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Handily etching nickel foams into catalyst-substrate fusion self-stabilized electrodes toward industrial-level water electrolysis

Zexuan Zhu¹, Xiaotian Yang¹, Jiao Liu¹, Mingze Zhu² & Xiaoyong Xu¹✉

The key challenge of industrial water electrolysis is to design catalytic electrodes that can stabilize high current density with low power consumption (i.e., overpotential), while industrial harsh conditions make the balance between electrode activity and stability more difficult. Here we develop an efficient and durable electrode for water oxidation reaction (WOR), which yields a high current density of 10000 A m⁻² at an overpotential of only 284 mV and shows robust stability even in 6 M KOH strong alkaline electrolyte with elevated temperature up to 80 °C. This electrode is fabricated from cheap nickel foam (NF) substrate through a simple one-step solution etching method, resulting in the growth of ultrafine phosphorus doped nickel-iron (oxy)hydroxide (P-NiFeOOH) nanoparticles embedded into abundant micropores on surface, featured as a self-stabilized catalyst-substrate fusion electrode. Such self-stabilizing effect fastens highly active P-NiFeOOH species on conductive NF substrate with significant contribution to catalyst fixation and charge transfer, realizing a win-win tactics for WOR activity and durability at high current densities in harsh environments. This work affords a cost-effective WOR electrode that can well work at large current densities, suggestive for rational design of catalyst electrodes toward industrial-scale water electrolysis.

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Human's over-dependence on fossil fuels leads to serious energy crisis and environmental hazards. Renewable electricity generation from natural sources through solar panels, wind turbines, hydropower, etc., shows great promise for sustainable and green energy supplies for the world^{1,2}. Further using surplus renewable electricity to produce fuels via electrochemical techniques will provide more room for power storage and utilization, attracting extensive interest in both academia and industry³⁻⁶. In this regard, electrochemical water splitting that promises for high-purity green hydrogen production offers an attractive prospect of eco-friendly hydrogen economy with zero carbon emitting⁷⁻¹⁰. However, water electrolysis generally exhibits sluggish kinetics especially for the energy-intensive water oxidation reaction (WOR) on the anode^{11,12}, resulting in high electricity consumption inadequate for large-scale commercialization. The noble Ru/Ir-based catalysts are capable of reducing the WOR overpotentials, but hardly meet practical application scale-up due to their scarcity and high cost¹³. Recent years have witnessed a striking upsurge of exploring earth-abundant inexpensive catalysts used for alkaline water electrolysis (AWE)¹⁴⁻²⁰, and notably many transition-metal compounds (TMCs), including oxides²¹, sulfides²², carbides²³, nitrides²⁴, phosphides²⁵, and alloys^{26,27} etc., have been developed as effective candidates to expedite WOR.

Despite great achievements, it remains an open question to apply these promising WOR catalysts in practical water electrolysis due to the criteria gap between lab- and industrial-scale performance²⁸⁻³⁰. Most of reported catalysts were shown to be active and stable only at low current densities (e.g., typical 10 mA cm^{-2})^{31,32}, which might not necessarily translate into practical performance at industrial-level large current densities. Indeed, there are limited catalysts reported so far to meet the strict industrial standard of large current densities over 500 mA cm^{-2} operating at low overpotentials

less than 300 mV³³. Moreover, the catalyst electrode stability would encounter more serious trials at high current densities under industrially relevant harsh conditions (i.e., temperature between 70–80 °C and alkalinity in 25–30 wt.% KOH)^{34,35}.

Hence, paired success of high activity and long durability to deliver large current densities under industrial conditions is imperative to develop catalyst electrodes for practical application³⁶. But, seeking such an activity-stability balance at high current densities becomes more challenging because of solid-liquid-gas interface exchange kinetics complicated in the context of intense mass/charge transfer and effervescence³⁷. To this end, self-supported electrodes in which active catalysts directly grown on conductive substrates have been considered to form their intimate contact beneficial for mechanical adhesion and charge/mass delivery without binders or additives^{38,39}. Several efficient self-supported electrodes have been noticeably emerged for large-current-density WOR in combination with some strategies, such as geometrical/structural design^{40,41}, hetero assembly^{42,43} and electronic modulation⁴⁴. Overall, most traditional approaches like electrodeposition and hydrothermal synthesis were generally adopted to guide the surface loading of active catalysts on support frameworks, whereas such hierarchical assembly might be still inadequate for robust solid-liquid-gas interface dynamics under industrial conditions because large-current-density WOR electrodes steady in strong alkali ($\geq 500 \text{ mA cm}^{-2}$ for over 100 h in $\sim 6 \text{ M KOH}$) are rarely reported to date. Along this line, we suppose that an etching strategy on metal substrates with targeted catalyst layer to construct catalyst-substrate fusion electrodes might enable strong self-stabilizing effects on mechanical adhesion and charge transfer for industrial criterions.

In addition, species reported as WOR promoters at high current densities are few and are most limited to NiFe-based (oxy)hydroxides^{40,43}, but their durability has yet to be

further examined in industrially relevant harsh environments with strong alkali and high temperature. Hence, we preferentially target to NiFe (oxy)hydroxide configuration through the rational etching design over nickel foams (NF). Moreover, most synthetic methods for previously reported metal (oxy)hydroxides usually involve multi-step procedures even including post treatment or reconstruction^{45,46}, which are inferior in respect to time-energy input, cost-effectiveness and scale-up, in comparison with etching process.

