Electronic Supplementary Information

Experimental Section

Materials: Potassium hydroxide (KOH), nitric acid (HNO₃), and ethanol (C_2H_5OH) were purchased from Chengdu Kelong Chemical Reagent Factory. Sodium hypophosphite (NaH₂PO₂), ammonium fluoride (NH₄F), urea (CO(NH₂)₂), CuCl₂·2H₂O and CeCl₂·7H₂O were provided by 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 reagents were used as received without further purification. Nickle foam (NF) 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. Ultrapure water was utilized to prepare all solutions.

Preparation of Cu₃P/NF, CeO₂-CuO/NF, and CeO₂-Cu₃P/NF: Specifically, 1.25 mmol CuCl₂·2H₂O, 2.5 mmol CeCl₂·7H₂O, 1.25 mmol urea, and 0.75 mmol NH₄F were dissolved in 30 mL ultrapure water under magnetic stirring to form a uniform solution. The above solution and a piece of cleaned NF (2 cm × 3 cm) were transferred to a 50 mL Teflon-lined stainless-steel autoclave. The autoclave was sealed and placed in an oven at 130 °C for 8 h and then cooled down naturally. The resulting product was taken out and washed with ultrapure water and dried at 60 °C. After that, the sample was calcinated at 300 °C for 2 h and CeO₂-CuO/NF was obtained. To obtain CeO₂-Cu₃P/NF, the resulting product and NaH₂PO₂ were put at two separate positions in a porcelain boat with 0.5 g NaH₂PO₂ at the upstream side of the furnace. After added with Ar, the center of the furnace was elevated to 260 °C at a ramping rate of 2 °C min⁻¹ and held at this temperature for 2 h, and then naturally cooled to ambient temperature under Ar. Cu₃P/NF was converted from corresponding precursor.

Preparation of Pt/C: To prepare Pt/C electrode, 20 mg Pt/C and 10 μ L 5 wt% Nafion solution were dispersed in 1 mL 1:1 v water/ethanol solvent by 30-min sonication to form an ink finally. Then 105 μ L catalyst ink was loaded on bare NF.

Characterizations: XRD measurements were performed using a RigakuD/MAX 2550 diffractometer with Cu K α radiation (λ =1.5418 Å). SEM measurements were carried out on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM measurements were carried out on a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical measurements: Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system using a CeO₂-Cu₃P/NF as the working electrode, a graphite sheet as the counter electrode and a Hg/HgO as the reference electrode. The potentials reported in this work were calibrated to reversible hydrogen electrode (RHE), using the following equation: E (RHE) = E (Hg/HgO) + (0.098 + 0.059 pH) V. Polarization curves were obtained using linear sweep voltammetry with a scan rate of 5 mV s⁻¹. All experiments were carried out at room temperature (25 °C).

FE determination: The generated gas was confirmed by gas chromatography (GC) analysis and measured quantitatively using a calibrated pressure sensor to monitor the pressure change in the cathode compartment of a H-type electrolytic cell. The FE was calculated by comparing the amount of measured hydrogen generated by potentiostatic cathode electrolysis with calculated hydrogen (assuming 100% FE). GC analysis was carried out on GC–2014C (Shimadzu Co.) with thermal conductivity detector and nitrogen carrier gas. Pressure data during electrolysis were recorded using a CEM DT-8890 Differential Air Pressure Gauge Manometer Data Logger Meter Tester with a sampling interval of 1 point per second.

DFT computation details: The plane-wave DFT computations were carried out using CASTEP module (Ab Initio Total Energy Program, code version: 6546), for the calculation of hydrogen binding energy.¹ The Perdew-Burke-Ernzerhof (PBE)

functional and generalized-gradient approximation (GGA) methods were used to treat the electron exchange correlation interactions. A Monkhorst–Pack grid k-points (3×3×1) and 400 eV plane-wave basis set cut-off energy were applied for the Brillouin zone integration. The structures were optimized for force and energy convergence set at 1.0×10^{-5} eV and 0.03 eV/Å, respectively. A 2.0×10^{-6} eV/atom self-consistence field (SCF) was used. To avoid periodic interactions, a vacuum space of 15.0 Å was used along the direction normal to the catalyst surface. To consider the influence of van der Waals interaction, the semi-empirical DFT-D force-field approach was applied.^{2,3} The hydrogen absorption free energy ΔG_{H^*} was calculated as; $\Delta G_{H^*} = \Delta E_{H^*} + \Delta ZPE - T\Delta S$

$$\Delta E_{H^*} = (E_{(cat + H^*)} - E_{(cat)} - \frac{1}{2}E_{H2})$$

Where the symbols represent the binding energy (ΔE), zero-point energy (ΔE_{ZPE}), temperature (T), and the entropy change (ΔS), respectively.

