Fast synthesis of nickel phosphide nanosheets for ultra-stable hydrogen evolution in seawater splitting

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Experimental

Materials

Ni foam (thickness: 1.6 mm), red phosphorous powder (P, AR, 98.5%, Aladdin), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 99.99%, Aladdin), iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, 99.99%, Aladdin), potassium hydroxide (KOH, 50% w/v, Aladdin), graphite rod (diameter: 6 mm, length: 90 mm), and Pt wire (diameter: 0.5 mm, length: 30 mm, CH Instrument) were used. Deionized water (resistivity: 18.2 MΩ cm) and sea water (Dongtou District, Zhejiang Province, China) were used for all of the aqueous solutions.

Characterization

X-ray diffraction (XRD, MiniFlex600, Regaku), X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha), scanning electron microscopy (SEM, Phenompharos, Phenom) coupled with energy-dispersive X-ray spectroscopy (EDS), and transmission electron microscopy (TEM, FEI TalosF200x) coupled with EDS were employed.

Electrochemical measurements

All electrochemical performance parameters were tested in alkaline seawater (1 M KOH) using a three-electrode electrochemical station. The alkaline seawater (1 M KOH) is the mixture of 26.2 mL 50% w/v KOH solution and 473.8 mL seawater. Graphite rod and a Hg/HgO electrode served as the counter electrode and the reference electrode, respectively. All potentials were converted to a reversible

hydrogen electrode (RHE) by the Nernst equation ($E_{RHE} = E_{Hg/HgO} + 0.0591\ pH + 0.098$) and all measurements were conducted with iR compensation. The polarization curves were tested by sweeping the potential from 0.065 to -0.325 V *vs.* RHE at a rate of 2 mV s^{-1}. The cyclic voltammetry (CV) curves were conducted from 1.025 to 1.125 V *vs.* RHE at different rates. Electrochemical impedance spectroscopy (EIS) was performed at -150 mV *vs.* RHE from 100 KHz to 10 mHz with an amplitude of 10 mV.

Supplementary Figures

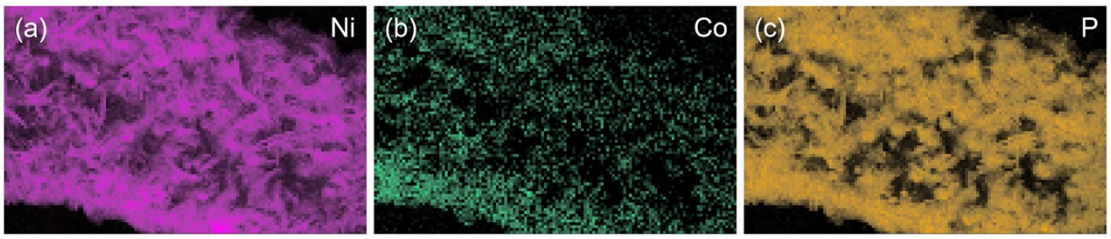

Figure S1. EDS mapping images of Ni foam from SEM.

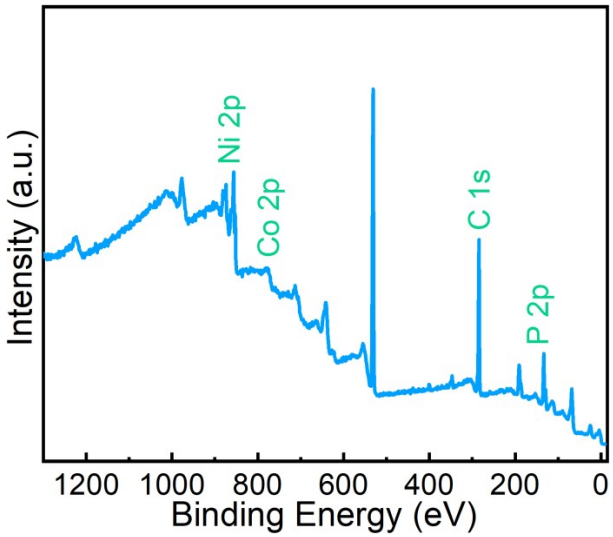

Figure S2. XPS spectrum of Co-Ni_5P_4-5m.