In this work, we develop a self-stabilized catalyst-substrate fusion electrode with industrially relevant WOR activity and durability through directly etching NF substrates, which in situ derives ultrafine phosphorus doped nickel-iron (oxy)hydroxide (P-NiFeOOH) nanoparticles embedded into abundant macropores etched on NF surface. The P-NiFeOOH electrode achieves large current density 1000 mA cm⁻² at a low overpotential of only 284 mV and exhibits robust durability at least 150 hours under industrial-level conditions. Such a self-stabilized electrode design strategic for industrial high current density features with several advantages as following. First, the surface etching method is extremely facile for targeted synthesis of active (oxy)hydroxides that differs from traditional hydrothermal or electrodeposition, more amenable to scaled-up production with economy. Second, the support-stabilizing catalyst construction avoids utilization of an expensive polymer binder (e.g., Nafion) that generally induces adverse effects of shielding active sites, deteriorating conductivity and insufficient stability especially at large currents in strong corrosive alkali. Third, the embedded fusion of catalyst-rooting at conductive substrate guarantees structural integrity with robust contact, favorable for electron transfer and catalyst fixation to overcome low conductivity and easy agglomeration commonly associated with metal (oxy)hydroxides. Fourth, the hierarchically porous structure

offers large specific surface areas to maximize active-site exposure, electrolyte permeation and gas product release, which are especially useful under high current densities and violent gas evolution conditions. In addition, the targeted NiFeOOH is widely accepted as the most efficient WOR catalyst⁴⁷, and here the trace P dopant into NiFeOOH species may improve electrical conductivity and optimize absorption energies for reaction intermediates, and the formed P-O bonds can contribute to resistance to corrosion^{10,48}.

Fig. 1. Morphology and structural characterizations. (A) Low- and (B) High-magnification SEM images, and (C) XRD pattern of as-prepared P-NiFeOOH@NF electrode. (D) TEM and (E-G) HRTEM images of P-NiFeOOH catalyst. (H) EDS elemental mappings for Fe, Ni, P, and O elements in P-NiFeOOH catalyst.

Results

Morphology and structural characterizations of P-NiFeOOH electrode. The support-stabilized P-NiFeOOH catalyst was prepared via chemically etching NF in

mixture solution with specific amounts of $\text{Fe}(\text{NO}_3)_3$ and Na_3PO_4 . The commercial NF presents a three-dimensional (3D) network with macropore structure and smooth surface under scanning electron microscopy (SEM) characterization (Supplementary Fig. 1). After etching reaction for 10 minutes, the treated NF maintains the overall 3D skeleton (Supplementary Fig. 2), but the surface is etched with many pores several micrometers in size (Fig. 1A). The amplified SEM image shows a large number of nanoparticles (200 to 400 nm in diameter) embedded in these micropores (Fig. 1B). The X-ray diffraction (XRD) pattern displays that the newly emerged broad peaks after etching can be assigned to FeOOH (PDF#26-0792) and $\text{Ni}(\text{OH})_2$ (PDF#14-0117), indicating the formation of NiFe-(oxy)hydroxide species (Fig. 1C). Transmission electron microscopy (TEM) image in Fig. 1D shows that the nanoparticle-interconnected assembly creates abundant interspaces with nanopores accessible to electrolyte diffusion. The high-resolution TEM (HRTEM) image (Fig. 1E) reveals the coexistence of crystalline and amorphous textures in single nanoparticle, which yields plenty of grain boundaries commonly rich in catalytic active sites. The exposed interplanar spacings of 0.23 and 0.20 nm in crystalline domains can be well indexed to the (002), (101) planes of $\text{Ni}(\text{OH})_2$ and the (120) plane of FeOOH , respectively. The selected area electron diffraction (SAED) pattern (Supplementary Fig. 3) further discloses the polycrystalline and low-crystalline characteristics in generated nanoparticles. The energy dispersive X-ray spectroscopy (EDS) elemental mappings (Fig. 1F) visualize the uniform distributions of Fe, Ni, P and O elements existing in nanoparticles.

The X-ray photoelectron spectroscopy (XPS) was employed to probe the surface chemical composition and valence states (Supplementary Fig. 4). The signals of Ni, Fe, O and P elements appear in the survey spectrum, consistent with the EDS elemental

mapping. The Ni-2p spectrum displays two spin-orbit peaks at 873.5 eV for Ni 2p_{1/2} and 855.8 eV for Ni 2p_{3/2}, in addition to two satellite peaks (marked as Sat.), which are indicative of mainly existing in Ni²⁺ state. Another small peak at 852.2 eV is the response to metallic Ni⁰ content. The Fe-2p spectrum shows a pair of Fe 2p_{1/2} and Fe 2p_{3/2} peaks located at 726.0 and 712.1 eV, respectively, characteristic of an existent in Fe³⁺ state. The O-1s spectrum can be deconvoluted to the two peaks at 532.4 and 531.3 eV, which are assigned to metal-hydroxyl (M-OH) and metal-oxygen (M-O) coordinations, respectively. In the P-2p spectrum, two small peaks at 131.0 and 130.0 eV for spin-orbit P 2p_{1/2} and P 2p_{3/2} reveal a small amount of P conjugated by metals, and another noticeable peak at 133.1 eV as an indicator of P-O bonds suggests that P species mostly coordinates with O. The electronegative P dopant may improve the electronic conductivity and promote the deprotonation kinetics in WOR¹⁰. Moreover, surface P is easy to be oxidized to form P-O species, which is not only active for water oxidation but also resistance to oxide dissolution⁴⁹.

