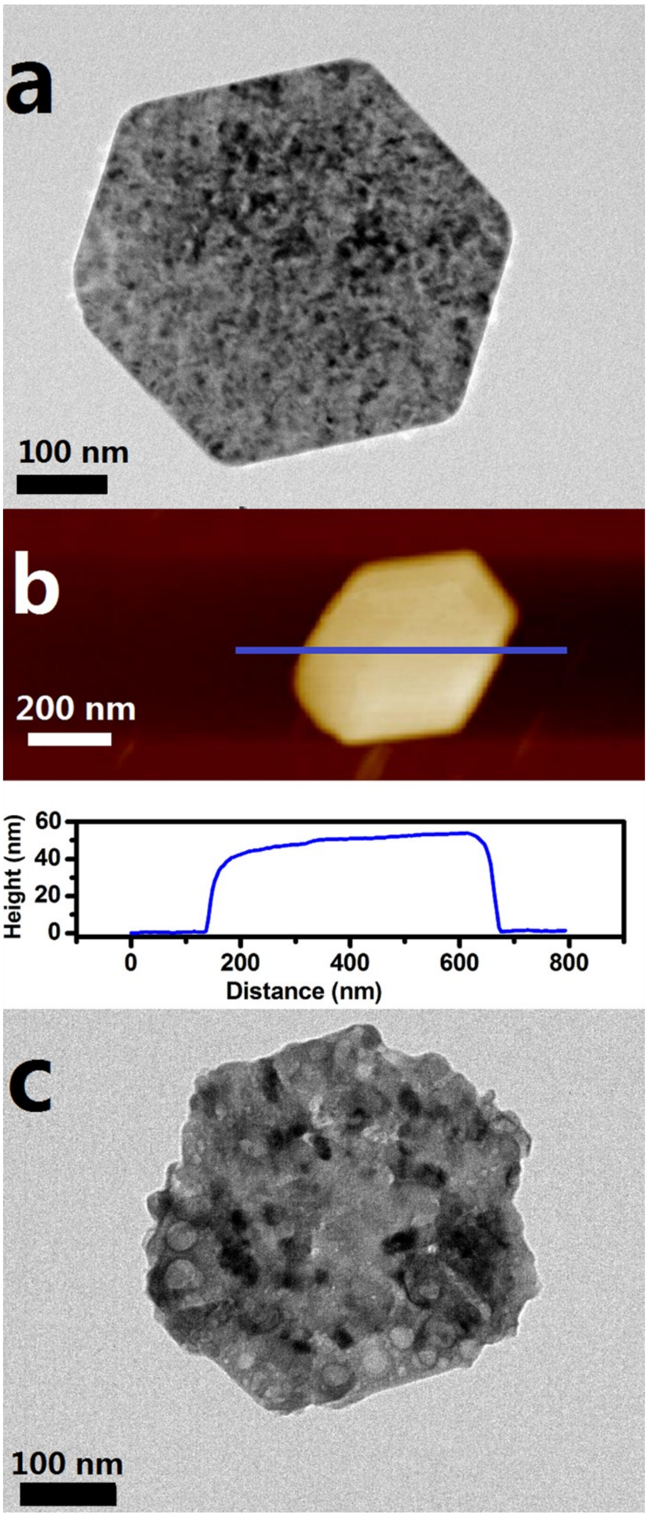

Fig. S1. (a) TEM and (b) AFM images of the Co(OH)2 nanoplate. (c) TEM image of the CoP nanoplate.

