Electronic Supplementary Material

Iron doped cobalt phosphide ultrathin nanosheets on nickel foam for overall water splitting

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Experimental section

Reagents and chemicals

Sodium hypophosphite monohydrate ($NaH_2PO_2 \cdot H_2O$) and potassium hydroxide (KOH) were obtained from Sinopharm Chemical Reagent Co., Ltd. Commercial RuO_2 nanoparticles (RuO_2 NPs) were supplied from Aladdin Industrial Co. Commercial 20% Pt on Vulcan XC-72 carbon (Pt/C) was purchased from Cabot Corp. Nickel foam (NF) substrate was obtained from Kunshan Deping Lake Electronic Technology Co., Ltd. Prior to synthesis, a piece of nickel foam (NF, 1cm×1cm) was cleaned by sonication successively in acetone, 1 M HCl, ethanol, and DI water for 15 min in order to remove the impurity like nickel oxides on the surface of the nickel foam and finally dried at 70 °C in vacuum oven for 5 h.

Materials characterization

X-ray diffraction (XRD) measurements were conducted on a DX-2700 power X-ray diffractometer using Cu Kα radiation source (λ=0.154 nm). The structural information and morphology of samples were investigated by energy-dispersive X-ray (EDX, TECNAI G2 F20 instrument), scanning electron microscopy (SEM, SU-8020 instrument), and high-angle-annular-dark-field (HAADF)-scanning transmission electron microscopy (STEM, TECNAI G2 F20 instrument). The thickness of the samples was measured by atomic force microscopy (AFM, Dimension Icon instrument). The surface element analysis was conducted by X-ray photoelectron spectroscopy (XPS, AXIS ULTRA spectrometer). The surface area analysis of samples was carried out by nitrogen adsorption and desorption isotherm (N_2-ADI) tests using Micro-meritics ASAP 2020 HD88 system.

Electrochemical measurements

The electrocatalytic performance of the samples was measured on CHI-660 electrochemical workstation at 30°C in a standard three-electrode system, including a saturated calomel electrode as the reference electrode, a graphite rod as the counter electrode, and electrocatalyst on NF substrate was directly as the working electrode. The measured potentials were converted to reversible hydrogen electrode (RHE) according to the following equation: $E_{RHE}=E_{SCE}+0.0591pH+0.242$. In all LSV curves, iR drop was compensated at 95% through the positive feedback model using the CHI 660E electrochemical analyzer. Electrochemical impedance spectroscopy was performed over a frequency range of 0.01−100000 Hz with an amplitude of 5 mV.

The Pt/C/NF and RuO_2 NPs/NF working electrode with 1.4 mg cm^{-2} loading mass were prepared according to previous report. [1] As follows, the Pt/C and RuO_2 NPs electrocatalyst suspensions were acquired by dispersing 3 mg sample in deionized water (790 μL), 5 wt% Nafion (10 μL) and isopropyl alcohol (200 μL) under the condition of strong ultrasound. Then, 467 μL of electrocatalyst suspension was uniformly deposited on NF substrate and then dried at room temperature.

The Fe-CoP UNSs/NF and CoP UNSs/NF without Fe doping were used directly as the working electrode. The accurate mass calculation showed the load amount of Fe-CoP UNSs and CoP UNSs on NF substrate was ca. 1.4 mg cm^{-2}.

Synthesis of iron doped cobalt phosphide ultrathin nanosheets on NF substrate (Fe-CoP UNSs/NF)

Iron doped cobalt oxides ultrathin nanosheets on NF substrate ($Fe\text{-}Co_3O_4$ UNSs/NF) were prepared according to our previous report.[1] The as-prepared $Fe\text{-}Co_3O_4$ UNSs/NF was further annealed for the phosphidation reaction with $NaH_2PO_2\cdot H_2O$. In a typical synthesis, a piece of $Fe\text{-}Co_3O_4$ UNSs/NF was placed in the porcelain boat, and 50 mg $NaH_2PO_2\cdot H_2O$ was placed in another porcelain boat. Two porcelain boats were then put into a tube furnace, and the temperature of the tube furnace was set at 300°C for 2 h. The reaction has taken place in a flow of nitrogen atmosphere, and the excess of PH_3 in the product was absorbed by the saturated copper (II) sulfate solution after treatment at the end of the gas circle.