In addition, SEM images of P-NiFeOOH@NF electrodes prepared with different etching times of 3, 5, 8 and 10 minutes are shown in the Supplementary Fig. 5, which suggest that the NF surface appears rougher with enlarged pores as etching time increases until abundant macropores are cultivated in the 10-minute sample. With further prolonging etching time, the treated NF became brittle with poor mechanical elasticity. Thus, an optimum sample etched for 10 minutes was used for further study unless otherwise noted. To sum up, this simple etching method enables fast surface reconstruction into porous P-NiFeOOH embedded layer, which consists of FeOOH and Ni(OH)₂, along with P dopant inside and outside. This NF-stabilized P-NiFeOOH catalyst was directly employed as an electrode to examine its intrinsic WOR activity and further applicable ability relevant to industrial conditions.

Fig. 2. WOR performance measurements. (A) Polarization curves and (B) Tafel plots for NF, IrO₂, and P-NiFeOOH electrodes in 1 M KOH. (C) The $\Delta\eta/\Delta\log|j|$ ratios for IrO₂ and P-NiFeOOH electrodes in different current density ranges. (D) Polarization curves, and (E) comparison of required overpotentials at various current densities (10–1000 mA cm⁻²) in different electrolytes (1–6 M KOH) for P-NiFeOOH electrode. (F) Polarization curves for P-NiFeOOH electrode in 6 M KOH with different temperatures (25, 40, 60 and 80 °C). (G) CP durability tests for P-NiFeOOH electrode at 5000 and 10000 A m⁻² in 1 M and 6 M KOH electrolytes with varying temperatures from 25 to 80 °C.

WOR performance of P-NiFeOOH electrode. The WOR performance of as-fabricated P-NiFeOOH electrode was first assessed in 1 M KOH electrolyte, with NF-supported commercial IrO₂ catalyst as a benchmark electrode for comparison. From the polarization curves shown in Fig. 2A, it can be seen that P-NiFeOOH electrode exhibits

an evident increase in WOR activity compared to pristine NF, and it is also much superior to IrO₂ benchmark. For instance, small overpotentials of 221 and 251 mV are required for P-NiFeOOH to deliver current densities of 10 and 100 mA cm⁻², which are much lower than those for NF (375 and 553 mV) and IrO₂ (310 and 408 mV) (Supplementary Fig. 6). Especially, at an overpotential of 284 mV, P-NiFeOOH can achieve a large current density up to 1000 mA cm⁻², two orders of magnitude higher than that of IrO₂ benchmark. Accordingly, P-NiFeOOH displays a smaller Tafel slope of 25.1 mV dec⁻¹ than NF (114.2 mV dec⁻¹) and IrO₂ (97.2 mV dec⁻¹), indicating faster catalytic WOR kinetics. These super parameters make P-NiFeOOH among the best for transition metal-based electrodes reported for alkaline WOR (Supplementary Table 1). We further compare the $\Delta\eta/\Delta\log|j|$ ratio that is defined by the slope of overpotential versus logarithm current density for different electrodes with different current densities to appraise the overpotential required to raise the current intensity, which is an important descriptor of catalytic performance especially at large current densities and critically significant for practical availability. The ratio for IrO₂ increases sharply as the current densities exceed 100 mA cm⁻², and reaches 455 mV dec⁻¹ at 500 mA cm⁻² (Fig. 2C), whereas that for P-NiFeOOH remains small, only ~32 mV dec⁻¹ at 1000 mA cm⁻², which indicates its remarkable WOR activity at large current densities.

We also tested the WOR activity of P-NiFeOOH electrodes obtained with different etching times. Longer etching treatment brings about higher WOR activity, and the NF etched with 10 minutes reaches an optimum (Supplementary Fig. 7), beyond which the NF appears brittle upon excessive etching. Thus, 10-minute-etched electrode achieves a balance between the surface porosity and mechanical strength balance, and equips with desirable pore-rich surface serving for active species embedment and site exposure (Supplementary Fig. 5). The double-layer capacitances (C_{dl}

cyclic voltammetry (CV) method (Supplementary Fig. 8). The C_{dl} values increase with incremental etching times, and the 10-minute-etched electrode has a maximum of 12.6 mF cm^{-2} , which is over 3 times that of pristine NF (3.6 mF cm^{-2}), offering a larger electrochemically active surface area (ECSA) with more active sites exposing to electrolyte. This suggests that the creation of abundant cavities embedded with active nanoparticles is very useful to maximize accessible active sites favorable for mass/charge transfer in catalysis.