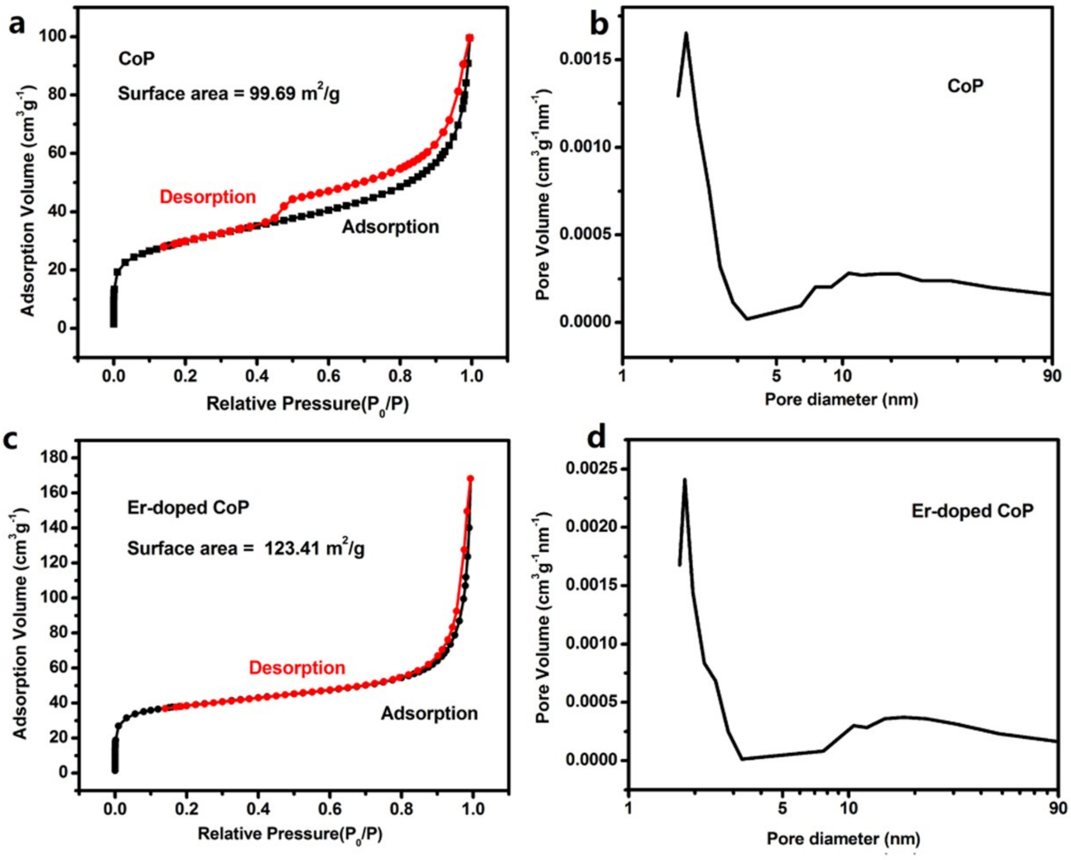

Fig. S2. Nitrogen adsorption and desorption isotherms and corresponding pore size distribution curve of CoP (a, b) and Er-doped CoP (c, d).

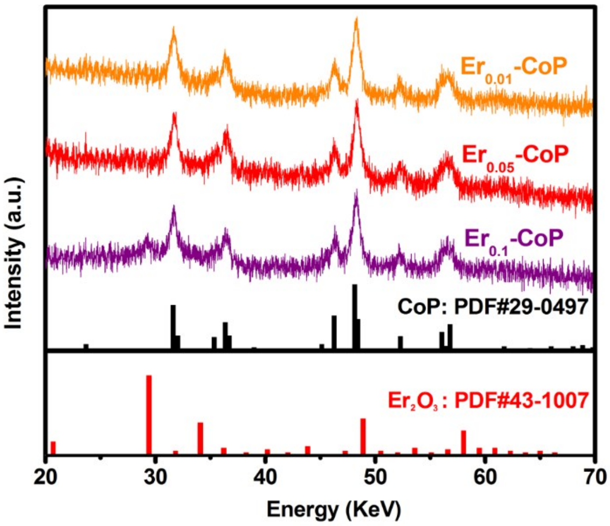

Fig. S3. XRD patterns of Er-doped CoP with Er:Co ratios 0.01, 0.05 and 0.1 respectively.