Figure

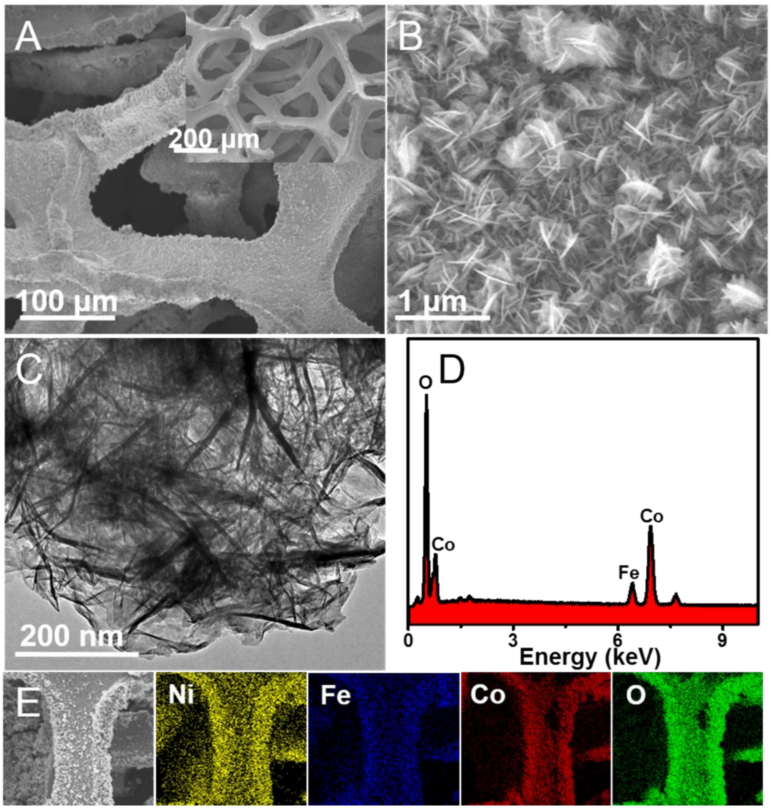

Fig. S1 (A) SEM image, (B) magnified SEM image, (C) TEM image, (D) EDX spectrum and (E) SEM-EDX mapping of Fe-Co_3O_4 UNSs/NF.

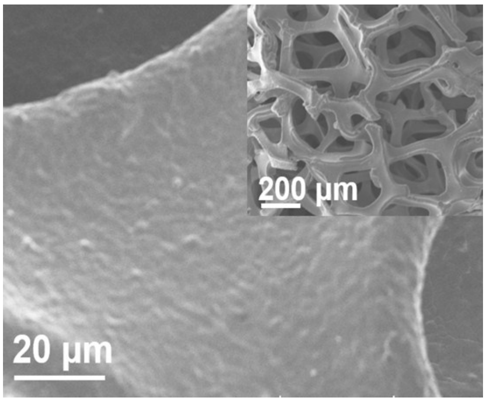

Fig. S2 SEM image of NF substrate.

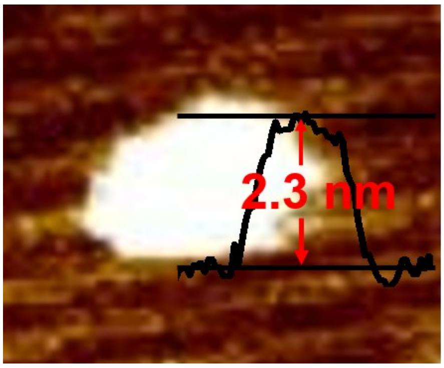

Fig. S3 AFM image of the Fe-CoP UNSs. Fe-CoP UNSs were obtained by strong sonication from NF substrate.

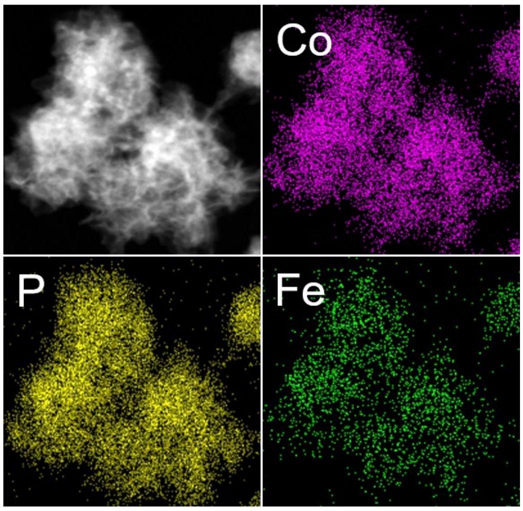

Fig. S4 STEM-EDX mapping image of Fe-CoP UNSs. Fe-CoP UNSs were obtained by strong sonication from NF substrate.