The surface hydrophilicity and aerophobicity become very critical for the active-site utilization and mass transfer when catalytic electrode coping with high current densities. The surface wettability of P-NiFeOOH electrode was examined through vacuolar contact manner tracked by a high-speed camera (Supplementary Fig. 9). Time sequence images exhibit ultra-fast water wetting process within 13 ms with almost invisible vacuole formation on the surface of P-NiFeOOH electrode while one vacuole remains on bare NF surface over 26 ms, which indicates the superhydrophilicity of P-NiFeOOH electrode favorable for electrolyte permeability. In addition, we recorded the videos for dynamic releases of oxygen bubbles on the pristine NF and P-NiFeOOH electrodes, which reflects the ability of active sites re-exposing to the electrolyte (Supplementary Movie 1 and 2). As shown in the photos of electrodes bubbling (Supplementary Fig. 10), oxygen bubbles stick firmly to the NF surface and appear very large size (mostly over 0.5 mm), shielding intermittently many catalytic sites on the surface. In sharp contrast, much smaller oxygen bubbles below 0.2 mm easily leave away from P-NiFeOOH surface, which guarantees a constant exposure of reactive sites to the surrounding media. Basing on the solid–liquid–gas interface theory^{50,51}, surface roughness at nanoscale or microscale can not only induce capillary force to benefit electrolyte diffusion, but also reduces bubble adhesion at interface to facilitate gas

$R_{ct} \sim 1.2 \ \Omega$), much smaller than commercial IrO_2

and pristine NF (Supplementary Fig. 11), indicating its efficient charge-transport ability favorable to WOR dynamics.

Industrial adaptability of P-NiFeOOH electrode. We then tested the WOR performance of P-NiFeOOH electrode in industrially relevant strong alkali electrolytes (3 M and 6 M KOH). Fig. 2D shows that the polarization activity gradually enhances with increasing alkali concentration, and the performance of P-NiFeOOH remains excellent against strong alkali corrosion. Note that the overpotentials required at even industrial-scale high current densities from 500 up to 1000 mA cm^{-2} are essentially smaller than 300 mV (Fig. 2E). In particular, an ultralow overpotential of only 250 mV can deliver a large current density of 1000 mA cm^{-2} under strong mass transfer in 6 M KOH. Furthermore, the temperature rise in industrial electrolysis is inevitable, and so the electrolyte with heating was used to examine P-NiFeOOH electrode. As shown in Fig. 2F, the elevated temperature can further optimize polarization capability in 6 M KOH in accordance with the Arrhenius law, and when the temperature up to 80 °C, the overpotentials are reduced to 164 and 173 mV for delivering 500 and 1000 mA cm^{-2} current densities, respectively (Supplementary Fig. 12), which represent a record-high performance for current alkaline WOR (Supplementary Table 2). The chronopotentiometry (CP) tests demonstrates the steady WOR catalysis on P-NiFeOOH electrode at both 500 and 1000 mA cm^{-2} for 100 h in 1 M KOH (Fig. 2G). The succedent CP test at 1000 mA cm^{-2} for 100 h in 6 M KOH with varying

temperatures from 25 to 80 °C further verifies the electrode durability with industrial-level large current densities under strong alkali and high temperature conditions. After testing, the P-NiFeOOH electrode basically maintains its structural and component characteristics, as evidenced by SEM, TEM and EDS imaging (Supplementary Fig. 13). Furthermore, the post-characterizations of XRD and XPS (Supplementary Fig. 14) show no detectable phase and valence changes. Of course, there are also little subtle changes noticed for active species, such as more flocculent morphology, clearer crystal domains and less P content. These micro-evolutions, though not reconstructing, may contribute to uncover atomic-scale catalytic centers and deserve further study in the future. The current work focuses on the applicability of P-NiFeOOH electrode to industrial harsh conditions, suggesting its potential practical application. Moreover, compared with other advanced electrodes reported recently, our P-NiFeOOH electrode exhibits both superior activity and stability that are among the best for alkaline WOR (Supplementary Table 2). These results confirm the exceptional WOR performance of P-NiFeOOH electrode especially suitable for industrial AWE, which mainly thanks to the targeted design with multiple advantages including the highly porous structure, as well as the robustly embedded contact and strong catalytic activity and corrosion resistance.

Fig. 3. Practical application of water electrolyser. (A) Schematic diagram of an electrolyzer cell using P-NiFeOOH and Pt as the anode and cathode, respectively. (B) Polarization curves in 1 M KOH of electrolytic cells using different anodes of P-NiFeOOH, benchmark IrO₂ and industrial Ni mesh, respectively, with same Pt foils as cathodes. (C) Numbers of reacting and conducting electrons over the P-NiFeOOH || Pt electrolyser at 100 mA cm⁻² current density. (D) CP durability tests for P-NiFeOOH || Pt electrolyzer at 10000 and 5000 A m⁻² in 6 M KOH with varying temperatures. (E) Comparison of large-current overpotential and stability performance in 1 M and 6 M KOH for P-NiFeOOH and other WOR electrodes.

Practical application of water electrolyser. To demonstrate overall water electrolysis application, we assemble a two-electrode electrolyser using the present P-NiFeOOH as the anode coupled with the Pt foil as the benchmark cathode (Fig. 3A). Notably, as shown in Fig. 3B, the designed P-NiFeOOH || Pt electrolyser displays remarkable activity for overall alkali water splitting in 1 M KOH, requiring small cell voltages of 1.653, 1.714, and 1.746 V to achieve current densities of 100, 500, and 1000 mA cm⁻², respectively, which are much lower than those for two benchmarks of IrO₂ || Pt and Ni mesh || Pt. When in 6 M KOH, the cell voltages of P-NiFeOOH || Pt electrolyser drop to

1.584, 1.652 and 1.692 V for delivering current densities of 100, 500, and 1000 mA cm⁻², respectively, even with only 1.743 V required to reach 2000 mA cm⁻² (Supplementary Fig. 15). Gaseous produces were measured with an online gas chromatography for water electrolysis over P-NiFeOOH || Pt electrolyzer operated at 100 mA cm⁻² current density. As shown in the Supplementary Fig. 16, H₂ and O₂ evolving amounts match well with a stoichiometric ratio of 2:1 by overall water splitting, and the number of reacting electrons in catalysis is almost equal to that conducting in the circuit (Fig. 3C), indicating an almost 100% Faraday efficiency for overall water splitting.

