Electrochemically Reconstructed Cu-FeOOH/Fe₃O₄ Catalyst for Efficient Hydrogen Evolution in Alkaline Media

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Surface self-reconstruction via incorporating an amorphous structure on the surface of a catalyst can induce abundant defects and unsaturated sites for enhanced hydrogen evolution reaction (HER) activity. Herein, an electrochemical activation method is proposed to reconstruct the surface of a Cu-Fe₃O₄ catalyst. Following a “dissolution–redeposition” path, the defective FeOOH is formed under potential stimulation on the surface of the Cu-Fe₃O₄ precursor during the electrochemical activation process. This Cu-FeOOH/Fe₃O₄ catalyst exhibits excellent stability as well as extremely low overpotential toward the alkaline HER (e.g., 129 and 285 mV at the large current densities of −100 and 500 mA cm⁻², respectively), much superior to the Pt/C catalyst. The experimental and density functional theory calculation results demonstrate that the Cu-FeOOH/Fe₃O₄ catalyst has abundant oxygen vacancies, featuring optimized surface chemical composition and electronic structure for improving the active sites and intrinsic activity. Introducing defective FeOOH on the surface of a Cu-Fe₃O₄ catalyst by means of an electrochemical activation method decreases the energy barrier of both H₂O dissociation and H₂ generation. Such a surface self-reconstruction strategy provides a new avenue toward the production of efficient non-noble metal catalysts for the HER.

1. Introduction

The hydrogen evolution reaction (HER) from water splitting under large current densities plays a vital role in industrial hydrogen production in that it is an efficient approach to solve the challenges of climate change and meanwhile to achieve carbon neutrality.[1–3] Unfortunately, the HER features slow kinetics, especially in alkaline media. Pt-based materials have been thus utilized and further recognized as the most effective HER catalysts, although their high price and scarcity severely restrict widespread and industrial applications of the HER.[4–6] In this regard, earth-rich and cheap HER catalysts are still on great demand from scientific and industrial orientations. For example, the earth-abundant Fe₃O₄ shows up as a possible alternative to noble metal-based catalysts since its octahedral Fe sites can facilitate the H₂O dissociation process to provide hydrogen intermediates in alkaline media.[7–8] On the other hand, the HER kinetics of Fe₃O₄ is limited by adverse hydrogen adsorption, inefficient H₂ generation during a Heyrovsky step or a Tafel step, and its unsatisfactory electrical conductivity.[9] Hence, the electron structures of Fe₃O₄-based catalysts have to be designed and modulated to boost the HER for efficient hydrogen production, especially under large current densities.

Among various strategies to regulate the electronic structures of HER catalysts, reconstruction of the catalyst surface via incorporating an amorphous structure is one of the most effective approaches up to date.[10,11] This process can induce abundant defects and unsaturated sites, which are identified as the active centers, leading to significantly improved HER activity.[12–16] As one of the most effective and controllable surfaces reconstruction strategies, electrochemical activation has been attracted great interest.[17–21] Under potential stimulation, this optimal method can let some components of the precursor leach at the catalyst-electrolyte interface and react with the electrolyte to form an amorphous phase on the surface of the precursor.[22–24] Leaching of the active components actually triggers this activation process. Therefore, a relatively weak chemical bond in the precursor is necessary to overcome the constraints of the crystal lattice.[24,25] The introduction of heteroatoms or vacancies can destabilize the original structures and thus accelerate the dissolution of the active components and subsequent redeposition. Using electrochemical activation Fe₃O₄ is expected to be reconstructed, where defects or...
active sites will be introduced into the Fe$_3$O$_4$ precursor. In this way, the electronic structure of a Fe$_3$O$_4$ catalyst is feasible to be tuned and the HER kinetics of a Fe$_3$O$_4$ catalyst will be accelerated.

Herein, an electrochemical activation strategy is proposed to self-reconstruct a Cu-Fe$_3$O$_4$ catalyst. In the first step, Cu atoms and oxygen vacancies are introduced into Fe$_3$O$_4$ (Cu-Fe$_3$O$_4$) by the means of a hydrothermal method. This precursor is applied for its electrochemical activation. During the HER process, the defective FeOOH is then formed on the surface of Cu-Fe$_3$O$_4$ in alkaline media, followed by a “dissolution–redeposition” route. This as-obtained Cu-FeOOH/Fe$_3$O$_4$ catalyst exhibits the superior HER activity (e.g., low overpotential, small Tafel slope, high faradaic efficiency) to the market-available noble metal Pt/C catalyst, especially under large current densities. This is because the Cu-FeOOH/Fe$_3$O$_4$ catalyst owns abundant oxygen vacancies and features optimized surface chemical composition and electronic structure, leading to increased active sites and enhanced intrinsic activity. Theoretical calculations demonstrate that the enhancement of HER catalytic activity of the Cu-FeOOH/Fe$_3$O$_4$ catalyst stems from the defective FeOOH introduced into the surface of the Cu-Fe$_3$O$_4$ catalyst decreases the energy barrier of both H$_2$O dissociation and H$_2$ generation. This study thus presents an efficient approach to optimize the surface structure of non-noble, earth-rich, and cheap catalysts for superior HER activity, especially under high current densities.