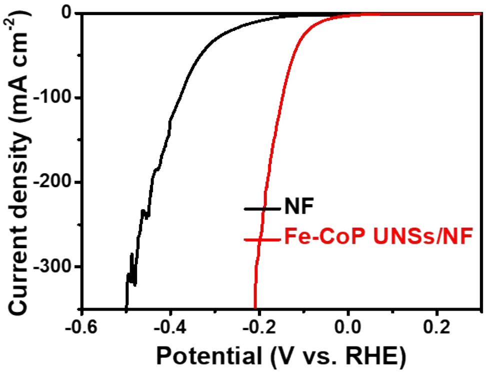

Fig. S5 iR-corrected LSV curves of Fe-CoP UNSs/NF and NF in N_2-saturated 1 M KOH electrolyte at 5 mV s^{-1}.

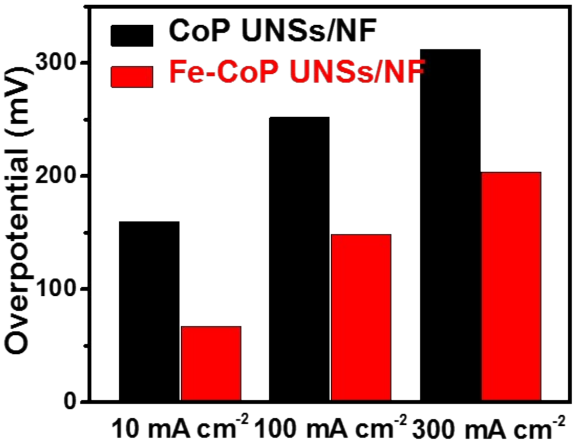

Fig. S6 Comparison of the HER overpotential at the current densities of 10, 100 and 300 mA cm^{-2} at Fe-CoP UNSs/NF and CoP UNSs/NF.

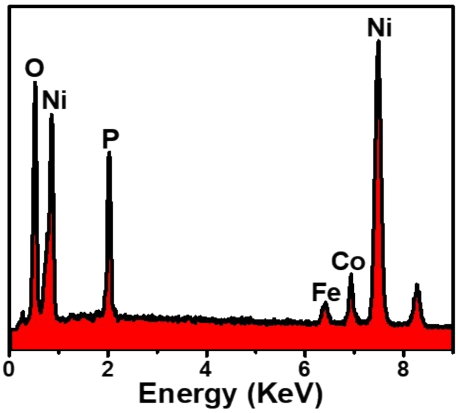

Fig. S7 EDX spectrum of Fe-CoP UNSs/NF after the HER test.

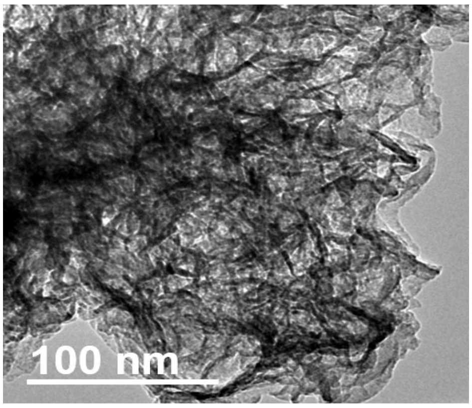

Fig. S8 TEM image of Fe-CoP UNSs/NF after the HER test. Fe-CoP UNSs were obtained by strong sonication from NF substrate.

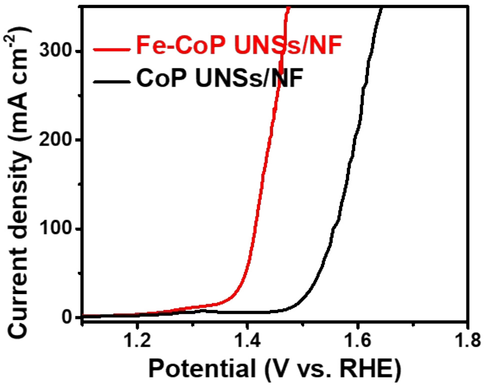

Fig. S9 iR-corrected LSV curves of Fe-CoP UNSs/NF and CoP UNSs/NF in O_2-saturated 1 M KOH aqueous solution at the scan rate of 5 mV s^{-1}.