Furthermore, the P-NiFeOOH || Pt electrolyser proceeds long-term stable water electrolysis in the CP model with no noticeable performance decay for 150 h at large current densities of 500 and 1000 mA cm⁻² in 6 M KOH electrolyte with different temperatures of 25 and 80 °C (Fig. 3D), and the polarization curve after the CP test is very close to the pristine level before stability test (Supplementary Fig. 17). The unit electricity consumption per cubic meter of H₂ (W_u) and corresponding electricity-to-hydrogen energy conversion efficiency (ETH) were calculated to be 3.9 kW h and 90% (Supplementary Fig. 18), respectively, whereas current commercial electrolyzers commonly operate at an W_u of over 4.5 kW h m⁻³ with an STH less than 80%⁵⁴. We summarize the cell voltages and durable times at industrial-level large current densities for reported water electrolyzers consisting of transition-metal-based anodes with various cathodes for alkaline water splitting (Supplementary Table 3). The P-NiFeOOH electrode exhibits as a preferable alternative to costly IrO₂/RuO₂ anodes used in commercial hydrogen generators. In order to highlight the advantages of P-NiFeOOH in balancing activity and stability toward practical applications, we further compared the overpotentials and steady times at high current densities (5000 and 10000 A m⁻²) with other state-of-the-art WOR electrodes reported recently (Fig. 3E and

Supplementary Table 2). Evidently, the P-NiFeOOH electrode stands out from them and has evident superiorities both in high-current-density activity and long-term stability. Moreover, such win-win performance is creditable especially in 6 M KOH because large-current-density WOR electrodes steady in strong alkali are rarely reported to date. Combined with the simple and scalable preparation process (Supplementary Fig. 19), the self-stabilized P-NiFeOOH electrode exhibits overall competitive advantages both from super performance and low capital cost toward practical applications.

Discussion

In summary, we have developed a non-noble metal based WOR electrode via facilely etching NF for industrially-relevant AWE with large current densities and harsh environments, by light of the support-stabilizing catalyst combination and porosity-enabling catalysis acceleration. The produced electrode with in-situ-grown active P-NiFeOOH nanoparticles embedded in surface micropores exhibits an overpotential as low as only 284 mV to achieve high current density of 1000 mA cm⁻² in 1 M KOH, which is among the best records for alkaline WOR, and also shows long durability for over 150 h at industrial-level large current densities in strong alkaline 6 M KOH electrolyte with elevated temperature up to 80 °C. The time-saving and low-cost production can be scaled up and make this electrode more cost-effective in commercial practice for massive water electrolysis to generate hydrogen. In particular, a new concept of "catalyst-substrate fusion electrode" based on targeted etching metal substrates was proposed to enable strong self-stabilizing effect on mechanical adhesion and charge/mass transfer at catalytic interfaces, which is instructive for designing high-performance electrodes competent for industrial-scale electrolysis.

Methods

Synthesis of P-NiFeOOH electrode. The P-NiFeOOH electrode was fabricated through a simple and scalable one-step etching method. Before synthesis, several pieces of small nickel foam (NF) were cut with same size of $1 \times 2 \text{ cm}^2$, and then washed for 10 minutes with sonication using successively acetone, dilute hydrochloric acid, ethanol and deionized water (DW) each, and finally dried under vacuum for later use. Typically, 0.3 mmol of Na_3PO_4 and 0.87 mmol of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved into 10 mL DW with continuous stirring to prepare a homogeneous solution. The cleaned NF was put into the above mixed solution, with controllable etching reaction times varying from 3 to 15 minutes to adjust etching degree and screen performance optimum. In this reaction, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and Na_3PO_4 feed the Fe and P sources, respectively. The NF provides the Ni source and meanwhile serves as the conductive substrate. After ten minutes of etching reaction, the NF was washed fully using in turn DW/ethanol, and was finally dried at 80°C overnight in a vacuum oven.

Synthesis of $\text{IrO}_2@\text{NF}$ electrode. 60 μL Nafion, 40 mg IrO_2 , 400 μL deionized water and 540 μL ethanol were mixed with ultrasonication for 90 min to prepare a homogeneous solution. The dispersion was then dripped onto the NF substrate and dried overnight under vacuum to obtain the NF-supported IrO_2 electrode. The commercial Ni mesh electrode (General purpose alkaline electrolyser electrode) was provided from China Electric Hydrogen Production Co. LTD.

Structural characterizations. Field-emission scanning electron microscopy (SEM) was carried out on Hitachi S-4800II at 15 kV acceleration voltage. Low- and high-resolution transmission electron microscopy (TEM) were performed on a Tecnai F30 with EDS spectroscopy at 200 kV acceleration voltage. XPS spectroscopy was conducted on an Escalab 250Xi using an Al $K\alpha$ x-ray irradiation (1486.60 eV). X-ray

diffraction (XRD) was recorded using a XRD-7000 diffractometer (Shimadzu) using a monochromatic Cu K α beam ($\lambda = 0.154$ nm).