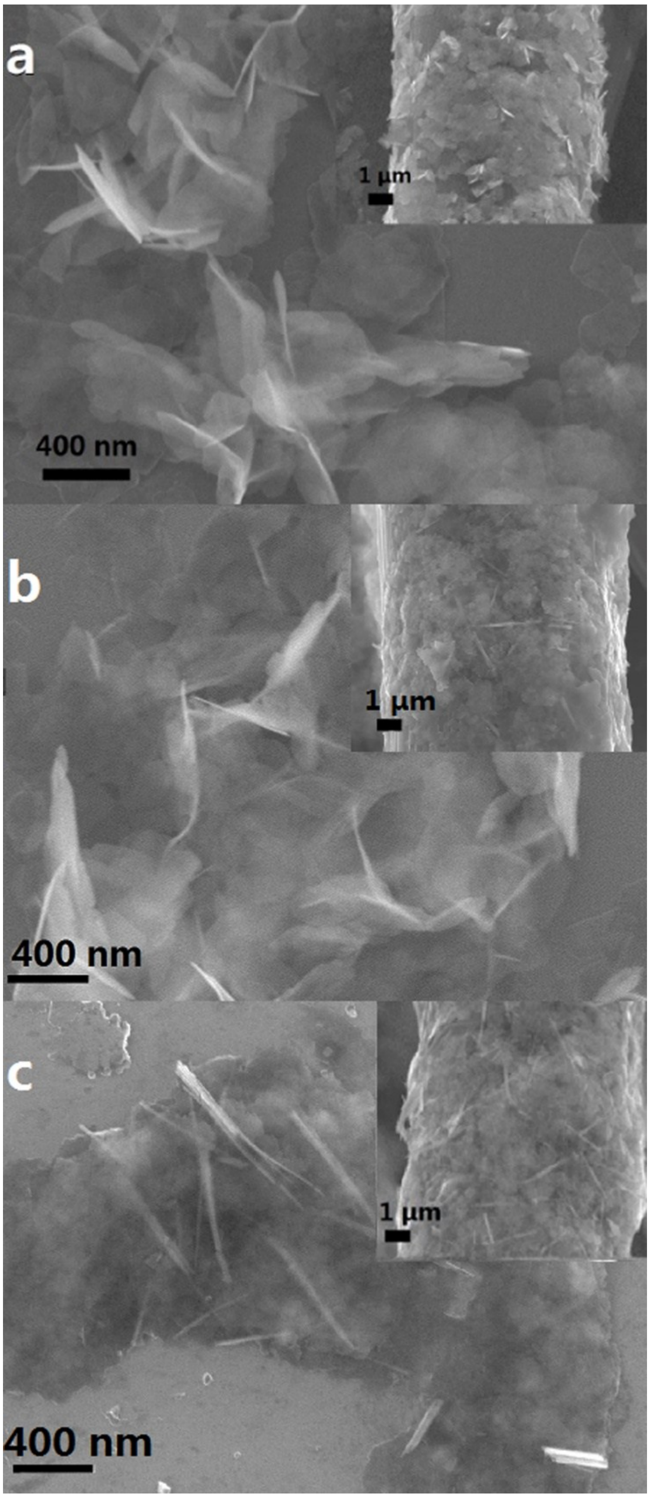

Fig. S4. SEM images of the Er-doped $Co(OH)_2$ and corresponding phosphide supported on CC (inset) with an Er:Co ratios of 0.01 (a), 0.05 (b) and 0.1 (c) respectively.

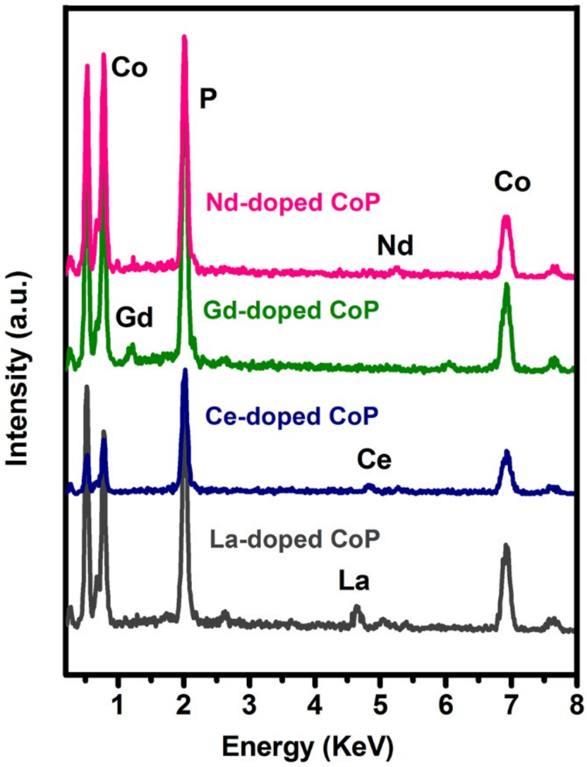

Fig. S5. EDX spectrums of Nd, Gd, Ce and La doped CoP.

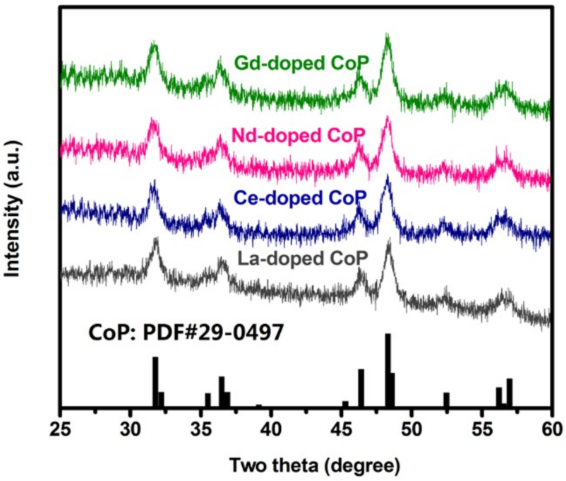

Fig. S6. XRD patterns of Er, Nd, Gd, Ce and La doped CoP.

