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## **Supporting Information**

## Universal synthesis of rare earth-doped FeP nanorod arrays for hydrogen evolution reaction

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## **Experimental section**

#### Reagents and chemicals

All the reagents were of analytical reagent grade and used without further purification. Iron (III) chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O) was supplied by Macklin Biochemical Co. Ltd. (Shanghai, China). Samarium (III) chloride (SmCl<sub>3</sub>) was brought from Aladdin Ltd. (Shanghai, China). Sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), and Glycine were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Commercial Ruthenium oxide (RuO<sub>2</sub>) and 20% Pt/C were obtained from Johnson Matthey Corporation. All the water used in the experimental section was deionized.

## Preparation of FeO(OH)@CC

The FeO(OH)@CC was prepared via a facile hydrothermal method. Briefly, 1.2 mmol (0.324 g) FeCl<sub>3</sub>·6H<sub>2</sub>O and 4 mmol (0.568 g) Na<sub>2</sub>SO<sub>4</sub> were dissolved in 40 mL of deionized (DI) water and mixed uniformly by ultrasound to obtain a red clarification solution. Subsequently, the above mixture and a piece of nitric acid-treated carbon cloth ( $2 \times 4 \text{ cm}^2$ ) were sealed in a Teflon-lined steel autoclave and heated at 120 °C for 8 h in an oven. After cooling down to room temperature, the as-fabricated FeO(OH)@CC was washed several times with ethanol and deionized water.

## Preparation of Sm-FeP@CC and FeP@CC

For the synthesis of Sm-FeP@CC, a piece of FeO(OH)@CC was first exposed to the energetic Ar plasma at the power of 60 W for 3 min. Subsequently, the as-treated FeO(OH)@CC was immersed into 30 mL 0.003 mol  $L^{-1}$  SmCl<sub>3</sub> and 1 wt% glycine mixed water solution and then transferred into a Teflon-lined steel autoclave at 80°C for 60 min. Subsequently, the as-treated carbon cloth was dried at room temperature and finally annealed at 350 °C for 30 min in an Ar atmosphere to obtain Sm-FeP@CC. For comparison, the FeP@CC was also synthesized with a similar procedure without SmCl<sub>3</sub> and glycine solution.

### Characterization

X-ray diffraction (XRD) was operated by a D/max-rC X-ray diffractometer (Cu Ka radiation,  $\lambda = 1.5406$  Å). Scanning electron microscopy (SEM) images were captured by JEOL JSM7500F. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), high angle annular dark-field scanning TEM (HAADF-STEM), and energy dispersive X-ray spectroscopy (EDS) elemental mapping/line scan were acquired through JEOL JEM-2100F with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was carried out on Thermo VG Scientific ESCALAB 250 spectrometer with an Al Ka light source. Electron spin resonance (ESR) spectra were recorded using Bruker A300-10 at 77 K.

### Electrochemical measurements

All electrochemical measurements were tested on a CHI 760E electrochemical workstation by a typical three-electrode system in 1.0 M KOH solution at room temperature. The catalyst-modified carbon cloth with a geometric area of  $1 \times 1$  cm<sup>2</sup> was employed as the working electrode, while a carbon rod and a saturated calomel electrode (SCE) were used as the auxiliary electrode and the reference electrode, respectively. The potential was operated to the reversible hydrogen electrode (RHE) by following the Nernst equation:  $E_{RHE} = E_{SCE} + 0.0592 \times pH + 0.242$ . The overpotential ( $\eta$ ) was calculated according to the following formula:  $\eta = E_{RHE} - 1.23$  V. The HER activity of catalysts was evaluated by the linear sweep voltammetry (LSV) with a scan rate of 5 mV s<sup>-1</sup> between -0.9 and -1.6 V *vs.* SCE. All data presented were corrected for iR loss. Faradaic Efficiency was calculated H<sub>2</sub>. Theoretically, it will take 300 s to produce 1.52 ml hydrogen at 20 mA (the molar volume of gas is 24.5 L mol<sup>-1</sup> at 25 °C). The electrochemical double-layer capacitances (Cdl) were converted through a series of CV tests (scan rate: 2-10 mV s<sup>-1</sup>). The ECSA of catalysts have been calculated via the following equation:

$$ECSA = \frac{C_{dl}}{40 \ \mu F \ cm^{-2} \ per \ cm^2}$$

The electrochemical impedance spectroscopy (EIS) was obtained over a scanning frequency range of 0.01 Hz to 100 kHz at -1.17 V.

### Theoretical calculation

Spin-polarized density functional theory (DFT) calculations were investigated via Vienna ab initio Simulation Package (VASP).<sup>1, 2</sup> The exchange-correlation term in the Hamiltonian operator is described by the generalized gradient approximation (GGA) method<sup>3</sup> with the revised Perdew-Burke-Ernzerhof (RPBE) functional developed by Nørskov et al.<sup>4</sup> The interaction between the ionic state and core electrons was described by the projector augmented wave (PAW) method.<sup>5, 6</sup> The behavior of valence electrons was described by expanding the Kohn-Sham wavefunctions in the plane-wave basis set. Therefore, the energy cutoff for the plane-wave basis set was set to 500 eV. The convergence for the forces of each atom is lower than 0.03 eV/Å, while the electronic self-consistency is below  $10^{-5}$  eV. The *k*-point sampling for the first Brillouin zone accepts the Monkhorst Pack method<sup>7</sup> with the density of 5×5×1 for the slab model. The van deer Waals dispersion correction is DFT-D3 method provided by Grimme et al with Becke-Johnson damping function.<sup>8</sup> To describe the strong on-site Coulombic interaction of 3d and 4f electrons, the Hubbard model was used according to Dudarev et al<sup>9</sup>, where the effective U values (Ueff) for Fe and Sm are 3 eV and 6 eV respectively. The computational hydrogen electrode (CHE) proposed by Nørskov et al<sup>10</sup> was used to calculate the free energy of electrochemical hydrogen evolution progress. The correction for the free energy of \*H follows G(\*H) = E(\*H) + 0.24eV according to Nørskov et al.11

# Fig.s and Tables



**Fig. S1** (a) XRD pattern of Sm-FeP and FeP without CC, (b) XRD patterns comparison of (211) facet: Sm-FeP and FeP without CC.