Electrochemical measurements. All electrochemical measurements were conducted in three- and two-electrode models on an electrochemical workstation (CHI 660E, China). The water oxidation reaction (WOR) performance of electrodes was examined via conventional three-electrode model, in which the as-fabricated electrodes, a graphite rod (99.9995%, Alfa Aesar) and an Ag/AgCl (Penglai, Shanghai) were employed as working electrodes, counter electrode and reference electrode, respectively. Electrolytes with different alkali concentrations (1-6 M KOH) and temperatures (25-80 °C) were prepared to simulate industrial operating environments. The electrolyte temperatures were adjusted or maintained by a temperature-controlling platform. The polarization curves were obtained from backward branches by cyclic voltammetry (CV) scanning at a slow rate of 10 mV s⁻¹. The durability tests were conducted in long-term chronopotentiometry (CP) model. Electrochemical impedance spectroscopy (EIS) was recorded within the frequency range of 10⁻²-10⁵ Hz, with 5 mV voltage amplitude. The two-electrode systems were constructed to operate overall water splitting by using the prepared P-NiFeOOH, commercial IrO₂ and Ni mesh as compared anodes, respectively, with same Pt foils as the cathodes. All reported potentials were calibrated with 90% *iR* compensation by Formula 1 and converted against reversible hydrogen electrode (RHE) by Formula 2 unless otherwise mentioned as following:

$$E_{\text{calibrated}} = E_{\text{measured}} - iR_s \quad (1)$$

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}}^0 + E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} \quad (2)$$

where $E_{\text{Ag/AgCl}}^0$ is the benchmark potential of Ag/AgCl reference electrode (0.1976 V versus RHE at 25 °C), R_s is the series resistance determined by the EIS. Tafel slopes

were estimated by Tafel plots from the linear portion fitting overpotential (η) against $\log|j|$ (j , current density) by the Formula 3:

$$\eta = b \log|j| + a \quad (3)$$

CV curves were recorded at a potential range from 0.1 to 0.2 V versus RHE without Faradic current, using different scanning rates (ν) of 10-110 mV s⁻¹ with double-layer charging currents (Δj) to calculate the double-layer capacitances (C_{dl}) by the following Formula 4:

$$C_{dl} = \Delta j / \nu \quad (4)$$

The electrochemically active surface areas (ECSA) were further evaluated as the ratio of C_{dl} to a constant specific capacitance (C_s , 0.04 mF cm⁻²) by the following Formula 5:

$$ESCA = C_{dl} / C_s \quad (5)$$

Real-time monitoring of gas evolution with a photocatalytic platform and gas chromatograph (Labsolar-IIIAG, Perfectlight Beijing; FULI 9790H) with a sealed electrolyser operating at 100 mA cm⁻² current density from 0 to 60 minutes.

Calculation method. To evaluate the Faradaic efficiency (ξ_F), the reacting electron number (N_{re}) and conducting electron number (N_{ce}) were calculated and compared based on the following Formulas 6-8:

$$N_{re} = 4M_O N_A \quad (6)$$

$$N_{ce} = jst/e \quad (7)$$

$$\xi_F = N_{ce} / N_{re} \times 100\% \quad (8)$$

where M_O is the mole amount of evolved O_2 , N_A is the avogadro number, e is the electron charge, as well as j , s , and t is the current density, effective electrode area, and the time, respectively.

The unit electricity consumption (W_u , $\text{kW} \cdot \text{h m}^{-3}$) required to produce one standard cubic meter of H_2 was calculated using the unit electric quantity (Q_u , $\text{A} \cdot \text{h m}^{-3}$) and cell voltage (V , V) at a certain current density of 500 mA cm^{-2} that is commonly operated in industrial alkali water electrolysis, according to the following Formula 9. The volume per mole of H_2 in standard state is $22.43 \times 10^{-3} \text{ m}^3$, so Q_u was calculated by the following Formula 10.

$$W_u = Q_u \times V / 1000 \text{ kW} \cdot \text{h m}^{-3} \quad (9)$$

$$Q_u = 2N_A e / (3600 \times 22.43 \times 10^{-3}) = 2390 \text{ A} \cdot \text{h m}^{-3} \quad (10)$$

Further, the electricity-to-hydrogen energy conversion efficiency (ETH) was estimated with a standard thermal neutral voltage ($V = 1.48 \text{ V}$) at which no waste heat is generated only for water splitting through the following Formula 11.

$$\text{ETH} = \frac{1.48 \times Q_u}{W_u \times 1000} \times 100\% \quad (11)$$

Data availability. All data supporting the results of this study are available from the corresponding authors upon reasonable request.

References

1. Chow, J., Kopp, R. J. & Portney, P. R. Energy resources and global development. *Science* **302**, 1528–1531 (2003).
2. Seh, Z. W. et al. Combining theory and experiment in electrocatalysis: insights into materials design. *Science* **355**, eaad4998 (2017).
3. Wu, H. et al. Non-noble metal electrocatalysts for the hydrogen evolution reaction in water electrolysis. *Electrochem. Energy Rev.* **4**, 473–507 (2021).