2. Results and Discussion

The schematic diagram for the preparation of Cu-Fe$_3$O$_4$ and Cu-FeOOH/Fe$_3$O$_4$ catalysts is depicted in Figure 1a. In the step, a Cu-Fe$_3$O$_4$ precursor is grown through a simple hydrothermal reaction on an iron foam (IF) substrate, of which thickness is 2 mm. A subsequent electrochemical activation process (e.g., under −120 mV vs. RHE in 1 M KOH) results in the formation of FeOOH on the surface of the Cu-Fe$_3$O$_4$ precursor, namely the
generation of a Cu-FeOOH/Fe₃O₄ catalyst. This potential-driven electrochemical self-reconstruction follows a dynamic “dissolution–redepotition” route.[22] In more detail, partial Fe species in the Cu-Fe₃O₄ precursor leaches at the catalyst-electrolyte interface and subsequently reacts with OH⁻ ions, leading to the electrolysissynthesis of FeOOH on the surface of the Cu-Fe₃O₄ precursor. Since FeOOH features a narrow bandgap, abundant defects, and strong adsorption hydrogen capacity,[26–28] this electrochemical introduction of FeOOH into the Cu-Fe₃O₄ precursor reconstructs the surface of the Cu-Fe₃O₄ precursor, modulates electronic structures of the Cu-Fe₃O₄ precursor, and provides more active sites towards HER.[29] On the Cu-FeOOH/Fe₃O₄ catalyst, boosted HER kinetics is thus expected.

Prior to the investigation of the HER performance on this Cu-FeOOH/Fe₃O₄ catalyst, it was characterized using different electron microscopes. From recorded scanning electron microscopy (SEM) images of the as-mentioned catalysts, one can see that the untreated IF substrate owns a continuous 3D porous structure (Figure 1b), in favor of increasing the specific surface area and exposing active catalyst sites of a loaded catalyst. The as-synthesized in Fe₃O₄ and Cu-Fe₃O₄ catalysts are ultra-thin and uniform. These nanosheets have an average thickness of ~0.5 μm (Figure 1c) and 1 μm (Figure 1d), respectively.

To better understand the dynamics of the proposed electrochemical activation process, the microstructures of a Cu-Fe₃O₄ precursor was monitored when different activation times were applied. For example, the catalyst prepared with an activation time of 20 h (named as Cu-Fe₃O₄-20) features a new polygonal nanoflake structure, of which thickness is ~20 nm and its height is ~3 μm (Figure 1e). The ultra-thinning nanosheets of Cu-Fe₃O₄ precursor gradually dwindle. These polygon nanoflakes are identified as the microstructures of the Cu-FeOOH/Fe₃O₄ catalyst. These polygon nanoflakes (Cu-FeOOH/Fe₃O₄ catalyst) dominate after an activation time of 50 h is applied, whereas the original nanosheets structure disappears piece by piece (Figure 1f). Compared with a Cu-FeOOH/Fe₃O₄ catalyst, the microstructure change of the catalyst with an activation time of 100 h (named as Cu-Fe₃O₄-100) can be ignored (Figure 1g). This confirms that the catalyst reaches a stable state after an activation time of 50 h is applied, suggesting the outstanding durability of a Cu-FeOOH/Fe₃O₄ catalyst.

The microstructure of Cu-Fe₃O₄ and Cu-FeOOH/Fe₃O₄ catalysts were further characterized by transmission electron microscopy (TEM). The denoted lattice fringe with a spacing of 0.25 nm (Figure 1h) is indexed to the (311) plane of Fe₃O₄. The d-spacings of 0.25 and 0.33 nm (Figure 1i) match well with the (311) and (310) lattice planes of FeO₂ and FeOOH, respectively. These results confirm the successful introduction of FeOOH into a Cu-Fe₃O₄ precursor. More importantly, the lattice mismatch between FeOOH and Fe₃O₄ is only 0.32%. This well-matched interface on the Cu-FeOOH/Fe₃O₄ catalyst can thus accelerate the electron redistribution and further optimize the electronic structure of this catalyst, resulting in improved HER performance. Furthermore, the corresponding energy-dispersive X-ray spectroscopy mapping images clearly demonstrate that the Fe, Cu, and O elements are homogeneously distributed over the entire structure of both a Cu-Fe₃O₄ precursor (Figure S1, Supporting Information) and a Cu-FeOOH/Fe₃O₄ (Figure S2, Supporting Information) catalyst. In short, the structural transformation of a Cu-Fe₃O₄ precursor during the electrochemical activation process is expected as follows (Figure 1j). As a longer activation time is applied, the ultra-thinning nanosheets of the Cu-Fe₃O₄ precursor disappear piece by piece, while the polygon nanoflake of a Cu-FeOOH/Fe₃O₄ catalyst dominates after an activation time of 50 h.