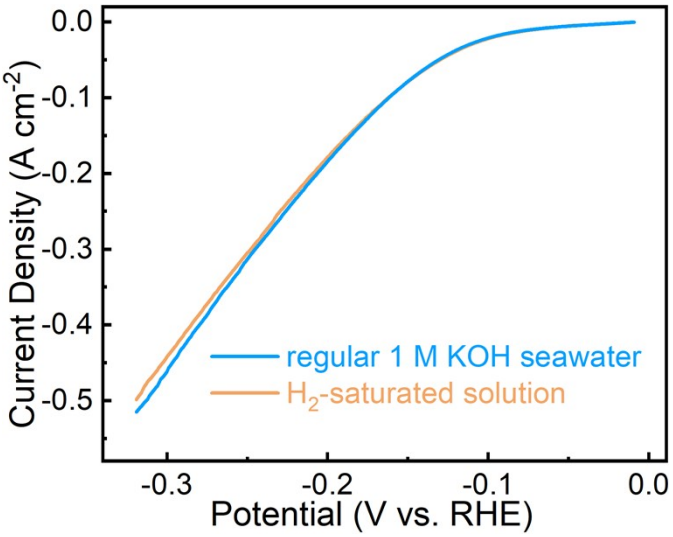

Figure S3. LSV curves of Co-Ni_5P_4-5m in H_2-saturated solution and regular 1 M KOH seawater solution.

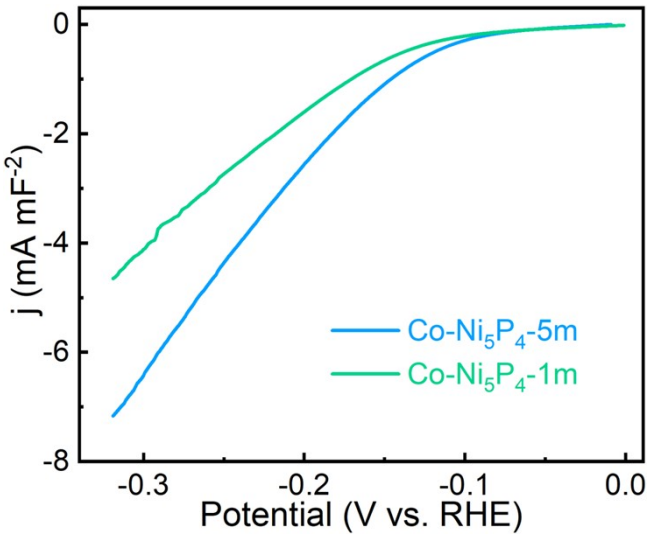

Figure S4. ECSA normalized LSV curves of Co-Ni_5P_4-5m and Co-Ni_5P_4-1m.

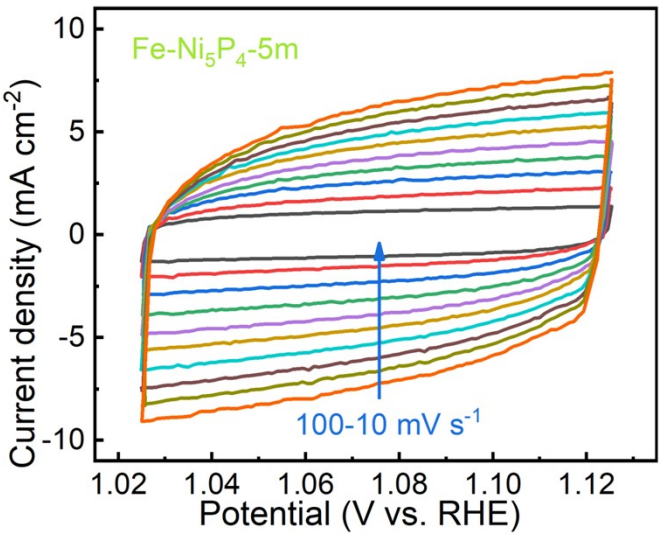

Figure S5. CV curves recorded for Fe-Ni_5P_4-5m electrodes over the potential range between 0.045 and -0.055 V *vs.* RHE at different rates in 1 M KOH seawater.

