## **Electronic Supplementary Information**

## **Experimental section**

**Materials:**  $Co(NO_3)_2 \cdot 6H_2O$ ,  $Ce(NO_3)_3 \cdot 6H_2O$ ,  $CO(NH_2)_2$ , KOH (90%), purified KOH (99.9%) and NaH<sub>2</sub>PO<sub>2</sub> were purchased from Aladdin Ltd. (Shanghai, China). Pt/C (10 wt% Pt) was purchased from Alfa Aesar (China) Chemicals Co. Ltd. Nafion (5 wt%) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. All chemicals were used as received without further purification. Ti mesh was purchased from Phychemsi Hong Kong Company Limited and was cleaned by sonication sequentially in acetone, water and ethanol several times to remove the surface impurities. The water used throughout all experiments was purified through a Millipore system.

Synthesis of  $Co_3O_4$ -CeO<sub>2</sub>/Ti, CoP-CeO<sub>2</sub>/Ti and CoP/Ti: In a typical synthesis process,  $Co(NO_3)_2 \cdot 6H_2O(1.019 \text{ g})$ ,  $Ce(NO_3)_3 \cdot 9H_2O(0.76 \text{ g})$ , and  $CO(NH_2)_2(1.051 \text{ g})$ were dissolved in deionized water (100 mL). After continuously stirring for 30 min, the solution was then transferred to a 50 mL Teflon-lined stainless steel autoclave with a piece of Ti mesh (2 cm × 3 cm). Then autoclave was sealed and maintained at 120 °C for 10 h in an oven. After the autoclave cooled down to room temperature, the sample was taken out and thoroughly washed with deionized water and ethanol several times alternatively, then dried at 60 °C for 6 h in air. After that, the sample was calcinated at 350 C for 2 h and grey  $Co_3O_4$ -CeO<sub>2</sub> was obtained. Next, the  $Co_3O_4$ -CeO<sub>2</sub>/Ti was placed in an alumina boat and the other alumina boat containing 700 mg NaH<sub>2</sub>PO<sub>2</sub> was placed at the upstream of the tube furnace. The two alumina boats were calcined at 300 °C for 2 h with a heating speed of 2 °C min<sup>-1</sup> under Ar flow and then cooled down to room temperature naturally. CoP/Ti were made under identical conditions with no cerium salts added for hydrothermal preparation.

**Characterizations:** XRD measurements were performed using a LabX XRD-6100 Xray diffractometer with Cu K $\alpha$  radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan). SEM measurements were carried out on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM images were collected on a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. To study the water adsorption of catalyst in the electrolyte, CoP and CoP-CeO<sub>2</sub> were immersed in 1.0 M KOH for 60 min before XPS analysis. XPS measurements were performed using an ESCALABMK II X-ray photoelectron spectrometer with the exciting source of Mg. ICP-AES analysis was performed on ThermoScientific iCAP6300. TG curves were collected on a TG 208F1 Iris (Netzsch, German) from 30 to 370 °C with the ramp rate of 5°C/min under N<sub>2</sub> atmosphere. FT-IR spectra were acquired on a Perkin-Elmer 580B spectrophotometer (Perkin-Elmer, United States).

**Electrochemical measurements:** Electrochemical measurements were performed with a CHI660E potentiostat (CH Instruments, China) in a standard three-electrode setup, with the use of CoP-CeO<sub>2</sub>/Ti as the working electrode, a graphite rod as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The KOH electrolyte was purged with Ar for 30 min before measurements. In all measurements, SCE was calibrated with respect to RHE as following: in 1.0 M KOH aqueous solution, E(RHE) = E(SCE) + 1.068 V. The presented current density referred to the geometrical area of the Ti mesh.

To acquire the electrochemical active surface areas (ECSAs) of CoP-CeO<sub>2</sub>/Ti, CoP/Ti, and CeO<sub>2</sub>/Ti, the roughness factors were firstly determined according to the equation: ECSA =  $R_f \times S$ , where S is the geometric area of electrode (here S is 1 cm<sup>2</sup>). The  $R_f$ was determined by  $R_f = C_{dl}/40 \ \mu F \ cm^{-2}$  based on the double-layer capacitance (C<sub>dl</sub>) of a smooth oxide surface (60  $\mu F \ cm^{-2}$ ).<sup>1,2</sup>

TOF values were calculated according to the previous work<sup>2</sup>

TOF = FE determination: The amount of hydrogen evolved from the cathode was measured in air-tight H-cell with a gas chromatograph (Shimadzu, GC-2014). The Faradaic efficiency was calculated by comparing the amount of experimentally detected hydrogen with the theoretically calculated hydrogen.