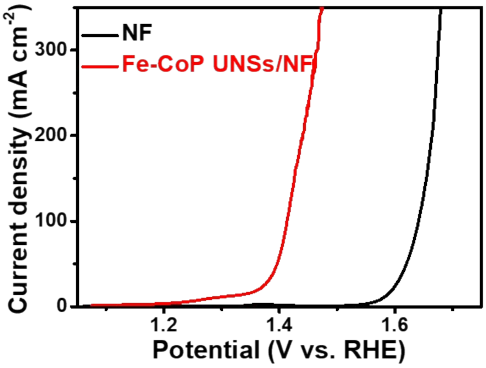

Fig. S10 iR-corrected LSV curves of Fe-CoP UNSs/NF and NF in O_2-saturated 1 M KOH electrolyte at 5 mV s^{-1}.

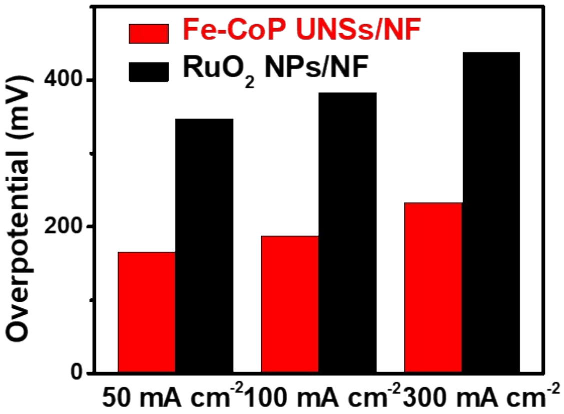

Fig. S11 Comparison of the OER overpotential at the current densities of 50, 100 and 300 mA cm^{-2} at Fe-CoP UNSs/NF and RuO_2 NPs/NF.

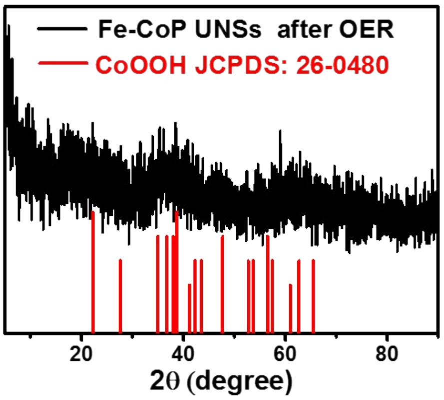

Fig. S12 XRD images of Fe-CoP UNSs after OER test. Fe-CoP UNSs were obtained by strong sonication from NF substrate.

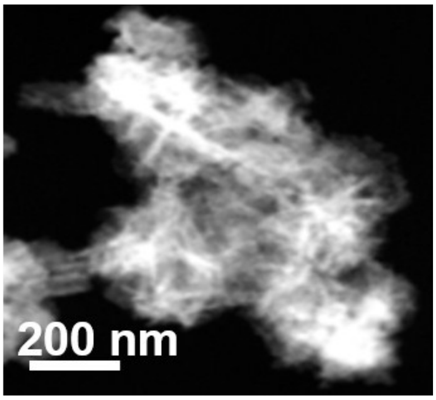

Fig. S13 STEM-EDX image of Fe-CoP UNSs after the OER test. Fe-CoP UNSs were obtained by strong sonication from NF substrate.

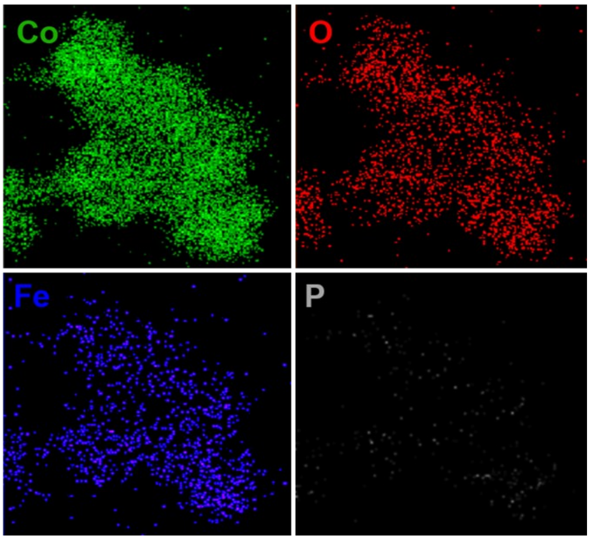

Fig. S14 STEM-EDX mapping images of Fe-CoP UNSs after the OER test. Fe-CoP UNSs were obtained by strong sonication from NF substrate.

References

1. Y. Li, F. M. Li, X. Y. Meng, X. R. Wu, S. N. Li, Y. Chen, *Nano Energy*, 2018, **54**, 238-250.