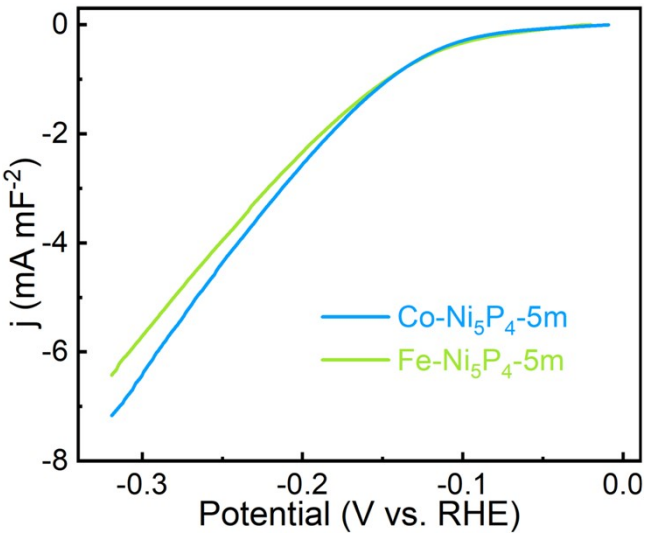

Figure S6. ECSA normalized LSV curves of Co-Ni_5P_4-5m and Fe-Ni_5P_4-5m.

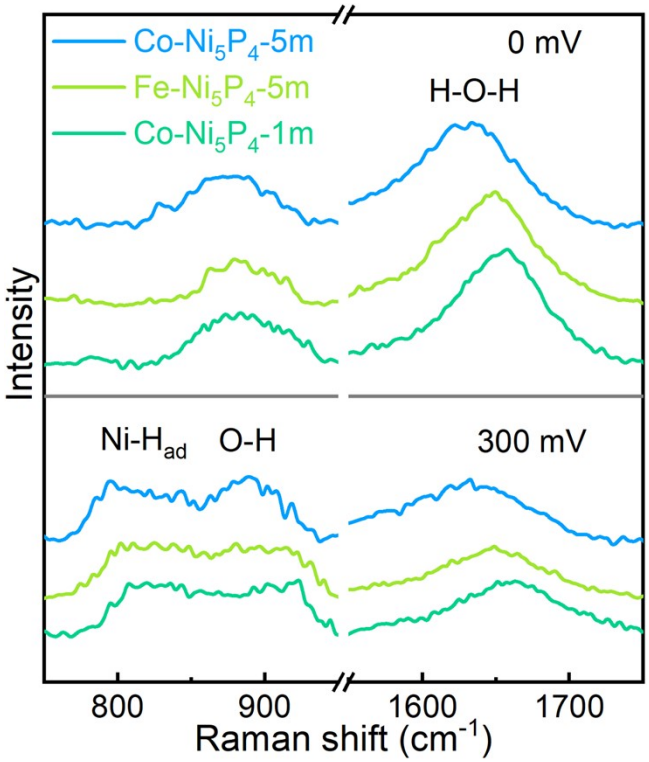

Figure S7. In-situ Raman spectra of Co-Ni_5P_4-5m, Fe-Ni_5P_4-5m and Co-Ni_5P_4-1m at the overpotential of 0 and 300 mV.