It is approximated that the vibrational entropy of hydrogen in the adsorbed state is negligible such that $\Delta S_H \approx S_{H^*} - \frac{1}{2}(S_{H2}) \approx -\frac{1}{2}(S_{H2})$, where S_{H2} is the entropy of $H_{2(g)}$ at standard conditions (TS_(H2)~0.41 eV) for H₂ at 300 K and 1 atm.^{4,5}

Detail of theoretical model construction: Correlative theoretical models were built to simulate CeO₂, Cu₃P, and composite CeO₂-Cu₃P catalysts phases. Typically, the (111) facet with Ce-termination is adopted to act as active surface for the CeO₂ nanoparticle, which was modeled by the slab with three layers of Ce-O bonding atoms. For Cu₃P, the (110) facet was used in the creation of the slab model. To build the representative model of the CeO₂-Cu₃P composite, the respective Cu₃P phases was laid on the (111) facet of the CeO₂ slab layer. To minimize the effects of lattice mismatch, an interface periodicity of 3×2 supercell for the Cu₃P and 3×1 supercell for CeO₂ in CeO₂-Cu₃P model were applied. A vacuum space of 15.0 Å was applied along the direction normal to the catalyst surface. The optimized model of the composite structure of the CeO₂-Cu₃P composite with atomic bonding model is as displayed in Fig. 4e of the main text. The final lattice parameters for the model catalyst are presented in **Table S1**.



Fig. S1. XRD patterns for (a) CeO_2 -CuO/NF, (b) CeO_2 /NF, and (c) CuO/NF.



Fig. S2. Low-magnification SEM images of (a) NF, (b) CeO_2 -CuO/NF, and (c) CeO_2 -Cu₃P/NF.



Fig. S3. EDX spectrum for CeO_2 - Cu_3P/NF .



Fig. S4. (a) LSV curve for CeO_2 - Cu_3P/NF in 0.1 M KOH with *iR* correction. (b) LSV curve for CeO_2 - Cu_3P/NF in 1.0 M PBS with *iR* correction.



Fig. S5. LSV curves recorded for CeO_2 - Cu_3P/NF before and after 1000 CV cycles in 1.0 M KOH with *iR* correction.



Fig. S6. SEM images for CeO_2 - Cu_3P/NF after long-term stability test.



Fig. S7. The amount of gas theoretically calculated and experimentally measured versus time for hydrogen evolution of CeO_2 -Cu₃P/NF.

| Catalant | j (mA | ··· (V/) | | D-f |
|--|--------------------|-----------|-------------|------------|
| Catalyst | cm ⁻²) | η (mv) | Electrolyte | Kei. |
| | 20 | 148 | | |
| | 50 | 228 | 1.0 M KOH | |
| | 20 | 237 | | TT1 · 1 |
| CeO ₂ -Cu ₃ P/NF | 50 | 297 | 0.1 M KOH | I his work |
| | 20 | 205 | | |
| | 50 | 304 | 1.0 M PBS | |
| Cu ₃ P NS/NF | 20 | 160 | 1.0 M KOH | 6 |
| Cu ₃ P NB/Cu | 20 | 151 | 1.0 M KOH | 7 |
| Cu ₃ P/CF | 50 | 412 | 0.1 M KOH | 8 |
| Cu ₃ P | 20 | 162 | 1.0 M KOH | 9 |
| Pr _{0.5} BSCF | 20 | 250 | 1.0 M KOH | 10 |
| Ni@NiO/Cr2O3 | 20 | 270 | 1.0 M KOH | 11 |
| NiO/Ni-CNT | 20 | 270 | 1.0 M KOH | 12 |
| CoO _x @CN | 20 | 220 | 1.0 M KOH | 13 |
| MnNi | 20 | 410 | 1.0 M KOH | 14 |
| N-CG-CoO | 10 | 340 | 1.0 M KOH | 15 |
| Co-NRCNTs | 20 | 480 | 1.0 M KOH | 16 |
| M ₀ B | 50 | 239 | 1.0 M KOH | 17 |
| CoP ₄ N ₂ | 5 | 750 | 1.0 M KOH | 18 |

Table S1. Comparison of HER performance for CeO_2 - Cu_3P/NF with other non-noble-metal electrocatalysts in alkaline electrolyte.

| Model | a | b | c |
|-------------------------------------|-------|-------|--------|
| CeO ₂ | 7.732 | 7.732 | 18.946 |
| Cu ₃ P | 7.732 | 8.004 | 19.410 |
| CeO ₂ -Cu ₃ P | 8.999 | 7.868 | 21.955 |

 Table S2. Lattice parameters (Å) of supercells for all model systems.



Fig. S8. Structural models of pure CeO_2 , Cu_3P , and CeO_2 - Cu_3P .

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