The X-ray diffraction (XRD) was used to investigate the phase composition of this as-obtained Fe₃O₄, Cu-FeOOH, and Cu-FeOOH/Fe₃O₄ catalysts. The diffraction peaks at 44.6°, 65.0°, and 82.3° (Figure S3, Supporting Information) correspond to the (110), (200), and (211) facets of cubic Fe metallic (PDF#06-0696), respectively. They are actually originated from the used IF substrate. The peaks located at 30.2°, 35.6°, and 62.9° (Figure 2a) are indexed to (220), (311), and (440) facets of the standard Fe₃O₄ (PDF#39-1346) in Fe₃O₄, Cu-Fe₃O₄ and Cu-FeOOH/Fe₃O₄ catalysts, respectively. As shown in XRD patterns of the Cu-FeOOH/Fe₃O₄ catalyst (Figure 2a and Figure S4, Supporting Information), the diffraction peaks locating at 26.7°, 34.1°, and 46.7° are assigned to (310), (400), and (411) planes of a FeOOH phase (PDF#34-1266), respectively. It identifies that the formation of FeOOH occurs on the surface of the Cu-Fe₃O₄ precursor during the electrochemical activation process. Such amorphous FeOOH is beneficial to increase the number of active sites and eventually to improve the intrinsic activity of the Cu-FeOOH/Fe₃O₄ catalyst for the HER. However, no FeOOH phase is observed in XRD patterns of the Fe₃O₄-50 catalyst (Figure S5, Supporting Information), demonstrating that the electrochemical activation process is difficult to take place on pure Fe₃O₄.

The contents of Fe and other impurities in IF were determined by inductively coupled plasma-mass spectrometry (ICP-MS). The obtained mass fraction of Fe is 99.432 wt.% (Table S1, Supporting Information). The content of the other impurities in IF is less than 0.60 wt.%, which contains 0.401 wt.% Ni. To further identify the exact position of Ni impurities, the IF substrate was separated from the Cu-Fe₃O₄ (denoted as IF[Cu-Fe₃O₄]) and Cu-FeOOH/Fe₃O₄ (denoted as IF[Cu-FeOOH/Fe₃O₄]) catalysts by ultrasonic treatment. According to their ICP-MS analysis (Table S2, Supporting Information), the Ni contents of IF[Cu-Fe₃O₄] and IF[Cu-FeOOH/Fe₃O₄] substrates are 0.436 and 0.437 wt.%, respectively. They are similar to that of an untreated IF substrate (0.40 wt.%). On the contrary, the contents of Ni in the separated Cu-Fe₃O₄ (0.087 wt.% and Cu-FeOOH/Fe₃O₄ (0.066 wt.% powers are thimbleful and most likely introduced during the ultrasonic treatment. Therefore, the influence of IF impurities during the preparation process on the contribution to the HER performance of this catalyst can be ignored.
Cu-Fe$_3$O$_4$ precursor for maintaining the electric neutrality of the catalyst. This result provides evidence that Fe atoms are substituted by Cu atoms. In this regard, the oxygen vacancies always appear around Cu atoms. Moreover, the amplified and broadened signal of the Cu-FeOOH/Fe$_3$O$_4$ catalyst indicates an increased concentration of oxygen vacancies. These results illustrate that the oxygen vacancies are derived from the introduction of Cu heteroatoms and the defective FeOOH. The FeOOH-incorporation and the oxygen vacancies then regulate the chemical composition and electronic structure of a Cu-FeOOH/Fe$_3$O$_4$ catalyst, leading to its enhanced HER activity.