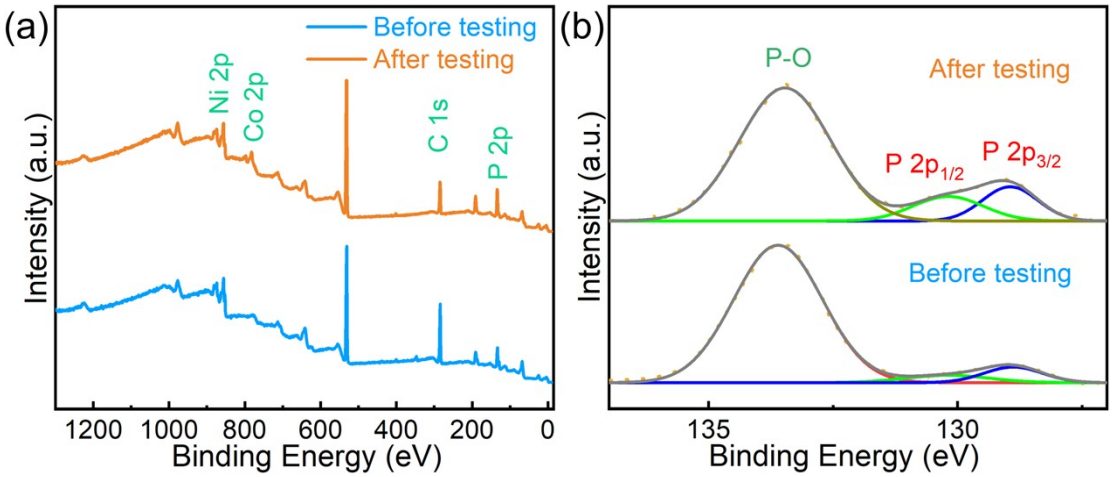

Figure S8. (a) XPS spectra of Co-Ni_5P_4-5m and (b) high-resolution XPS spectra of P 2p in Co-Ni_5P_4-5m after testing.

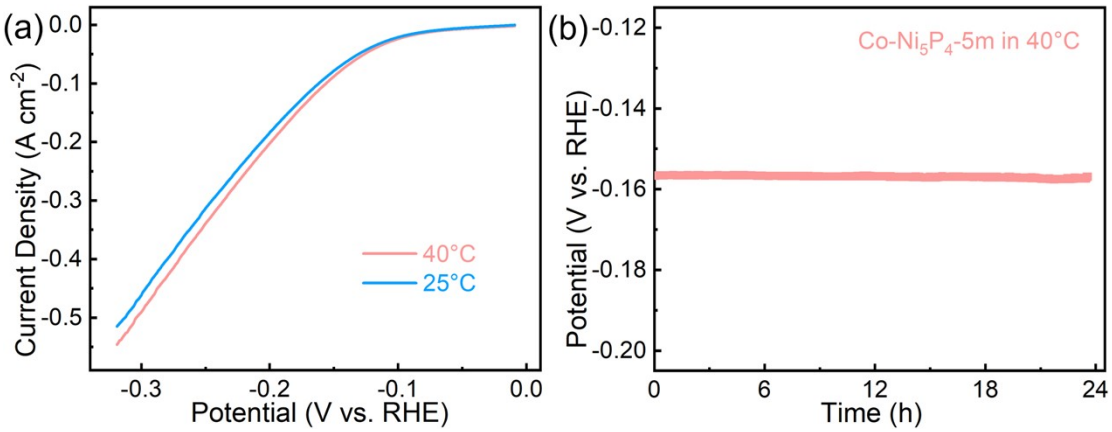

Figure S9. (a) Polarization curves of Co-Ni_5P_4-5m at different temperature. (b) Chronopotentiometry curve at the current density of 100 mA cm^{-2} in 40°C electrolyte.

