Spontaneously separated intermetallic $\text{Co}_3\text{Mo}$ from nanoporous copper as versatile electrocatalysts for highly efficient water splitting

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Developing robust nonprecious electrocatalysts towards hydrogen/oxygen evolution reactions is crucial for widespread use of electrochemical water splitting in hydrogen production. Here, we report that intermetallic $\text{Co}_3\text{Mo}$ spontaneously separated from hierarchical nanoporous copper skeleton shows genuine potential as highly efficient electrocatalysts for alkaline hydrogen/oxygen evolution reactions in virtue of in-situ hydroxylation and electrooxidation, respectively. The hydroxylated intermetallic $\text{Co}_3\text{Mo}$ has an optimal hydrogen-binding energy to facilitate adsorption/desorption of hydrogen intermediates for hydrogen molecules. Associated with high electron/ion transport of bicontinuous nanoporous skeleton, nanoporous copper supported $\text{Co}_3\text{Mo}$ electrodes exhibit impressive hydrogen evolution reaction catalysis, with negligible onset overpotential and low Tafel slope ($\sim 40$ mV dec$^{-1}$) in 1 M KOH, realizing current density of $-400$ mA cm$^{-2}$ at overpotential of as low as 96 mV. When coupled to its electro-oxidized derivative that mediates efficiently oxygen evolution reaction, their alkaline electrolyzer operates with a superior overall water-splitting output, outperforming the one assembled with noble-metal-based catalysts.
Electrochemical water splitting powered by electricity from renewable energy sources (e.g., solar or wind) is an attractive energy-conversion technology that makes use of molecular hydrogen as a clean energy carrier in the energy framework of the water cycle. Itpromises a sustainable scenario to store/deliver renewable energy without any greenhouse-gas emission for meeting future energy demands. However, its widespread implementation is persistently plagued by the low efficiency of water electrolysis, particularly in water–alkali electrolyzers with nickel and/or stainless steel as electrodes or electrocatalysts, due to their high operation overpotentials and poor durability for the electrocatalytic hydrogen/oxygen evolution reactions (HER/OER) in alkaline environments. Such dilemma urgently calls for developing more efficient HER/OER electrocatalytic materials to lower the overall-splitting overpotential, with the versatile requirements of amenable accessible surface, highly reactive sites and fast electron-transfer and mass-transport pathways. To date, nanostructured noble-metal platinum (Pt) and iridium/ruthenium oxides (IrO2 or RuO2) are the benchmark HER and OER catalysts with the highest intrinsic activities, respectively, but the scarcity and high cost substantially hinder their widespread utilization. Moreover, nanostructured Pt, typically carbon-supported Pt nanoparticles (Pt/C), not only suffers from poor durability but encounters 2 or 3 orders of magnitude lower HER activity in alkaline media than in acidic electrolytes, with an aim to replace these noble-metal catalysts by Earth-abundant and cost-effective catalysts, many non-noble transition-metal compounds (such as Mo, W, Fe, Co, and Ni carbides, phosphides, and sulfides) and their derivatives have been developed for the HER/OER in alkaline environments. Nevertheless, few of these materials satisfy the practical requirements, i.e., high current density at low working overpotential, due to either poor electron transfer and/or insufficient catalytic activity. Despite nanostructuring as a general strategy could improve their HER/OER catalysis by increasing active sites, most nanocatalysts usually have to be immobilized on a conductive substrate using insulative polymer binders, which inevitably leads to supplementary interfaces linked to conductivity issues.