Meanwhile, the X-ray photoelectron spectra (XPS) survey patterns reveal that the Fe and O elements dominate these three catalysts, while the XPS signal of Cu atoms appears in both Cu-Fe$_3$O$_4$ and Cu-FeOOH/Fe$_3$O$_4$ catalysts (Figure S6, Supporting Information). No Ni signal was observed in the XPS spectra of these catalysts, confirming again that the Ni impurities in the IF substrate do not exist on the surface of these catalysts during their synthesis processes. In the O 1s XPS spectra of these catalysts, three peaks can be identified (Figure 2d). The peak at about 529.7 eV is attributed to the Cu/Fe-O bond, while the peak at about 530.9 eV corresponds to the oxygen vacancies, and the peak at about 532.8 eV is associated with the surface oxygen.[34] For the Fe 2p XPS spectra of these catalysts (Figure 2e), the visible peaks located at about 710.0, 711.6, 721.8, and 724.2 eV are corresponding to Fe$^{2+}$ 2p$_{3/2}$, Fe$^{3+}$ 2p$_{3/2}$, Fe$^{2+}$ 2p$_{1/2}$, and Fe$^{3+}$ 2p$_{1/2}$, respectively.[35,36] In their Cu 2p$_{3/2}$ XPS spectra (Figure 2f), the peaks at 933.1,
934.9, and 942.3 are ascribed to Cu$^0$/Cu$^+$ 2p$_{3/2}$, Cu$^{2+}$ 2p$_{1/2}$, and Cu$^{2+}$ 2p$_{3/2}$, respectively.[17,38] The existence of Cu$^{2+}$ and Cu$^+$ in Cu-Fe$_2$O$_4$ and Cu-FeOOH/Fe$_3$O$_4$ catalysts indicate that the Cu atoms are introduced into the lattices by the formation of Cu–O bonds, suggesting that the Fe atoms are substituted by Cu. Furthermore, the XPS spectra of the Cu-Fe$_2$O$_4$-100 catalyst were also recorded (Figure S7, Supporting Information), where no obvious changes are found in its O 1s, Fe 2p, and Cu 2p XPS spectra compared with those of a Cu-FeOOH/Fe$_3$O$_4$ catalyst. These results again demonstrate the excellent durability of the Cu-FeOOH/Fe$_3$O$_4$ catalyst.

A schematic diagram of crystal structure transform at an atomic level is then proposed and illustrated (Figure 2g). It is known that Fe$_3$O$_4$ is a perfect cubic crystal. Fe atoms of Fe$_2$O$_4$ exist in octahedral or tetrahedron (Figure S8, Supporting Information). The tetrahedron or octahedron interstice in Fe$_3$O$_4$ crystal lattice is too small to accommodate a Cu atom. Additionally, the atomic radius of Cu is close to Fe, which makes it easier to substitute Fe atoms by Cu atoms. The composition changes of the catalyst during the surface reconstruction process were investigated by ICP-MS. The presence of Fe and Cu species in the electrolyte increases with the increased electrochemical activation time (Figure S9a, Supporting Information). It remains unchanged even after the formation of the Cu-FeOOH/Fe$_3$O$_4$ catalyst. In comparison with those in the Cu-Fe$_2$O$_4$ catalyst, the contents of Fe and Cu decrease in the Cu-FeOOH/Fe$_3$O$_4$ catalyst (Figure S9b, Supporting Information). These results suggest the leaching of Fe and Cu species during the formation of the Cu-FeOOH/Fe$_3$O$_4$ catalyst. During the electrochemical activation process (namely under potential stimulation), the destabilized Cu-Fe$_2$O$_4$ precursor has a relatively weak bond to overcome the restraint of the crystal lattice, triggering the leaching of Fe and Cu species from the precursor. Once these Fe species react with the electrolyte (OH$^-$), the defective FeOOH is synthesized on the surface of a Cu-Fe$_2$O$_4$ precursor, resulting in the formation of a Cu-FeOOH/Fe$_3$O$_4$ catalyst (Figure S10, Supporting Information). This is consistent with a typical “dissolution-redeposition” path.[39]

The electron states of Fe$_2$O$_4$ (Figure S11, Supporting Information), Cu-Fe$_2$O$_4$ (Figure S12, Supporting Information), and Cu-FeOOH/Fe$_3$O$_4$ (Figure 2h,i) catalysts were then examined by use of a slice of 2D charge difference isosurface, where the electron-rich and deficient areas are marked in red and blue, respectively. Clearly, the electrons accumulate around the oxygen vacancies and rearrange at the interface in a Cu-FeOOH/Fe$_3$O$_4$ catalyst. Hence, the surface self-reconstruction of a Cu-Fe$_2$O$_4$ precursor by means of electrochemical activation can significantly optimize the electronic structure of the Cu-FeOOH/Fe$_3$O$_4$ catalyst. Its improved HER performance is thus expected.