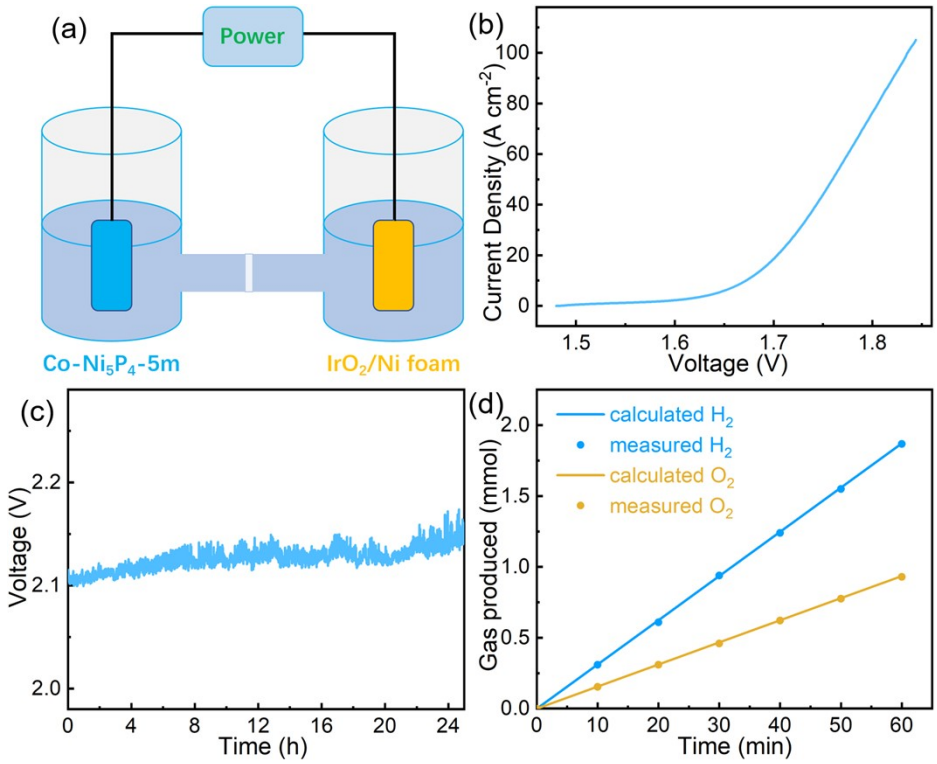

Figure S10. (a) The schematic of two-compartment electrochemical cell. (b) Polarization curve for overall water splitting. (c) Chronopotentiometry curve at the current density of 500 mA cm^{-2} for overall water splitting. (d) Experimental and theoretical amounts of H_2 and O_2 at the current density of 100 mA cm^{-2}.

Turnover frequency calculations

The turnover frequency (TOF) was calculated by the following formula according to previous reports.[1, 2]

$$TOF\ per\ site = \frac{\#\ Total\ Hydrogen\ Turnovers/cm^2 geometric\ area}{\#\ Surface\ Sites\ /cm^2\ geometric\ area}$$

Here, the total number of hydrogen turnovers is calculated as follows:

$$\#_{H_2} = \left(j\frac{mA}{cm^2}\right)\left(\frac{1C\ s^{-1}}{1000\ mA}\right)\left(\frac{1\ mol\ e^-}{96485.3\ C}\right)\left(\frac{1\ mol\ H_2}{2\ mol\ e^-}\right)\left(\frac{6.022\ \times 10^{23}\ H_2\ m}{1\ mol\ H_2}\right.$$
$$\times 10^{15}\ \frac{H_2/s}{cm^2}\ per\ \frac{mA}{cm^2}$$

The surface sites are calculated through the following equation:

$$\frac{\#\ Surface\ sites}{cm^2\ geometric\ area} = \frac{\#\ Surface\ sites\ (flat\ standard)}{cm^2\ geometric\ area} \times Roughness\ factor$$

Here, the roughness factor is related to the double-layer capacitance (C_{dl}), which we can set as 40 μF cm^{-2} for a flat electrode according to the previous reports, and the corresponding number of surface sites per cm^2 is known to be 2 × 10^{15} from the previous reports.[3, 4] The surface active sites for Co-Ni_5P_4-5m can then be calculated to be $\frac{7.19\ \times\ 10^4}{40}$ × 2 × 10^{15} surface sites/cm^2 = 3.60 × 10^{18} surface sites/cm^2.

Thus, the TOF for Co-Ni_5P_4-5m at the overpotential of 300 mV is calculated as follows:

$$\text{TOF} = \left(3.12\ \times 10^{15}\ \frac{H_2/s}{cm^2} \Big/ \frac{mA}{cm^2}\right)\left(461.6\ \frac{mA}{cm^2}\right)\left(\frac{1\ cm^2}{3.60\ \times\ 10^{18}\ surface\ sites}\right) = 0.40\ s^{-1}$$

Similarly, the TOF values for Co-Ni_5P_4-1m and Fe-Ni_5P_4-5m are calculated as 0.26 and 0.36 s^{-1}.

References

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