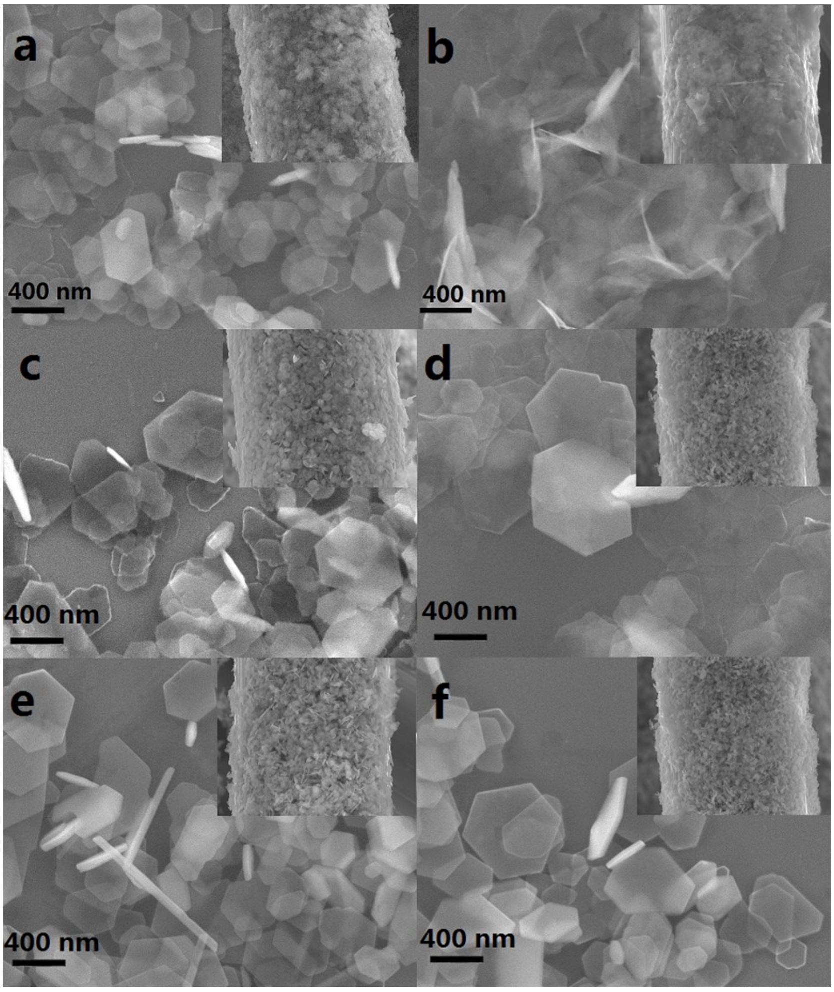

Fig. S7. SEM images of $Co(OH)_2$ (a), Er (b), Ce(c), Gd (d), La (e), Nd (f) doped $Co(OH)_2$ and corresponding phosphide supported on CC (inset).

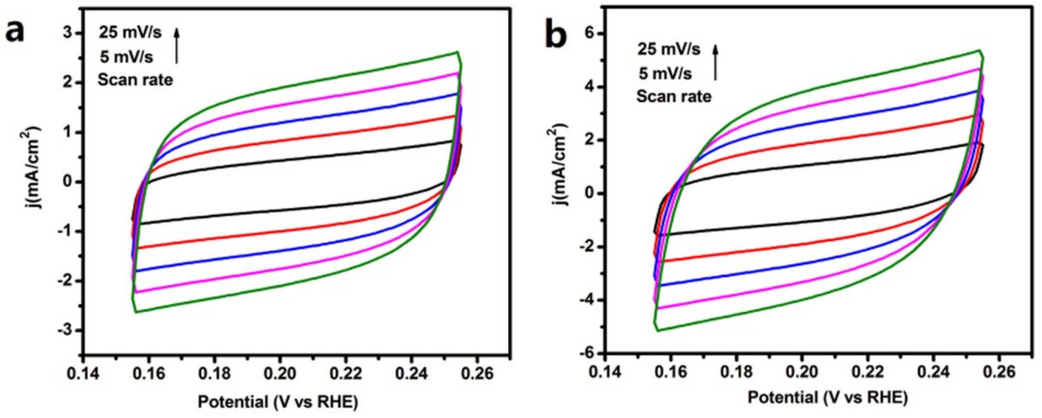

Fig. S8. CV curves of CoP (a) and Er-doped CoP (b) with various scan rates in 1.0 M KOH solutions.

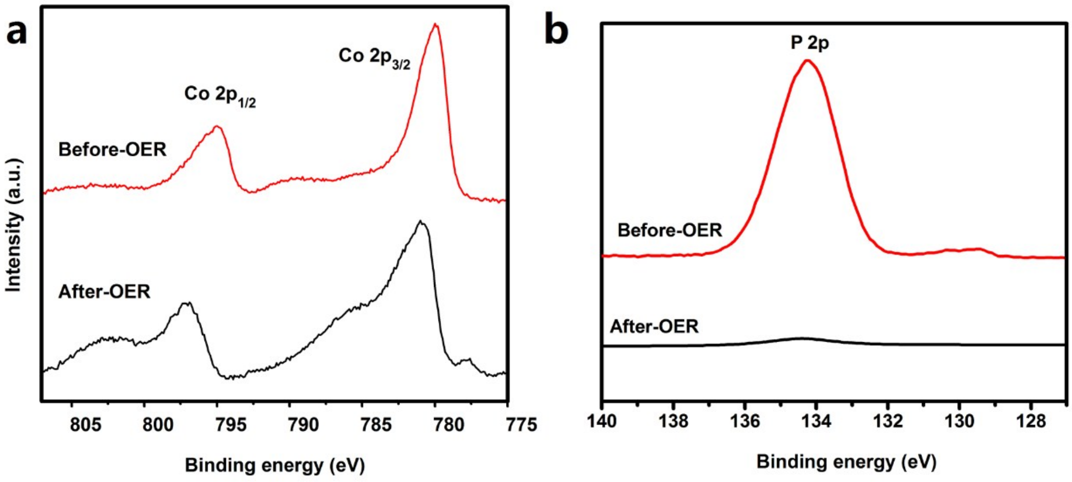

Fig. S9. XPS spectra of (a) Co core level spectra and (b) P 2p core level spectra of Er-doped CoP before and after OER test.