Here, we report intermetallic Co3Mo nanoparticles that are seamlessly integrated on the surface of hierarchical nanoporous Cu skeleton (Co3Mo/Cu) via a spontaneous phase separation during a chemical dealloying process as high-performance HER/OER electrocatalytic materials in alkaline media as a consequence of in situ hydroxylation and electro-oxidation. Owing to the hydroxylated Co3Mo having an optimal hydrogen-binding energy (HBE) associated with the fast HER reaction rate and the hierarchical nanoporous Cu skeleton facilitating electron transfer and OH−/H2O mass transport, the self-supported nanoporous Co3Mo/Cu electrodes exhibit negligible onset overpotential and low Tafel slope of 40 mV decade−1 in 1 M KOH. They reach a current density of −400 mA cm−2 at the iR-corrected overpotential of as low as 96 mV. When triggered by electro-oxidation, there in-situ forms Molybdenum oxide nanoflakes on the nanoporous CuO/Cu skeleton to accelerate the OER. The alkaline electrolyzer assembled with the nanoporous Co3Mo/Cu as the cathode and its derivative oxide as the anode only takes 1.65 V to achieve −145 mA cm−2, along with good stability, in a brine electrolyte containing 1 M KOH and 0.5 M NaCl. These electrochemical properties outperform some of the best electrocatalysts previously reported and make them promising candidates for overall electrochemical water splitting.

**Results**

**Preparation and structural characterization.** To develop electrocatalytic materials for practical application, self-supported monolithic nanoporous Co3Mo/Cu electrodes are fabricated by a facial and scalable dealloying technology associated with a spontaneous phase separation, which can be extended to develop various monolithic nanoporous alloy/metal hybrid electrode materials. Therein, both the hierarchical structures and components are controlled by making use of quasi-eutectic Cu12−x−yCo3MoAl8x alloy precursors (Supplementary Fig. 1), which are primarily composed of immiscible multiphase α-Al and CuAl2 without/with additional intermetallic Co3Mo36,37, Co2Al9, and MoAl12 (Supplementary Fig. 2). As illustrated by representative scanning electron microscopy (SEM) backscattered electron image and transmission electron microscope (TEM) image for the Cu3Co3MoAl8 alloy (Supplementary Fig. 3a, b), there are two distinctly contrasted phases with ~300 nm width. One is α-Al phase and the other corresponds to Cu-rich mixture of intermetallic CuAl2, Co3Mo, Co2Al9, and MoAl12, attested by their XRD patterns (Supplementary Fig. 2b) and energy-dispersive X-ray spectroscopy (EDS) elemental mappings (Supplementary Fig. 3a). The quasi-eutectic multiphase structure enables a bimodal nanoporous Cu skeleton with large channels and small nanopores via a two-step etching process, i.e., the fast dissolution of sub-micrometer-sized α-Al phase and then the slow dealloying of less noble Al component in the intermetallic CuAl2 phase. Figure 1a shows a typical cross-sectional SEM image for nanoporous Co3Mo/Cu electrode that is prepared by chemically dealloying the Cu3Co3MoAl8 alloy in KOH electrolyte. It displays a hierarchical nanoporous Cu skeleton with ~300 nm large channels and ~25 nm small nanopores. Owing to the poor miscibility of intermetallic Co3Mo with Cu matrix37,42, ultrasmall intermetallic Co3Mo nanoparticles with diameter of ~10 nm are spontaneously separated and in situ integrated on the interconnective Cu ligaments as a result of the Cu surface diffusion during the etching processes (Fig. 1b). X-ray photoelectron spectroscopy (XPS) analysis demonstrates the presence of Cu and Mo with an atomic ratio of 25:3, beside Cu skeleton and residual Al (Supplementary Fig. 4). This is consistent with EDS elemental mapping (Supplementary Fig. 5) and inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements. Scanning TEM (STEM) EDS mapping of nanoporous Co3Mo/Cu electrode attests the formation of Co3Mo nanoparticle with diameter of ~10 nm on the protonatable Cu ligament (Fig. 1c), in addition to some Co and Mo atoms with some *OH ligands due to selectively removing the Al component in the Co2Al9 and MoAl12. While for the residual Al atoms, STEM-EDS mapping and low-energy ion scattering (LEIS) spectrum illustrate that they are mainly in the interior of Cu skeleton (Supplementary Fig. 6). The atomic structure of nanoporous Cu supported Co3Mo nanoparticles is further characterized by high-angle annular-dark-field STEM (HAADF-STEM). Figure 1d shows a representative HAADF-STEM image of intermetallic Co3Mo nanoparticles in-situ grown on Cu ligament, which are evidenced by their corresponding fast Fourier transform (FFT) patterns (Fig. 1e, f). There is no sharp Co3Mo/Cu interface to be observed, implying that the Co3Mo nanoparticles are highly coherent with the Cu substrate. Such unique architecture not only enables electron transfer but also maintains exceptional stability. X-ray diffraction (XRD) characterization of nanoporous Co3Mo/Cu electrode verifies the hybrid structure, with two sets of diffraction patterns (Fig. 1g): the evident diffraction peaks at 2θ = −40.6°, −44.0°, and −46.4° corresponding to the (200), (002), and (201) planes of intermetallic Co3Mo in space group P 63/mmc (ICPDS 29-0488)37,42,43, and the ones else assigned to Cu (ICPDS 04-0836). This is in contrast with the XRD patterns of nanoporous Cu with/without Mo or Co incorporation, wherein they cannot be detected due to either too little or too small clusters on the Cu ligaments despite their similar...
Fig. 1 Microstructures and chemical properties. a Typical cross-sectional SEM image of Co3Mo/Cu electrode prepared by chemically dealloying Cu9Co3MoAl8 alloy precursor, displaying a three-dimensional bicontinuous and bimodal nanoporous architecture. Scale bar, 200 nm. b High-resolution cross-sectional SEM image of Co3Mo/Cu electrodes with a number of intermetallic Co3Mo nanoparticles in-situ integrated on Cu ligaments. Scale bar, 100 nm. c STEM image and the corresponding STEM-EDS elemental mappings of Cu, Co and Mo, demonstrating the Co3Mo nanoparticles grown on Cu ligaments. Scale bar, 10 nm. d Atomic resolution HAADF-STEM image of intermetallic Co3Mo nanoparticles grown on Cu ligament with a coherent interface structure. Inset: atomic structure of intermetallic Co3Mo. Scale bar, 1 nm. e STEM image and the corresponding STEM-EDS elemental mappings of Cu, Co and Mo, demonstrating the Co3Mo nanoparticles grown on Cu ligaments. Scale bar, 290 nm. f FFT patterns of Co3Mo (e) and Cu (f) in the selected areas in (d). g XRD patterns of nanoporous Co3Mo/Cu hybrid electrode and bare nanoporous Cu electrode. The line patterns show reference cards 04-0836 and 29-0488 for Cu and Co3Mo phases according to JCPDS, respectively.