To disclose the detailed chemical state and coordination environment of Fe$_2$O$_4$, Cu-Fe$_2$O$_4$, and Cu-FeOOH/Fe$_3$O$_4$ catalysts, X-ray absorption fine structure spectroscopy analysis was performed. The Fe K-edge X-ray absorption near edge structure (XANES) spectra of Fe$_2$O$_4$, Cu-Fe$_2$O$_4$, and Cu-FeOOH/Fe$_3$O$_4$ catalysts (Figure 3a) were studied along with a Fe foil, a FeO film, and a Fe$_3$O$_4$ film as the reference substrates (Figure S13a–c, Supporting Information). The white line intensities of both Cu-FeOOH/Fe$_2$O$_4$ and Cu-Fe$_2$O$_4$ catalysts are lower than that of a Fe$_3$O$_4$ catalyst, illustrating that the introduction of Cu and oxygen vacancies significantly increases the electron density around Fe atoms, in favor of enhancing the bond of Fe–H and promoted HER kinetics. The Cu-FeOOH/Fe$_3$O$_4$ catalyst shows a negative absorption edge shift and an increased white line intensity relative to a Cu-Fe$_2$O$_4$ precursor. Such a phenomenon reveals that the valence state of Fe decreases in the Cu-FeOOH/Fe$_3$O$_4$ catalyst. Moreover, the Fe K-edge Fourier transform extended X-ray absorption fine structures (FT-EXAFS) curves of both Cu-Fe$_2$O$_4$ and Cu-FeOOH/Fe$_3$O$_4$ catalysts (Figure 3b) indicate a conspicuous peak at 1.51 Å. This peak is assigned to Fe–O, although it is longer than that (~1.37 Å) of a Fe$_3$O$_4$ catalyst. Furthermore, an obvious peak is observed in the FT-EXAFS curves of Fe$_2$O$_4$, Cu-Fe$_2$O$_4$, and Cu-FeOOH/Fe$_3$O$_4$ catalysts. It is located at about 2.61 Å, corroborating the Fe–Fe/Cu scattering contribution. The Cu-FeOOH/Fe$_2$O$_4$, Cu-Fe$_2$O$_4$, and Fe$_3$O$_4$ catalysts show the markedly different k space oscillation (Figure 3c), suggesting that the introduction of Cu and FeOOH can significantly regulate the local atomic environment of a Cu-FeOOH/Fe$_3$O$_4$ catalyst.

The Cu K-edge XANES curves of Cu-Fe$_2$O$_4$ and Cu-FeOOH/Fe$_3$O$_4$ catalysts (Figure 3d) were also compared with those of a Cu foil, a CuO film, and a Cu$_2$O film (Figure S13d–f, Supporting Information). The absorption energy ($E_0$) of the Cu-Fe$_2$O$_4$ and Cu-FeOOH/Fe$_3$O$_4$ catalysts are 8990.5 and 8989.5 eV, respectively. These $E_0$ values confirm that the oxidation state of Cu in the Cu-FeOOH/Fe$_3$O$_4$ catalyst has not changed even after the application of the proposed electrochemical activation process. The Cu K-edge FT-EXAFS curve of the Cu-Fe$_2$O$_4$ catalyst emerges a peak at about 1.3 Å, attributing to Cu–O. This bond is shorter than that in the Cu-FeOOH/Fe$_3$O$_4$ catalyst (Figure 3e). In other words, this electrochemical activation process effectively promotes the movement of oxygen vacancies. Compared with a Cu-Fe$_2$O$_4$ precursor, the amplitude of the k space oscillation for a Cu-FeOOH/Fe$_3$O$_4$ catalyst is increased (Figure 3f), suggesting a different coordinative configuration surrounding Cu atoms in the Cu-FeOOH/Fe$_3$O$_4$ catalyst.

The wavelet transforms (WT) for the k$^2$-weighted Fe K-edge EXAFS curves of Fe$_2$O$_4$, Cu-Fe$_2$O$_4$, Cu-FeOOH/Fe$_3$O$_4$ (Figure 3g), a Fe foil, a FeO film, and a Fe$_3$O$_4$ film (Figure S14, Supporting Information) were replotted. Their related peak locations were assigned (Table S3, Supporting Information). The intensity maximum at about 3.5 Å$^{-1}$ corresponds to the Fe–O bond in the Cu-Fe$_2$O$_4$ and Cu-FeOOH/Fe$_3$O$_4$ catalysts, which are similar to that (3.4 Å$^{-1}$) in Fe$_3$O$_4$. However, the Cu-FeOOH/Fe$_2$O$_4$ and Cu-Fe$_2$O$_4$ catalysts reveal the intensity maximum at 6.1 and 6.3 Å$^{-1}$, associated with the Fe–Fe/Cu bond, which are lower than that of Fe$_3$O$_4$ (70 Å$^{-1}$). Additionally, the intensity of Fe–Fe/Cu bond in Cu-Fe$_2$O$_4$ catalyst is weaker than that of Fe$_3$O$_4$ (Figure S15, Supporting Information). This result suggests an apparent local unsaturated coordination of the Cu-Fe$_2$O$_4$ catalyst, illustrating that more vacancies are introduced into this catalyst when introducing the Cu into the Fe$_3$O$_4$. The intensity maximum at about 4.3 Å$^{-1}$ in Cu-Fe$_2$O$_4$ and Cu-FeOOH/Fe$_3$O$_4$ catalysts (Figure 3h and Table S4, Supporting Information) correspond to the Cu–O bond, re-confirming that the Fe atoms in Fe$_3$O$_4$ are substituted by Cu atoms. The WT at 11.6 Å$^{-1}$ is considered as the Cu–Cu bond in the Cu-FeOOH/Fe$_3$O$_4$ catalyst. Compared to that (12.7 Å$^{-1}$) of
a Cu-Fe3O4 precursor, the negative shift of this WT value indicates a decrease of the bond length, in turn implying a faster electronic transfer in the Cu-FeOOH/Fe3O4 catalyst than in the Cu-Fe3O4 precursor. The peaks of Cu−O and Cu−Cu/Fe bonds are broader than those of a Cu-Fe3O4 precursor, re-confirming that the electrochemical activation brings in more vacancies in the Cu-FeOOH/Fe3O4 catalyst, ultimately resulting in its improved HER performance.