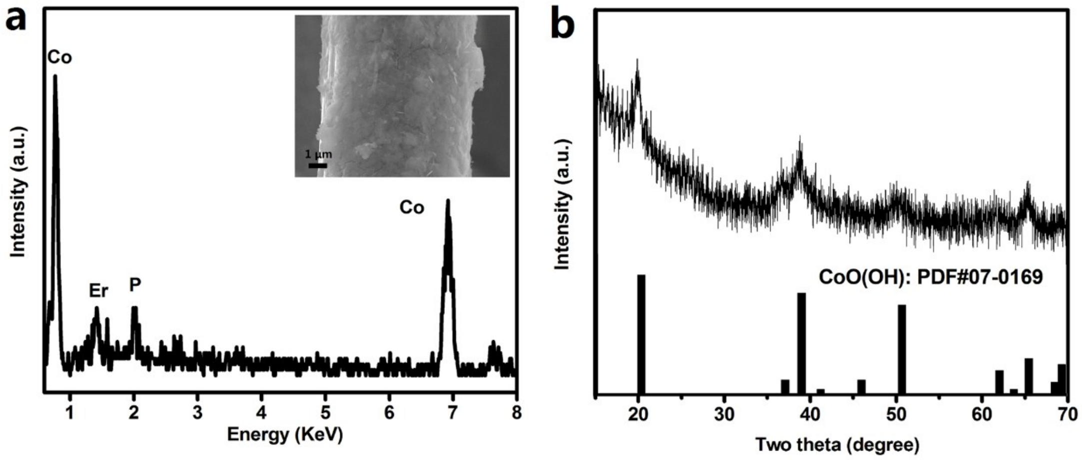

Fig. S10. EDX spectra (a), SEM image (b) and XRD pattern of Er-doped CoP after the OER stability test.

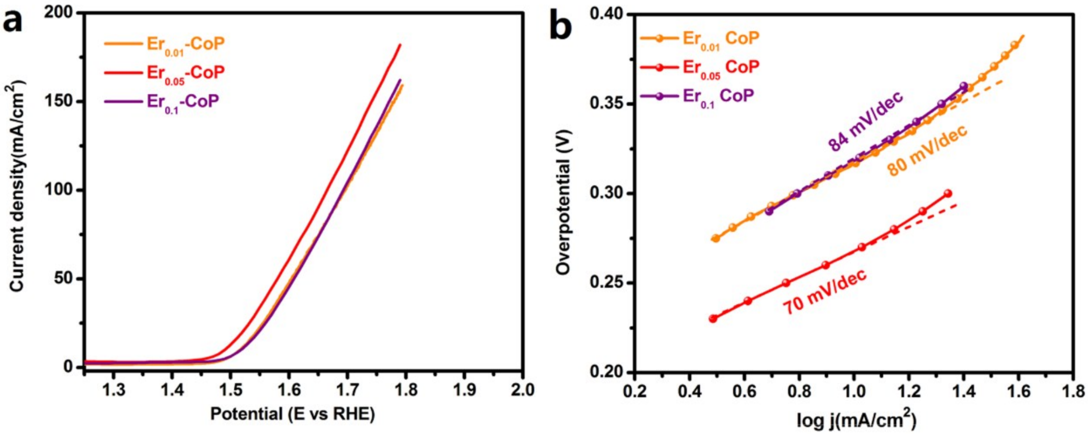

Fig. S11. Polarization curve of $Er_{0.01}$ CoP, $Er_{0.05}$ CoP and $Er_{0.1}$ CoP recorded in 1.0 M KOH.