geometric structure of nanoporous electrodes (Supplementary Figs. 7–9).

Figure 2a shows Co 2p and Mo 3d XPS spectra in the nanoporous Co3Mo/Cu electrode. In addition to their metallic states that correspond to the internal Co and Mo atoms in the intermetallic Co3Mo, the surface Co atoms exhibit Co2+ state 46,47 due to the surface adsorption of hydroxyl groups while surface Mo atoms are in Mo4+ and Mo6+ states (Supplementary Fig. 10) 46. Nevertheless, these oxidized Co and Mo surface atoms thermodynamically prefer to be electro-reduced to form partially hydroxylated Co3Mo surface in the HER potential region at pH = 14, as verified by initial two linear scanning voltammetry curves in 1 M KOH electrolyte (Supplementary Fig. 11) 47. As demonstrated by density functional theory (DFT) calculations based on the meta-generalized gradient approximation (meta-GGA) with strongly constrained appropriately normed (SCAN) functional (Supplementary Fig. 12a), the coverage of hydroxyl groups on the Co3Mo(002) surface decreases as the potential decreases from 0.6 to ~0.6 V vs. the reversible hydrogen electrode (RHE). At the potential of 0 V vs. RHE, DFT simulations demonstrate that the hydroxyl groups tend to be adsorbed on the Co–Co–Mo hollow sites with a coverage of 1/2 (Supplementary Fig. 12b). Considering that the practical catalyst surface is always in co-adsorption with OH− ions in alkaline environments 5,7,9,48,49, the free energy for atomic hydrogen adsorption (ΔGH*) for nonprecious metal catalysts is calculated on the basis of such atomic configuration. The ΔGH* for the partially hydroxylated Co3Mo(002) becomes almost thermoneutral, suggesting that it is more favorable for hydrogen adsorption/desorption than bare ones, as well as the monometallic Co and Mo (Fig. 2b). This is due to the adsorption of hydroxyl groups remarkably weakening the HBE (−0.36 eV) of their adjacent Co–Co–Mo hollow sites in comparison with the value of bare Co3Mo (002) surface (−0.77 eV), as illustrated in their partial density of states (PDOS) (Fig. 2c) and schematic atomic structures (Fig. 2d, e).