To evaluate the electrocatalytic performance of HER, the as-prepared Fe3O4, Cu-Fe3O4, and Cu-FeOOH/Fe3O4 catalysts were tested in alkaline solution (1 M KOH) using a typical three-electrode configuration. Note here that for all these catalysts no binder was required or added. For comparison, the HER performance of a commercial Pt/C catalyst loaded on the used IF was also estimated. The linear sweep voltammmograms (LSVs) of these catalysts recorded at a scan rate of 5 mV s−1 was further corrected with the iR-compensation. As a substrate, the overpotential and Tafel slope of the used IF substrate is huge (Figure S16, Supporting Information), illustrating its inferior HER activity. This result suggests that the contribution of IF impurities to the HER performance of this catalyst can be ignored. The overpotentials of Fe3O4, Cu-Fe3O4, Cu-FeOOH/Fe3O4 and Pt/C catalysts in 1 M KOH at the current densities of 50, 100, 500, and 1000 mA cm−2 were firstly compared (Table S5, Supporting Information). Significantly, the Cu-FeOOH/Fe3O4 catalyst achieves the best HER activity in 1 M KOH since it features the ultra-low overpotential. For example, it is only 129 and 285 mV at the current density of as large as −100 and −500 mA cm−2, respectively (Figure 4a). Differently, when a current density of −100 mA cm−2 is applied, the overpotential of the Pt/C catalyst is 198 mV, which is similar to the previous reports.[40–42] The overpotentials of 281 and 392 mV are required for Cu-Fe3O4 and Fe3O4 catalysts to gain a current density of 100 mA cm−2, respectively. To explore the effect of Cu content on the HER performance of the Cu-Fe3O4 and Cu-FeOOH/Fe3O4 catalysts, a varied Cu(NO3)2 powder were introduced during their synthesis process. Their LSVs were then

Figure 3. Structural characterization of the Cu-FeOOH/Fe3O4 catalyst: a) the normalized Fe K-edge XANES spectra, b) FT-EXAFS curves at Fe K-edge, and c) Fe K-edge EXAFS oscillation functions k2χ(k) of Fe3O4, Cu-Fe3O4, and Cu-FeOOH/Fe3O4 catalysts. d) the normalized Cu K-edge XANES spectra, e) FT-EXAFS curves at Cu K-edge, and f) Cu K-edge EXAFS oscillation functions k2χ(k) of Cu-Fe3O4 and Cu-FeOOH/Fe3O4 catalysts. g,h) the WT plots for the k2-weighted g) Fe K-edge and h) Cu K-edge of Cu-Fe3O4 and Cu-FeOOH/Fe3O4 catalysts.
tested in 1 M KOH. The as-obtained overpotentials decrease first and then increase with the increased Cu content in these series Cu-FeOOH/Fe3O4 catalysts and the minimum overpotential is found on Cu-FeOOH/Fe3O4 catalyst (Figure S17, Supporting Information). Moreover, the corresponding Tafel slope of the Cu-FeOOH/Fe3O4 catalyst is only 11 mV dec^{-1} (Figure 4b), which is obviously lower than that of Cu-Fe3O4 (47 mV dec^{-1}), Fe3O4 (67 mV dec^{-1}), and Pt/C (20 mV dec^{-1}) catalysts. In this context, the Cu-FeOOH/Fe3O4 catalyst shows an enhanced HER kinetics. A Volmer–Tafel route is assumed to occur on the Cu-FeOOH/Fe3O4 catalyst or after introducing defective FeOOH on the surface of a Cu-Fe3O4 precursor.[43] In terms of the overpotentials at a current density of −100 mA cm^{-2} and related Tafel slopes, the Cu-FeOOH/Fe3O4 catalyst (Figure 4c) surpasses most of the state-of-the-art Cu or Fe-based HER catalysts (Table S6, Supporting Information).[9,44–50] These results suggest that this surface reconstruction strategy through introducing defective FeOOH on the surface of a Cu-Fe3O4 precursor distinctly improves the HER performance of this catalyst. Again, it is worth highlighting here that the catalytic HER performance of this Cu-FeOOH/Fe3O4 catalyst is even much superior to the noble metal Pt/C catalyst. It thus provides the possibility for its large-scale industrial application for hydrogen production. To clarify the superior HER performance of this Cu-FeOOH/Fe3O4 catalyst, its double-layer
capacitance ($C_{dl}$), a vital criterion to identify the exposed active sites toward the HER, was estimated. It is known that this $C_{dl}$ value is proportional to the electrochemical active surface area (ECSA).[51,52] It was then calculated from the cyclic voltammograms (CVs) recorded at different scan rates within the non-faradaic potential region.[51–53] The estimated $C_{dl}$ of a Cu-FeOOH/Fe$_3$O$_4$ catalyst is 7.3 mF cm$^{-2}$ (Figure 4d), larger than that of Pt/C (4.8 mF cm$^{-2}$), Cu-Fe$_2$O$_3$ (2.4 mF cm$^{-2}$) and Fe$_2$O$_4$ (2.3 mF cm$^{-2}$) catalysts. Therefore, the Cu-FeOOH/Fe$_3$O$_4$ catalyst exhibits the largest ECSA or abundant exposed active sites. On the other hand, the electron transfer kinetics on Fe$_2$O$_3$, Cu-Fe$_2$O$_3$, and Cu-FeOOH/Fe$_3$O$_4$ catalysts were checked by means of electrochemical impedance spectroscopy (Figure 4e). The recorded Nyquist plot of the Cu-FeOOH/Fe$_3$O$_4$ catalyst exhibits the smallest charge transfer resistance within these three catalysts, demonstrating its outstanding charge transfer during the HER process.[56,57]