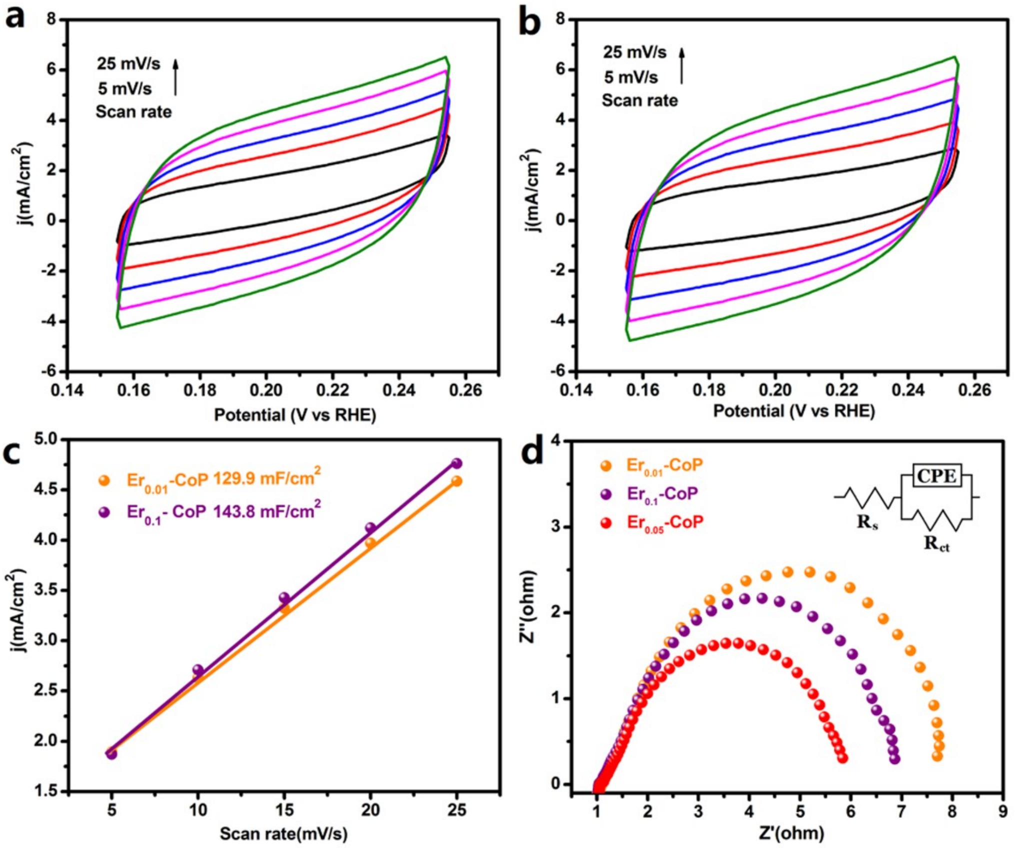

Fig. S12. CV curves of Er$_{0.01}$-CoP (a) and Er$_{0.1}$-CoP (b) with various scan rates in 1.0 M KOH. (c) Corresponding double layer capacitances (C_{dl}). (d)Nyquist plots for Er$_{0.01}$-CoP, Er$_{0.05}$-CoP and Er$_{0.1}$-CoP in 1.0 M KOH.

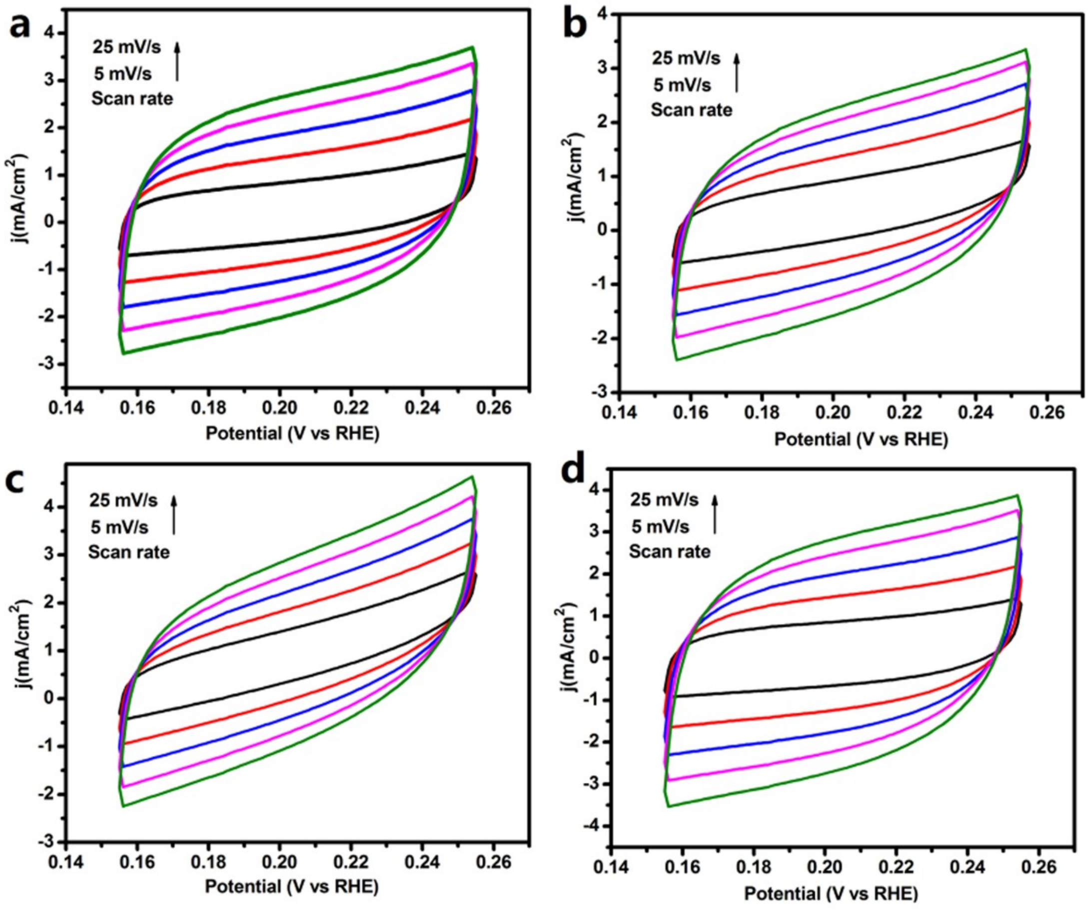

Fig. S13. CV curves of Ce (a), Gd (b), La (c) and La-doped CoP (d) with various scan rates in 1.0 M KOH solutions.