Electrochemical characterizations. To evaluate the electrocatalysis, all nanoporous electrode materials are directly used as working electrodes for electrochemical measurements, which are performed in N2-saturated 1 M KOH electrolyte in a classic three-electrode configuration with a graphite counter electrode and an Ag/AgCl reference electrode. According to the calibration experiment (Supplementary Fig. 13), all potentials are iR corrected and calibrated with respect to the RHE. Figure 3a compares typical HER polarization curve of nanoporous Co3Mo/Cu electrode with those of nanoporous Mo/Cu, Co/Cu, and bare Cu electrodes, as well as that of commercially available Pt/C catalyst immobilized on the nanoporous Cu electrode by dint of Nafion as polymer binder (Pt/C/Cu). Because of the presence of hydroxylated intermetallic Co3Mo nanoparticles, the nanoporous Co3Mo/Cu electrode exhibits an overpotential of as low as ~12 mV at current density of 10 mA cm−2, in sharp contrast with nanoporous Mo/Cu (~25 mV), Co/Cu (~116 mV), and Cu electrodes (~151 mV) with either too high or too low HBEs. Furthermore, this value is ~38 mV lower than that of nanoporous Pt/C/Cu despite the constituent Pt is usually expected as a benchmark catalyst to efficiently boost the HER. The superior electrocatalytic activity of nanoporous Co3Mo/Cu is also manifested by the low Tafel slope of ~40 mV dec−1 that corresponds to the Volmer–Heyrovsky mechanism (Fig. 3b) 5,6,10,12,13,25.
result, the nanoporous Co3Mo/Cu only takes the iR-corrected overpotential of ~96 mV to reach a current density of ~400 mA cm⁻², much lower than nanoporous Mo/Cu (~178 mV) and Co/Cu electrodes (~308 mV). The overpotential of the nanoporous Pt/C/Cu at ~400 mA cm⁻² is as high as ~286 mV probably due to the polymer binder that covers some electroactive sites. To demonstrate the reproducibility, ten nanoporous Co3Mo/Cu electrodes are produced by the same dealloying procedure. Supplementary Fig. 14 shows their HER polarization curves with almost the same overpotentials of ~65 and ~96 mV at ~100 and ~400 mA cm⁻² (Fig. 3c), respectively, indicating the excellent reproducibility. The substantially boosted reaction kinetics of the HER on the nanoporous Co3Mo/Cu is further revealed by electrochemical impedance spectroscopy (EIS) analysis. As shown in the Nyquist plots (Fig. 3d), the EIS spectrum of nanoporous Co3Mo/Cu displays a characteristic semicircle with a very small diameter that represent a low charge transfer resistance (R_{CT}). Based on the general descriptors in the equivalent circuit (inset of Fig. 3d), the R_{CT} value is determined to be ~1 Ω for the nanoporous Cu/Co3Mo, much lower than those of nanoporous Cu/Mo (~3 Ω), Cu/Co (~10 Ω), Cu (~39 Ω) electrodes (Supplementary Fig. 15).