Furthermore, the faradic efficiencies toward hydrogen generation on the Cu-Fe$_2$O$_3$ catalyst were calculated. When a potential of $-0.25, -0.30, -0.35, -0.40, -0.45$ V (vs. RHE) is applied, the faradic efficiency is 68%, 80%, 84%, 89%, and 85%, respectively. Differently, on the Cu-FeOOH/Fe$_3$O$_4$ catalyst, the faradic efficiency reaches almost 100% (Figure 4f). This result indicates that the Cu-FeOOH/Fe$_3$O$_4$ catalyst effectively improves the efficiency of hydrogen production. Namely, all electrical energy applied to the Cu-FeOOH/Fe$_3$O$_4$ catalyst is converted to generate hydrogen energy.

A continuous current-time measurement on the Cu-Fe$_2$O$_3$ catalyst was carried out to detect the variation of current densities under a constant potential stimulation during the electrochemical activation process (Figure 4g). The current density of the Cu-Fe$_2$O$_3$ catalyst reveals a dramatically increase at $-120$ mV (vs. RHE), approximately 100% after the application of 50 h activation time, when the Cu-FeOOH/Fe$_3$O$_4$ catalyst is obtained. The change of current density is negligible when the activation time is longer than 50 h, illustrating the excellent stability of this Cu-FeOOH/Fe$_3$O$_4$ catalyst. Beyond that, the change of current density between the Fe$_2$O$_3$ and Fe$_3$O$_4$-50 catalysts can be ignored, confirming again the introduction of Cu heteroatoms or vacancies is necessary for triggering the electrochemical activation process to synthesize the Cu-FeOOH/FeOOH catalyst by destabilizing the original structure of Fe$_2$O$_3$ (Figure S18, Supporting Information). All these results demonstrate that the Cu-FeOOH/Fe$_3$O$_4$ catalyst, generated from the electrochemical activation of a Cu-Fe$_2$O$_3$ precursor effectively features reconstructed surface, modulated electronic structure, and increased reaction sites, and eventually improved HER activity.

To get insight into the mechanism of the surface reconstructions of a Cu-Fe$_2$O$_3$ precursor as well as its effect on the HER performance, density functional theory (DFT) calculations were carried out. For example, the charge density difference and the Bader charge analysis were conducted for Fe$_2$O$_3$, Cu-Fe$_2$O$_3$ and Cu-FeOOH/Fe$_3$O$_4$ model catalysts (Figure 5a), where the purple and cyan regions represent electron accumulation and depletions domains, respectively. Compared with Fe$_2$O$_3$, the electron transfer of a Cu-Fe$_2$O$_3$ precursor is tremendously enhanced by introducing Cu heteroatoms and oxygen vacancies. Noticeably, for the Cu-FeOOH/Fe$_3$O$_4$ catalyst, the electron redistribution occurs at the interface between Fe$_2$O$_3$ and FeOOH. Partial electrons are transferred from Fe$_2$O$_3$ to FeOOH and accumulated on FeOOH. The abundant electrons on defective FeOOH thus favor optimizing the energy barrier of H$_2$O dissociation and hydrogen generation, or improved HER activity.[58–59]