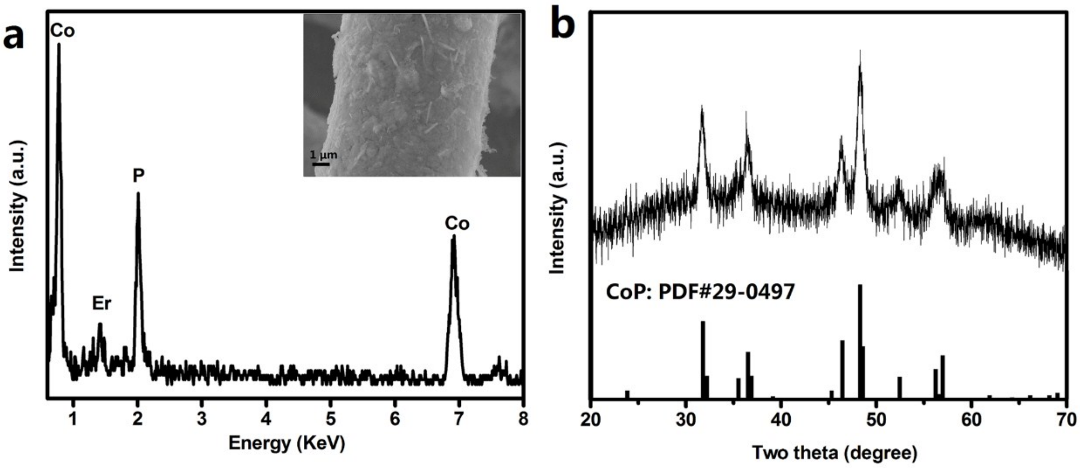

Fig. S14. EDX spectra (a), SEM image (a, inset) and XRD pattern (b) of Er-doped CoP after the HER stability test.

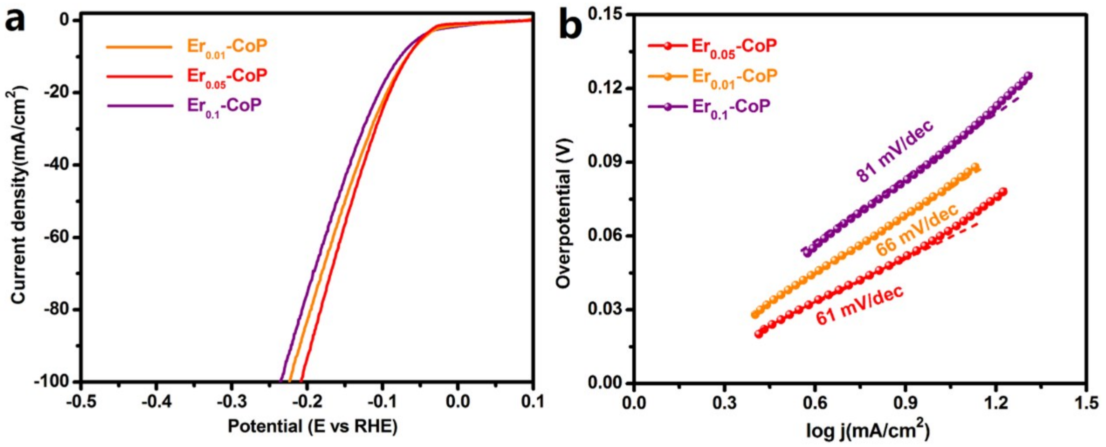

Fig. S15. Polarization curve of $Er_{0.01}$-CoP, $Er_{0.05}$-CoP and $Er_{0.1}$-CoP recorded in 1.0 M KOH.