Double-layer capacitance measurements demonstrate that the electrochemical surface area (ECSA) cannot account for ~6- or 46-fold enhancement in geometric current density of nanoporous Co3Mo/Cu electrode in view that its ECSA is only 0.7- or 1.1-fold that of nanoporous Mo/Cu or Co/Cu (Fig. 3e, Supplementary Fig. 16). This fact indicates the significant role of intermetallic Co3Mo in the exceptional HER activity of nanoporous Co3Mo/Cu, justified by H₂SO₄ treatment that partially removes the electroactive Co3Mo nanoparticles (Supplementary Fig. 17). As shown in Fig. 3f, the H₂SO₄-treated nanoporous Co3Mo/Cu exhibits evident degradation of HER catalysis, with about threefold reduction in current density at the overpotential of 100 mV, relative to the pristine one. With an assumption that the dramatic reduction in geometric current density results from the ECSA change due to the loss of both Co3Mo nanoparticles and Cu kinks or edges on ligament surface (Supplementary Fig. 18), the intrinsic activity of Co3Mo is evaluated to be 0.48 mA cm⁻² ECSA, ~830-fold higher than that of bare Cu (0.58 μA cm⁻² ECSA) (Supplementary Fig. 19a). The outstanding electrocatalytic activity of Co3Mo is also confirmed by the turnover frequency that is estimated to be 0.775 s⁻¹ at the overpotential of 100 mV (Supplementary Fig. 19b, Supplementary Note 1), higher than some of the best nonprecious HER catalysts reported previously in 1 M KOH (Supplementary Table 1).

The durability of nanoporous Co3Mo/Cu electrode is tested at ~60- and ~80 mV vs. RHE for 1000 and 500 h in 1 M KOH, respectively. As shown in Fig. 3g, there is not evident fluctuation in their corresponding current densities of ~60 and ~210 mA cm⁻² because of the steady nanoporous structure, in which the constituent intermetallic Co3Mo nanoparticles are seamlessly integrated on the firm metal skeleton. In the tested electrolyte, there are no Co and Mo ions to be detected by ICP-OES except for some detectable Cu and Al ions (Supplementary Table 2). Nevertheless, after the long-term durability measurements, the nanoporous Co3Mo/Cu electrode still keeps the original structure and exhibits almost the same polarization curve as the initial one (insets of Fig. 3g). All these electrochemical properties indicate that the nanoporous Co3Mo/Cu electrode can exhibit impressive electrocatalytic performance at mild conditions, i.e., in 1 M KOH electrolyte at room temperature, in contrast with Ni-Mo catalysts supported by stainless steel or Ni substrates even under higher temperatures or/and KOH concentrations³⁰-³³. Compared with state-of-the-art transition-metal compounds and alloys, the nanoporous Co3Mo/Cu electrode is one of the best nonprecious electrocatalytic materials (Fig. 3h, Supplementary Tables 3 and 4)⁶,⁸,¹⁰,¹³,¹⁵,²⁶-³¹.