**Computational methods:** Spin-polarized density functional theory calculations were performed using the Vienna ab initio simulation package (VASP).<sup>3-5</sup> We used the PBE functional for the exchange-correlation energy<sup>6</sup> and projector augmented wave (PAW) potentials.<sup>7,8</sup> The kinetic energy cutoff was set to 450 eV. The ionic relaxation

was performed until the force on each atom is less than 0.01 eV Å<sup>-1</sup>. The k-points meshes were  $2 \times 2 \times 1$  with Monkhorst-Pack method.<sup>9</sup> The climbing image nudged elastic band (cNEB)<sup>10</sup> method was used to examine the energy profiles along selected pathways for H<sub>2</sub>O dissociation. In order to evaluate the on-site Coulomb interaction in the 4f states of CeO<sub>2</sub>, we also implemented the DFT+U approach with a Hubbard parameter U=5.0 eV.

In order to build the CoP/CeO<sub>2</sub> interface, one CoP(211) layer was placed on the 3layer CeO<sub>2</sub>(111) slab. The free energy change for H\* adsorption on CoP(211) surface and CoP/CeO<sub>2</sub> interface ( $\Delta G_{\rm H}$ \*) was calculated as follows, which is proposed by Norskov and coworkers:<sup>11</sup>

$$\Delta G_{H^*} = E_{total} - E_{surf} - E_H^2/2 + \Delta E_{ZPE} - T\Delta S$$

where  $E_{total}$  is the total energy for the adsorption state,  $E_{surf}$  is the energy of pure surface,  $E_{H}^2$  is the energy of  $H_2$  in gas phase,  $\Delta E_{ZPE}$  is the zero-point energy change and  $\Delta S$  is the entropy change.



Fig. S1. EDX spectrum of CoP-CeO<sub>2</sub>/Ti.



Fig. S2. TG curves of CoP, CeO<sub>2</sub> and CoP-CeO<sub>2</sub>.



Fig. S3. FT-IR spectra of CoP, CeO<sub>2</sub> and CoP-CeO<sub>2</sub>.



Fig. S4. (a) XRD pattern for CoP. (b) SEM image for CoP/Ti.



Fig. S5. (a) XRD pattern for  $CeO_2$ . (b) SEM image for  $CeO_2/Ti$ .



Fig. S6. LSV curve for Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub>/Ti for HER in 1.0 M KOH.

Catalyst	<i>j</i> (mA cm <sup>-2</sup> )	Overpotential (mV)	Ref.
CoP-CeO <sub>2</sub> /Ti	10	43	This work
MoP <sub>2</sub> /CC	10	67	12
Ni <sub>0.33</sub> Co <sub>0.67</sub> S <sub>2</sub>	10	88	13
NiFe LDH/NF	10	92	14
NiMo HNRs/TiM	10	92	15
NiS nanoframes	10	94	16
NiSe/NF	10	96	17
$(CoP)_x$ - $(FeP)_{1-x}$	10	97	18
Ni/NiO-CNT	10	100	19
NiP <sub>2</sub> NS/CC	10	102	20
a-CoSe/Ti	10	121	21
HNDCM-Co/CoP	10	135	22
MoC <sub>x</sub>	10	151	23
O-Co <sub>2</sub> P-3	10	160	24
FeP NAs/CC	10	218	25
CoO <sub>x</sub> /CN	10	232	26

**Table S1.** Comparison of CoP-CeO<sub>2</sub>/Ti and other non-noble-metal catalysts for HER performance in 1.0 M KOH.



Fig. S7. LSV curves CoP-CeO<sub>2</sub> on Ti mesh with different atomic ratios of Ce/Co.



**Fig. S8.** (a) LSV and (b) chronopotentiometry curve for CoP-CeO<sub>2</sub>/Ti for HER in 1.0 M purified KOH.



**Fig. S9.** Polarization curves for CoP-CeO<sub>2</sub>/Ti and CoP/Ti before and after 1000 CV cycles.



**Fig. S10.** (a) SEM images of CoP-CeO<sub>2</sub>/Ti and (b) HRTEM image of CoP-CeO<sub>2</sub> after stability test.



Fig. S11. SEM image of CoP/Ti after stability test.

**Table S2.** ICP-AES data for the electrolyte after stability test.

Co (mg/L)	Ce (mg/L)	P (mg/L)
0.28	0.36	0.57



Fig. S12. XPS spectra of CoP-CeO<sub>2</sub> after stability test.



Fig. S13. Chronopotentiometry curves for CoP-CeO<sub>2</sub>/Ti and CoP/Ti in 1.0 M KOH.



Fig. S14. Theoretically calculated and experimentally detected amount of hydrogen versus time for the CoP-CeO<sub>2</sub>/Ti at the overpotential of 80 mV.



**Fig. S15.** Chronopotentiometry curves for CoP-CeO<sub>2</sub>/Ti and CoP/Ti in 1.0 M KOH in a two-compartment cell.



Fig. S16. Cyclic voltammograms for (a) CoP-CeO<sub>2</sub>/Ti, (b) CoP/Ti and (c) CeO<sub>2</sub>/Ti. (d) The calculated  $C_{dl}$  of CoP-CeO<sub>2</sub>/Ti, CoP/Ti and CeO<sub>2</sub>/Ti.



Fig. S17. ECSA normalized LSV curves for CoP-CeO<sub>2</sub>/Ti and CoP/Ti.



Fig. S18. TOF curves for CoP-CeO<sub>2</sub>/Ti and CoP/Ti.

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