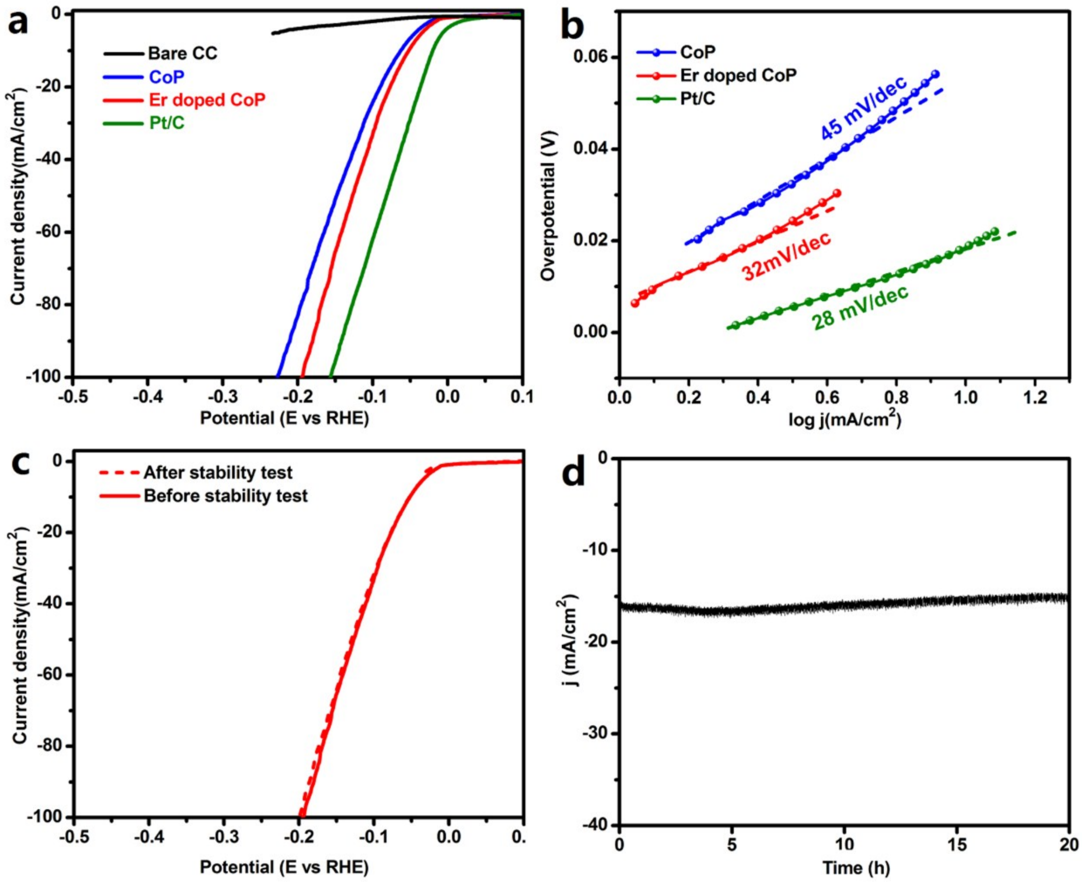

Fig. S16. Polarization curves (a) and corresponding Tafel curves (b) of bare CC, CoP, Er-doped CoP and Pt/C in 0.5 M H_2SO_4. (c) HER cycling stability of Er-doped CoP.

(d) Long-term electrochemical durability of Er-doped CoP for HER for 20 h.

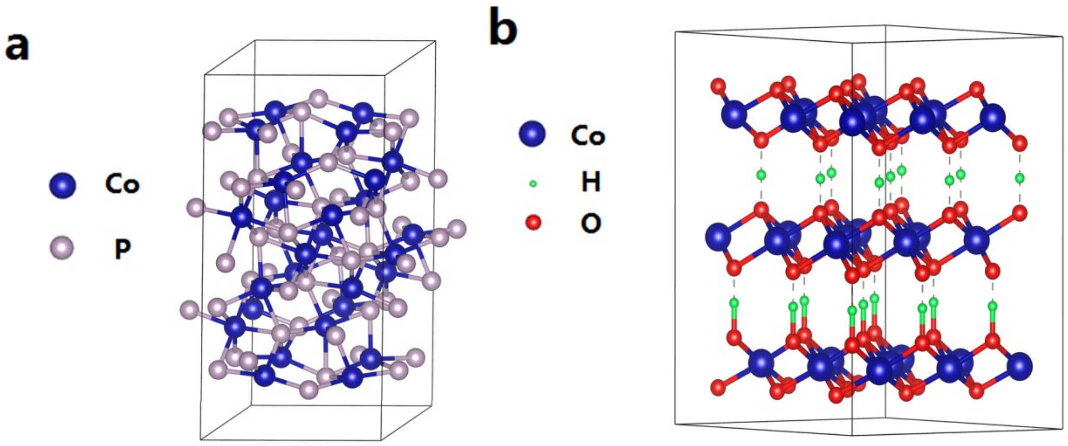

Fig.S17. (a) Side view of the CoP (211) surface. (b) Side view of the CoOOH (001) surface.

Table. S1. The elemental compositions of RE-doped CoP samples obtained by EDS analysis.

Sample	P (at. %)	Co (at. %)	RE (at. %)
CoP	51.70	48.30	
Er-CoP	49.01	48.24	2.76
Gd-CoP	46.66	51.23	2.21
Ce-CoP	51.33	46.31	2.36
La-CoP	46.75	50.55	2.70
Nd-CoP	50.08	47.79	2.13
Er$_{0.\ 1}$-CoP	46.21	47.91	5.88
Er$_{0.01}$-CoP	51.03	48.44	0.53

Supporting References

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