Besides directly working as the outstanding HER electrocatalyst, the nanoporous Co3Mo/Cu can also serve as a good pre-electrocatalyst for the OER. After a facile electro-oxidation
**Fig. 3** Electrochemical characterization on HER properties. **a** |R-corrected HER polarization curves for self-supported nanoporous Co$_3$Mo/Cu, Co/Cu, Mo/Cu, and Cu electrodes, as well as commercially available Pt/C immobilized on nanoporous Cu (Pt/C/Cu) in 1 M KOH. Scan rate: 1 mV s$^{-1}$. **b** Comparison of the Tafel plots of different electrocatalytic materials obtained from the HER polarization curves in panel **a**. **c** Overpotentials at current densities of 100 and 400 mA cm$^{-2}$ for ten nanoporous Co$_3$Mo/Cu electrodes that are prepared by the same alloying/dealloying procedure. **d** EIS spectra of nanoporous Co$_3$Mo/Cu, Co/Cu, Mo/Cu, and bare Cu electrodes and nanoporous Pt/C/Cu. **e** Comparison of current density at −100 mV for nanoporous Co$_3$Mo/Cu electrode with the values of nanoporous Cu, Co/Cu, Mo/Cu electrodes, and nanoporous Pt/C/Cu. **f** |R-corrected HER polarization curves of nanoporous Co$_3$Mo/Cu and bare Cu electrodes before and after H$_2$SO$_4$ treatment. **g** Long-term stability measurement of nanoporous Co$_3$Mo/Cu electrode at the overpotentials of 60 and 80 mV for more than 1000 and 500 h, respectively. The negligible current fluctuation is due to the depletion/replenishment of electrolyte. Insets: SEM image after the durability measurement at 60 mV for 1000 h and polarization curves before and after the durability measurement. Scale bar: 300 nm. **h** Tafel slope and overpotential at 100 mA cm$^{-2}$ of nanoporous Co$_3$Mo/Cu electrode, comparing with the values of representative HER catalysts reported previously.
procedure at a potential of 1.57 V vs. RHE (Supplementary Fig. 20a), there form a large number of Mo-doped Co₃O₄ nanoflakes to be integrated with partially oxidized CuO/Cu skeleton (EO Co₃O₄/Cu), as illustrated by SEM (inset of Fig. 4a) and high-resolution TEM images (Supplementary Fig. 20b). Distinguished from the CuO signals in the EO Co₃O₄/Cu electrode, which keep the same Raman characteristics as the ones in the EO Cu, the characteristic Raman bands at 183, 460, 502, and 658 cm⁻¹ remarkably blue shift relative to the ones of pristine Co₃O₄ (Supplementary Fig. 20c)⁵⁴, implying the incorporation of Mo into the Co₃O₄ nanoflakes⁵⁵. This is further verified by XPS analysis and SEM-EDS elemental mappings of Co, Mo, and O. As a result of uniform incorporation of Mo in the Co₃O₄ (Supplementary Fig. 21c–e), the XPS characteristic peaks of the Co 2p in the EO Co₃O₄/Cu electrode shift to lower binding energy compared with the ones in the EO Co/Cu (Supplementary Fig. 20d), suggesting the strong electron interactions between Mo and Co₃O₄⁵⁶. On account of the enhanced electrocatalytic activity of the Mo-doped Co₃O₄, the EO Co₃O₄/Cu electrode with a hierarchical nanoporous architecture shows a superior OER activity in 1 M KOH electrolyte, compared with the electro-oxidized nanoporous Co₃O₄/Cu, Cu electrodes (EO Co/Cu, EO Cu) (Fig. 4a). The OER current density of EO Co₃O₂/Cu electrode increases dramatically from the onset overpotential of ~261 mV, ~86 mV lower than that of Ir/C supported by nanoporous Cu (Ir/C/Cu) (~347 mV). As a result of low Tafel slope of ~82 mV dec⁻¹ (Fig. 4b), the EO Co₃O₄/Cu can deliver a geometric current density of ~164 mA cm⁻² only at the overpotential of 350 mV (Fig. 4c). Owing to the steady architecture, the EO Co₃O₂/Cu electrode exhibits a good electrocatalytic durability at the overpotentials of 300, 350, and 400 mV for each 10 h in 1 M KOH electrolyte (Fig. 4d). As shown in Supplementary Fig. 22, the EO Co₃O₂/Cu electrode keeps the initial morphology and elemental distributions of Co, Mo, and O after the durability test. Furthermore, there are not evident changes in Raman spectra and Co 2p, Mo 3d, and O 1s XPS spectra (Supplementary Figs. 23 and 24), demonstrating the stability of surface oxides. For comparison, nanoporous NiFe/Cu electrode and its electro-oxidized derivative (EO NiFe/Cu) are also prepared by the same methods (Supplementary Fig. 25a, c). Whereas the EO NiFe/Cu exhibits slightly higher OER activity than the EO Co₃O₂/Cu⁵⁶, the HER activity of nanoporous NiFe/Cu electrode is much lower than that of nanoporous Co₃O₂/Cu electrode (Supplementary Fig. 25b, d).