4. Hosseini, S. E. & Wahid, M. A. Hydrogen from solar energy, a clean energy carrier from a sustainable source of energy. *Int. J. Energy Res.* **44**, 4110–4131 (2020).
5. De Luna, et al. What would it take for renewably powered electrosynthesis to displace petrochemical processes? *Science* **364**, eaav3506 (2019).
6. Rabiee, H. et al. Gas diffusion electrodes (GDEs) for electrochemical reduction of carbon dioxide, carbon monoxide, and dinitrogen to value-added products: a review. *Energy Environ. Sci.* **14**, 1959–2008 (2021).
7. Luo, J. et al. Water photolysis at 12.3% efficiency via perovskite photovoltaics and earth-abundant catalysts. *Science* **345**, 1593–1596 (2014).
8. Wang, J. et al. Non-precious-metal catalysts for alkaline water electrolysis: operando characterizations, theoretical calculations, and recent advances. *Chem. Soc. Rev.* **49**, 9154–9196 (2020).
9. Kibsgaard, J. & Chorkendorff, I. Considerations for the scaling-up of water splitting catalysts. *Nat. Energy* **4**, 430–433 (2019).
10. Chang, J. et al. Dual-doping and synergism toward high-performance seawater electrolysis. *Adv. Mater.* **33**, 2101425 (2021).
11. Kuznetsov, D. A. et al. Tuning redox transitions via inductive effect in metal oxides and complexes, and implications in oxygen electrocatalysis. *Joule* **2**, 225–244 (2018).
12. Yao, Y. et al. Engineering the electronic structure of single atom Ru sites via compressive strain boosts acidic water oxidation electrocatalysis. *Nat. Catal.* **2**, 304 (2019).
13. Suen, N. T. Electrocatalysis for the oxygen evolution reaction: recent development and future perspectives. *Chem. Soc. Rev.* **46**, 337–365 (2017).
14. Chung, D. Y. et al. Dynamic stability of active sites in hydr(oxy)oxides for the

- oxygen evolution reaction. *Nat. Energy* **5**, 222–230 (2020).
15. Menezes, P. W. et al. Uncovering the nature of active species of nickel phosphide catalysts in high-performance electrochemical overall water splitting. *ACS Catal.* **7**, 103–109 (2017).
 16. Wu, T. et al. Spin pinning effect to reconstructed oxyhydroxide layer on ferromagnetic oxides for enhanced water oxidation. *Nat. Commun.* **12**, 3634 (2021).
 17. Song, J. et al. A review on fundamentals for designing oxygen evolution electrocatalysts. *Chem. Soc. Rev.* **49**, 2196–2214 (2020).
 18. Yu, L. et al. Non-noble metal-nitride based electrocatalysts for high-performance alkaline seawater electrolysis. *Nat. Commun.* **10**, 5106 (2019).
 19. Liu, Y. et al. Corrosion engineering towards efficient oxygen evolution electrodes with stable catalytic activity for over 6000 hours. *Nat. Commun.* **9**, 2609 (2018).
 20. Xiao, H., Shin, H. & Goddard, W. A. Synergy between Fe and Ni in the optimal performance of (Ni,Fe)OOH catalysts for the oxygen evolution reaction. *Proc. Natl. Acad. Sci. U.S.A.* **115**, 5872–5877 (2018).
 21. Yu, J. et al. Monoclinic SrIrO₃: an easily synthesized conductive perovskite oxide with outstanding performance for overall water splitting in alkaline solution. *Chem. Mater.* **32**, 11, 4509–4517 (2020).
 22. Wang, C. et al. Redox bifunctional activities with optical gain of Ni₃S₂ nanosheets edged with MoS₂ for overall water splitting. *Appl. Catal. B: Environ.* **268**, 118435 (2020).
 23. Lu, C. et al. Molybdenum carbide-embedded nitrogen-doped porous carbon nanosheets as electrocatalysts for water splitting in alkaline media. *ACS Nano* **11**, 3933–3942 (2017).
 24. Zhu, C. et al. Fe-Ni-Mo nitride porous nanotubes for full water splitting and Zn-air

- batteries. *Adv. Energy Mater.* **8**, 1802327 (2018).
25. Liang, H. et al. Amorphous NiFe-OH/NiFeP electrocatalyst fabricated at low temperature for water oxidation applications. *ACS Energy Lett.* **2**, 1035–1042 (2017).
 26. Bao, F. et al. Host, suppressor, and promoter-the roles of Ni and Fe on oxygen evolution reaction activity and stability of NiFe alloy thin films in alkaline media. *ACS Catal.* **11**, 10537–10552 (2021).
 27. Wang, B. et al. In situ structural evolution of the multi-site alloy electrocatalyst to manipulate the intermediate for enhanced water oxidation reaction. *Energy Environ. Sci.* **13**, 2200–2208 (2020).
 28. Masa, J., Andronescu, C. & Schuhmann, W. Electrocatalysis as the nexus for sustainable renewable energy: the gordian knot of activity, stability, and selectivity. *Angew. Chem. Int. Ed.* **59**, 15298–15312 (2020).
 29. Chen, F. Y., Wu, Z. Y., Adler, Z. & Wang, H. Stability challenges of electrocatalytic oxygen evolution reaction: From mechanistic understanding to reactor design. *Joule* **5**, 1–28 (2021).
 30. Yu, L. et al. Ultrafast room-temperature synthesis of porous S-doped Ni/Fe (oxy)hydroxide electrodes for oxygen evolution catalysis in seawater splitting. *Energy Environ. Sci.* **13**, 3439–3446 (2020).
 31. Zhang, X. et al. A simple synthetic strategy toward defect-rich porous monolayer NiFe-layered double hydroxide nanosheets for efficient electrocatalytic water oxidation. *Adv. Energy Mater.* **9**, 1900881 (2019).
 32. Zhang, B. et al. Homogeneously dispersed multimetal oxygen-evolving catalysts. *Science* **352**, 333–337 (2016).
 33. Luo, Y., Zhang, Z., Chhowalla, M. & Liu, B. Recent advances in design of