Fig. S2 XRD pattern of FeO(OH)@CC catalyst.



Fig. S3 EDS spectrum of Sm-FeP@CC.



Fig. S4 XPS survey spectrum of Sm-FeP@CC.



Fig. S5 Sm 3d XPS spectra comparison of Sm-FeP@CC and Sm<sub>2</sub>O<sub>3</sub>.



Fig. S6 SEM images of FeO(OH)@CC.



Fig. S7 SEM images of FeP@CC.



Fig. S8 Digital micrograph of a sealed assembly of drainage gas gathering system.



Fig. S9 I-t curve of FeP@CC.



Fig. S10 SEM images of Sm-FeP@CC after the stability test.



**Fig. S11** (a) XPS survey spectrum of Sm-FeP@CC after the stability test; (b) Fe 2p XPS spectra comparison of the initial and recovered Sm-FeP@CC.



**Fig. S12** CVs at different sweeping rates from 2 mV s<sup>-1</sup> to 10 mV s<sup>-1</sup> of (a) Sm-FeP@CC, (b) FeP@CC and (c) FeO(OH)@CC.



Fig. S13 PDOS of Fe-3d, P-3p and O-2p in FeP (011) + (\*H + \*OH).



Fig. S14 The optimized H<sub>2</sub>O adsorption configuration at Sm-FeP surface.



Fig. S15 I-t curves of Sm-FeP@CC || RuO<sub>2</sub>-based electrolyzer and FeP@CC || RuO<sub>2</sub>-based electrolyzer.



**Fig. S16** SEM images and element mapping profiles of (a) Yb-FeP@CC, (b) Eu-FeP@CC, (c) La-FeP@CC and (d) Er-FeP@CC.

Catalysts	η10	Tafel slope	Reference
	(mV)	(mV dec <sup>-1</sup> )	
Sm-FeP@CC	71	85.9	This work
Mn–FeP	173	95	ACS Sustainable Chem. Eng. 2019, 7, 12419.
N–FeP	226	84.8	Appl. Surf. Sci. 2020, <b>507</b> , 145096.
NiFe/NiCo <sub>2</sub> O <sub>4</sub> /NF	105	88	Adv. Funct. Mater. 2016, 26, 3515.
Fe-NiO/NF	183	105.5	Nano Energy. 2019, 66, 104118.
Fe-NC	347	128	Carbon. 2019, 146, 671.
(Ni, Fe)S2@MoS2	130	101.22	Appl Catal. B Environ. 2019, 247, 107.
Fe-Co <sub>2</sub> P BNRs	156	90	J Energy Chem. 2021, <b>55</b> , 92.
Fe-Ni <sub>5</sub> P <sub>4</sub> /NiFeOH-350	197	94	Appl Catal. B Environ. 2021, 291, 119987.
Fe-N4 SAs/NPC	202	123	Angew. Chem. Int. Ed. 2018, 57, 8614.
Fe, Al-NiSe <sub>2</sub> /rGO	288	103	Nanoscale. 2020, <b>12</b> , 13680.
Fe <sub>3</sub> O <sub>4</sub> -FeS/IF	~100	126.3	J Energy Chem. 2022, <b>68</b> , 96.
N-FeS <sub>2</sub>	126	124	J Energy Chem. 2021, <b>56</b> , 283.
Fe <sub>0.9</sub> Co <sub>0.05</sub> S <sub>1.05</sub>	342	114	Chem Eng J. 2020, <b>402</b> , 125069.
δ-FeOOH/Ni <sub>3</sub> S <sub>2</sub> /NF	106	82.6	J. Mater. Chem. A. 2020, 8, 21199.
Fe-Ni@NC-CNTs	202	113.7	Angew. Chem. Int. Ed. 2018, 57, 8921.
FeP	218	146	ACS Catal. 2014, <b>4</b> , 4065.
FeCo <sub>2</sub> O <sub>4</sub> @FeCo <sub>2</sub> S <sub>4</sub> @PPy-12	98.2	89.6	Nano Energy. 2020, <b>72</b> , 104715.
CdFe-BDC	148	128.99	ACS Appl. Mater. Interfaces. 2022, 14, 46374.
FeS2@CC	195	128	ACS Appl. Nano Mater. 2019, 2, 3889.
Fe <sub>0.1</sub> -NiS <sub>2</sub> NA/Ti	156	108	Nano Res. 2016, 9, 3346.
NiFe LDH@NiCo2S4/NF	200	101.1	ACS Appl. Mater. Interfaces. 2017, 9, 15364.
NiFe LDH@NiCoP/NF	120	88.2	Adv. Funct. Mater. 2018, 28, 1706847.
FeP/NCNSs	409	92	ACS Appl. Mater. Interfaces. 2018, 6, 11587.
FeP/NF	166	97	Chem Sci. 2018, <b>9</b> , 85909.
FePNPs@NPC	386	136	Nanoscale. 2017, <b>9</b> , 3555.

Table S1. Comparison of HER activity of Sm-FeP@CC with other catalysts reported.

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