**Electrochemical performance of alkaline electrolyzers.** The outstanding electrocatalytic properties of nanoporous Co₃O₂/Cu and its electro-oxidized derivative for the HER and OER demonstrate that they show genuine potential as cathode and anode materials for practical water electrolysis (Fig. 5a). Figure 5b presents a typical polarization curve of an alkaline electrolyzer that is constructed with the nanoporous Co₃O₂/Cu as the cathode and the EO Co₃O₂/Cu as the anode. Within the brine electrolyte containing 1 M KOH and 0.5 M NaCl, the onset overpotential of this electrolyzer is as low as ~230 mV, distinguished from most electrocatalysts that tend to be corroded and/or deactivated in such environments²⁸,³⁸. Notably, the nanoporous Co₃O₂/Cu-based electrolyzer delivers the current density of 100 mA cm⁻² at a low potential of 1.62 V for the overall water splitting, outperforming the ones assembled with nonprecious electrode materials previously reported (Fig. 5d, Supplementary Table 5)³³,³⁵,³⁶. At the overpotential of 420 mV, the water-splitting output of this electrolyzer reaches ~145 mA cm⁻², more than 7- or 10-fold higher than the one constructed with nanoporous NiFe/Cu and EO NiFe/Cu, or Pt/C/Cu and
Ir/C/Cu, respectively (inset of Fig. 5b). During the stability measurement at the voltage of 1.65 V, the output of this alkaline electrolyzer is highly stable at ~145 mA cm\(^{-2}\), in contrast with the poor behavior of Pt/C/Cu-Ir/C/Cu electrolyzer, which is performed at the same voltage but with much lower current densities (Fig. 5c). Moreover, both nanoporous Co\(_3\)Mo/Cu and EO Co\(_3\)Mo/Cu electrodes still maintain their initial microstructures after the stability measurement (insets of Fig. 5c).

**Discussion**

In the water electrolysis, the HER/OER taking place at the cathode/anode is always associated with mass transports of ions/molecules toward/from the electrochemical surface in the electrolyte, electron transfer from current collector to active sites in the solid electrode, and redox reactions at the active site/electrolyte interface

These indispensable processes require a versatile electrode design in both architecture and active site levels for highly efficient HER/OER electrocatalysis. In contrast with low-dimensional nanocatalysts that are usually immobilized on conductive substrate by polymer binder, our monolithic nanoporous Co\(_3\)Mo/Cu electrode not only simultaneously facilitates the electron transfer and the HO\(^*/\)H\(_2\)O mass transports of along the interconnective Cu ligaments and the interpenetrating channels, respectively, but raises the accessibility of intermetallic Co\(_3\)Mo nanoparticles by making use of small nanopores. Meanwhile, the seamless integration between the electroactive Co\(_3\)Mo nanoparticles and the conductive Cu ligaments with a coherently interfacial structure minimizes their contact resistance and improves the electrochemical durability. The multifunctional electrode architecture enlists the constituent intermetallic Co\(_3\)Mo nanoparticles to exhibit exceptional electrocatalysis towards the alkaline HER. Because of the ordered crystal structure, the intermetallic Co\(_3\)Mo nanoparticles have the precise surfaces composed of regular Co and Mo atoms, wherein their dissimilarity results in both ligand effect and strain effect to regulate the adsorption energies of HO\(^*/\)H\(^+\) intermediates. In view that Mo is more oxophilic than Co, the HO\(^*/\)thermodynamically prefers to be adsorbed at the Co-Co-Mo hollow sites with a coverage of 1/2. This unique surface structure benefits for the subsequent adsorption/desorption of H\(^+\) intermediates at the hollow sites nearby the hydroxylated Co–Co–Mo ones as a result of their optimum HBE and thermoneutral \(\Delta G_{\text{H}}\). While triggered by electro-oxidation, the hydroxylated Co\(_3\)Mo evolves into the Co\(_3\)O\(_4\) nanoflakes with the in-situ incorporation of Mo, which improves the electronic conductivity of Co\(_3\)O\(_4\) and adjusts the adsorption energy of HO\(^*/\)H\(^+\), remarkably boosting the OER electrocatalysis. The versatile properties of nanoporous Co\(_3\)Mo/Cu electrode demonstrate the feasibility of dealing with quasi-eutectic multiphase alloys as a facile and scalable strategy to develop high-performance intermetallic compound-based electrocatalysts for the HER/OER.