- electrocatalysts for high-current-density water splitting. *Adv. Mater.* <https://doi.org/10.1002/adma.202108133> (2021).
34. Godula-Jopek, A. Hydrogen production: by electrolysis, 1st ed., John Wiley & Sons, New Jersey (2015).
 35. Yang, F. et al. A durable and efficient electrocatalyst for saline water splitting with current density exceeding 2000 mA cm⁻². *Adv. Funct. Mater.* **31** 2010367 (2021).
 36. Luo, Y. et al. Morphology and surface chemistry engineering toward pH-universal catalysts for hydrogen evolution at high current density. *Nat. Commun.* **10**, 269 (2019).
 37. Shan, X. et al. An engineered superhydrophilic/superaerophobic electrocatalyst composed of the supported CoMoS_x chalcogel for overall water splitting. *Angew. Chem., Int. Ed.* **59**, 1659–1665 (2020).
 38. Yu, Q. et al. A Ta-TaS₂ monolith catalyst with robust and metallic interface for superior hydrogen evolution. *Nat. Commun.* **12**, 6051 (2021).
 39. Yang, H., Driess, M. & Menezes, P. W. Self-supported electrocatalysts for practical water electrolysis. *Adv. Energy Mater.* **11**, 2102074 (2021).
 40. Wang, Y. et al. NiFe (sulfur) oxyhydroxide porous nanoclusters/Ni foam composite electrode drives a large-current-density oxygen evolution reaction with an ultra-low overpotential. *J. Mater. Chem. A* **7**, 18816–18822 (2019).
 41. Yu, M. et al. A hierarchically porous and hydrophilic 3D nickel–iron/MXene electrode for accelerating oxygen and hydrogen evolution at high current densities. *Nano Energy* **63**, 103880 (2019).
 42. Zou, X. et al. Ultrafast formation of amorphous bimetallic hydroxide films on 3D conductive sulfide nanoarrays for large-current-density oxygen evolution electrocatalysis. *Adv. Mater.* **29**, 1700404 (2017).

43. Liang, C. Exceptional performance of hierarchical Ni-Fe oxyhydroxide@NiFe alloy nanowire array electrocatalysts for large current density water splitting. *Energy Environ. Sci.* **13**, 86–95 (2020).
44. Liu, P. et al. Tip-enhanced electric field: a new mechanism promoting mass transfer in oxygen evolution reactions. *Adv. Mater.* **33**, e2007377 (2021).
45. Xu, X., Song, F. & Hu, X. A nickel iron diselenide-derived efficient oxygen-evolution catalyst. *Nat. Commun.* **7**, 12324 (2016).
46. Liu, J. et al. Engineering self-reconstruction via flexible components in layered double hydroxides for superior-evolving performance, *Small* **17**, 2101671 (2021).
47. Liu, X. et al. Deep reconstruction of nickel-based precatalysts for water oxidation catalysis. *ACS Energy Lett.* **4**, 2585–2592 (2019).
48. Wu, L. et al. Heterogeneous bimetallic phosphide Ni₂P-Fe₂P as an efficient bifunctional catalyst for water/seawater splitting. *Adv. Funct. Mater.* **31**, 2006484 (2020).
49. Chang, J. et al. Core-shell structured Ni₁₂P₅/Ni₃(PO₄)₂ hollow spheres as difunctional and efficient electrocatalysts for overall water electrolysis. *Appl. Catal. B: Environ.* **204**, 486–496 (2017).
50. Lai, Y. et al. Designing superhydrophobic porous nanostructures with tunable water adhesion. *Adv. Mater.* **21**, 3799–3803 (2009).
51. David, Q. Non-sticking drops. *Rep. Prog. Phys.* **68**, 2495 (2005).
52. George, J. E., Chidangil, S., George, S. D. Recent progress in fabricating superaerophobic and superaerophilic surfaces. *Adv. Mater. Interfaces* **4**, 1601088 (2017).
53. Luo, Y., Li, J., Zhu, J., Zhao, Y. & Gao, X. Fabrication of condensate microdrop self-propelling porous films of cerium oxide nanoparticles on copper surfaces.

Angew. Chem. Int. Ed. **54**, 4876–4879 (2015).

54. Zhang, X. et al. Minimum allowable values of energy efficiency and energy efficiency grades for hydrogen producing systems by water electrolysis. National standards of the People's Republic of China (2017).

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Author contributions

X.X. conceived the idea, and directed the research. Z.Z., J.L. and X.Y. made sample synthesis, characterization and performance tests. M.Z. designed sample devices and assisted with operation analysis. X.X. and Z.Z. interpreted the data and co-wrote the manuscript. All of the authors discussed the results together and proofread the text.

Competing interests

The authors declare no competing interests.

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