Meanwhile, the density of states (DOS) of Fe$_2$O$_3$, Cu-Fe$_2$O$_3$, and Cu-FeOOH/Fe$_3$O$_4$ catalysts are continuous across the Fermi level, revealing their metallic behavior (Figure 5b). The electron-occupied states of the Cu-FeOOH/Fe$_3$O$_4$ catalyst at the Fermi level are higher than that of Fe$_2$O$_3$ and Cu-Fe$_2$O$_3$ catalysts, demonstrating its superior conductivity. This well facilitates electron transfer and accelerates the HER kinetics of the Cu-FeOOH/Fe$_3$O$_4$ catalyst.[60,61] The Gibbs free energies of H* ($\Delta G_{H*}$) on these three model catalysts were further calculated (Figure 5c and Figure S19, Supporting Information). It is known that a moderate $\Delta G_{H*}$ ($\Delta G_{H*} = 0$) stands for the superior HER activity.[62] After the electrochemical activation process, the calculated $\Delta G_{H*}$ values of O$_2$ site in a Cu-FeOOH/Fe$_3$O$_4$ catalyst (O$_2$-Cu-FeOOH/Fe$_3$O$_4$) is $-0.067$ eV, which is smaller than other sites in this catalyst (e.g., Cu, Fe, O$_2$ sites) and even superior to a Pt catalyst ($-0.09$ eV).[63] Therefore, the O$_2$-Cu-FeOOH/Fe$_3$O$_4$ site is identified as the active center for the HER on this Cu-FeOOH/Fe$_3$O$_4$ catalyst. Beyond that, the $\Delta G_{H*}$ values of Cu, Fe, and O sites in a Cu-Fe$_2$O$_3$ catalyst are $-1.299, 0.390$, and $-0.070$ eV, respectively. They are larger than that of O$_2$-Cu-FeOOH/Fe$_3$O$_4$. In other words, the improved HER activity of the Cu-FeOOH/Fe$_3$O$_4$ catalyst stems from its effectively optimized electronic structure on its surface.

The HER pathway in alkaline media involves three main stages: H$_2$O adsorption, H$_2$O dissociation, and H$_2$ evolution. The free energy diagram for the proposed HER pathways on the surface of Fe$_2$O$_3$, Cu-Fe$_2$O$_3$, and Cu-Fe$_2$O$_4$/FeOOH catalysts are then proposed (Figure 5d and Table S7, Supporting Information). The H$_2$O adsorption energies ($\Delta E_{H2O}$) of Fe$_2$O$_3$, Fe-Cu$_2$O$_3$, and Cu-Cu-Fe$_2$O$_3$/FeOOH catalysts are calculated to be $-0.15, -0.2, -0.08$, and $-0.0005$ eV, respectively. The negative $\Delta E_{H2O}$ value ensures the effective H$_2$O adsorption for subsequent hydrogen evolution. However, the $\Delta E_{H2O}$ of a Cu-Cu$_2$O$_3$/FeOOH catalyst is $0.578$ eV, which is difficult to adsorb H$_2$O. For the H$_2$O dissociation process, H$_2$O favorably adsorbs at the metal sites in these three catalysts (e.g., Fe-Cu$_2$O$_3$/FeOOH), due to their abundant electrons. Simultaneously, the cleavage of the O–H bonds allows H to bond with the nearby O, which readily facilitates the adsorbed *H$_2$O dissociation into H* and OH*. Finally, two H* radicals are combined to generate a hydrogen molecule through a Tafel step (Figure 5e). The calculated energy barriers of H$_2$O dissociation and H* adsorption on the Cu-Cu$_2$O$_3$/FeOOH catalyst are 0.36 and 0.17 eV, respectively. They are lower than those on the Cu-Fe$_2$O$_3$ and Fe$_2$O$_3$ catalysts. These DFT calculation results prove that the defective FeOOH on the surface of a Cu-Fe$_2$O$_3$ precursor introduced by the proposed electrochemical activation approach reduces the energy barrier of both H$_2$O dissociation and hydrogen generation.

### 3. Conclusion

In summary, an electrochemical activation method as a surface self-reconstruction strategy to promote the HER performance of a Cu-Fe$_2$O$_3$ catalyst. The applied potential during the HER process stimulates the formation of defective FeOOH on the surface of
a Cu-Fe\textsubscript{3}O\textsubscript{4} catalyst, following a dynamic “dissolution–redeposition” route. The structural configuration and electron distribution of such a Cu-FeOOH/Fe\textsubscript{3}O\textsubscript{4} catalyst are thus changed continuously during the electrochemical process. The FeOOH-incorporation and the oxygen vacancies synergistically regulate the chemical composition and electronic structure of the Cu-FeOOH/Fe\textsubscript{3}O\textsubscript{4} surface, leading to increased active sites and enhanced intrinsic activity. Remarkably, this binder-free Cu-FeOOH/Fe\textsubscript{3}O\textsubscript{4} catalyst exhibits excellent stability as well as extremely low overpotentials during the HER, even at high current densities as high as 500 mA cm\textsuperscript{-2}. Such performance is much superior to the traditional and market-available Pt/C catalyst. Consequently, electrochemical activation induced surface self-reconstruction is an efficient strategy to promote the performance of different HER catalyst systems and thus promising to be employed for mass-production of cheap HER catalysts in industries.

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**Conflict of Interest**

The authors declare no conflict of interest.

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Research data are not shared.

**Keywords**

electrochemical activation, hydrogen evolution, surface self-reconstruction

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**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.