In summary, we have developed nanoporous Cu supported intermetallic Co\(_3\)Mo as self-supported monolithic electrocatalytic materials for highly efficient electrochemical splitting water. As a consequence of the intermetallic Co\(_3\)Mo having exceptionally high intrinsic activity and the hierarchical nanoporous Cu skeleton offering fast electron-transfer and mass-transport pathways, the nanoporous Co\(_3\)Mo/Cu electrodes exhibit negligible onset
overpotential, and low Tafel slope of 40 mV dec⁻¹, with an excellent durability. They only take the overpotential of as low as 96 mV to reach -400 mA cm⁻². As a high-performance HER catalysts, the nanoporous Co₃Mo/Cu electrode is coupled with its electro-oxidized derivative, i.e., EO Co₃Mo/Cu, to construct an alkaline electrolyzer for the overall water splitting reaction. This alkaline electrolyzer delivers ~145 mA cm⁻² at a low overpotential of 420 mV, along with long-term stability in the electrolyte of 1 M KOH and 0.5 M NaCl. The outstanding electrochemical performance enlists them to be promising candidates as low-cost anode and cathode materials for wide applications in water splitting.

**Methods**

**Preparation of nanoporous electrocatalysts.** All nanoporous hybrid electrodes were prepared by a scalable alloying/dealloying procedure. Precursor alloys, i.e., Cuₓ₋ₓ₋ₓ₋₋ₓ₉₋₋₋₋₋ₓ₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋脱颖�-


**Structural characterizations.** Microstructure characterizations and chemical component analysis of nanoporous electrocatalyst electrodes were performed on a field-emission scanning electron microscope (SMI-6700F, JEOL, 7 keV) equipped with X-ray energy-dispersive spectroscopy (EDS), and a field-emission transmission electron microscope (EM-ARM300F, JEOL) equipped with double spherical-aberration correctors for both condenser and objective lens, respectively. XRD measurements of the nanoporous electrocatalyst electrodes were conducted on a D/max2500pc diffractometer with a monochromated Cu Kα radiation. Chemical states and distribution of surface elements were analyzed using XPS and LEIS on a Thermo ECSALAB 250 with an Al anode. Charging effects were compensated by inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo electron) analysis correcting according to the equations, and used to evaluate the ECSAs. The HER durability tests of nanoporous Co₃Mo/Cu electrode were performed at the overpotential of 300, 350, and 400 mV in 1 M KOH, respectively, for 10 h. As for the overall-splitting water, a two-electrode electrode was carried out at the overpotential of 300, 350, and 400 mV in 1 M KOH for 30 h. Pt/C and Ir/C catalyst inks were prepared by mixing commercially available Pt/C and Ir/C catalysts in 1 M KOH and 0.5 M NaCl, wherein the stability test was carried out at 1.65 V vs. RHE for 20 min. Pt/C and Ir/C catalysts were electro-oxidized derivative, i.e., EO Co₃Mo/Cu, to construct an alkaline electrolyzer for the overall water splitting reaction. This alkaline electrolyzer delivers ~145 mA cm⁻² at a low overpotential of 420 mV, along with long-term stability in the electrolyte of 1 M KOH and 0.5 M NaCl. The outstanding electrochemical performance enlists them to be promising candidates as low-cost anode and cathode materials for wide applications in water splitting.

**Data availability**

All relevant data are available from the corresponding authors upon request.

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