Constructing nickel–iron oxyhydroxides integrated with iron oxides by microorganism corrosion for oxygen evolution

Huan Yang, Chungli Dong, Hongming Wang, Ruijuan Qi, Lanqian Gong, Yingrui Lu, Chaohui He, Shenghua Chen, Junlong Yao, Xuehong Luo, Junlong Yao, Xueliang Jia, Xingpeng Guo, and Bao Yu Xia

Developing facile approaches for preparing efficient electrocatalysts is of significance to promote sustainable energy technologies. Here, we report a facile iron-oxidizing bacteria corrosion approach to construct a composite electrocatalyst of nickel–iron oxyhydroxides combined with iron oxides. The obtained electrocatalyst shows improved electrocatalytic activity and stability for oxygen evolution, with an overpotential of ∼230 mV to afford the current density of 10 mA cm⁻². The incorporation of iron oxides produced by iron-oxidizing bacteria corrosion optimizes the electronic structure of nickel–iron oxyhydroxide electrodes, which accounts for the decreased free energy of oxygenate generation and the improvement of OER activity. This work demonstrates a natural bacterial corrosion approach for the facile preparation of efficient electrodes for water oxidation, which may provide interesting insights in the multidisciplinary integration of innovative nanomaterials and emerging energy technologies.

Oxygen evolution reaction (OER) determines the efficiency and cost of water electrolyzers and rechargeable metal-air batteries. These electrochemical energy technologies are promising to realize the continuous and matching supply-on-demand for energy and power for sustainable society development (1–3). However, efficient electrocatalysts are required to promote the kinetically sluggish OER during the conversion of renewable electric energy to chemical energy (4–6). Consequently, extensive research has been devoted to exploring various OER electrocatalysts (7–10). Precious catalysts, including Ir-/Ru-based compounds, are sometimes employed (11, 12). However, their limited reserves and high price are a bottleneck for widespread industrial applications (13, 14). To this end, earth-abundant and cost-effective nonnoble metal composites attract tremendous attention for efficient OER electrocatalysis (15–18).

Among several kinds of candidates, transition-metal composites with higher flexibility and substitutability in their composition and structure have been developed as the most effective electrocatalysts (19–21). In particular, Fe doping into Ni hydroxides will modify the electronic structure and local environment around the Ni center, consequently stabilizing the intermediates and promoting the OER (22, 23). Therefore, different preparation strategies, such as hydrothermal treatment, have been reported (24–27). However, most of these candidate electrocatalysts are limited to ontology regulation by geometric structure and doping or defect engineering, while constructing heterojunctions can further enrich regulation strategies to optimize the local coordination atoms and modify their electronic structures. Moreover, these methods need delicate control in complex environments for the synthesis of Ni–Fe hydroxides (28, 29). Metal corrosion is a spontaneous process that produces metal oxides and hydroxides in nature (30, 31), and the presence of natural microorganisms can promote corrosion behaviors. For example, sulfate-reducing bacteria (SRB), which are anaerobic microorganisms, use sulfate as the electron acceptor, and an SRB-assisted corrosion approach can be adopted to construct an iron sulfides decorated Ni–Fe hydroxide electrode with highly efficient OER activity (32). However, unlike SRB, aerobic iron-oxidizing bacteria (IOB) oxidize Fe(II) into Fe(III) to obtain energy and use oxygen (O) as the final electron acceptor, which directly accelerates the metal corrosion process (33). More important, IOB is a common metal-depositing microorganism that usually deposits iron oxides (Fe₂O₃) extracellularly. The generation of an Fe₂O₃ species could be integrated into corroded electrodes to further increase the level of Fe doping and then improve the electrochemical activity cooperatively (34). In this regard, the microbial corrosion process can be designed as a facile top–down strategy to prepare Ni–Fe composites for improving catalytic activities and at the same time realize the transformation from destructive corrosion behavior to valuable electrocatalysts for emerging energy technologies.
In this work, we report the facile construction of Ni–Fe hydroxide nanosheets incorporated with Fe2O3 clusters (Ni(Fe)(OH)2-Fe2O3) through the natural microorganism-involved corrosion process. The corrosion-induced electrode shows excellent OER performance, and only an overpotential of 230 mV can deliver 10 mA cm−2, significantly exceeding that of bare Ni substrates. The integration of Fe2O3 clusters with Ni(Fe)(OH)2 nanosheets and their in situ transformation to Fe2O3-incorporated Ni–Fe oxyhydroxide (Ni(Fe)OOH-Fe2O3) are responsible for the improvement of electrochemical activity, in which Fe species optimize the electronic structure of the resultant Ni(Fe)OOH-Fe2O3 hybrid electrode to adsorb the oxygenate intermediates. This work demonstrates a facile corrosion strategy to construct efficient electrodes for the OER, which may stimulate extensive interest in the multidisciplinary integration of traditional corrosion engineering, innovative nanomaterials preparation, and emerging energy and sustainable environment technologies.

Fig. 1. Schematic and structural analysis of different products. (A) Schematic formation and transformation process, (B and E) SEM, and (C and D, F and G) high-resolution TEM images of Ni(Fe)(OH)2-Fe2O3 (B-D) and Ni(Fe)OOH-Fe2O3 (E-G).

In this work, we report the facile construction of Ni–Fe hydroxide nanosheets incorporated with Fe2O3 clusters (Ni(Fe)(OH)2-Fe2O3) through the natural microorganism-involved corrosion process. The corrosion-induced electrode shows excellent OER performance, and only an overpotential of 230 mV can deliver 10 mA cm−2, significantly exceeding that of bare Ni substrates. The integration of Fe2O3 clusters with Ni(Fe)(OH)2 nanosheets and their in situ transformation to Fe2O3-incorporated Ni–Fe oxyhydroxide (Ni(Fe)OOH-Fe2O3) are responsible for the improvement of electrochemical activity, in which Fe species optimize the electronic structure of the resultant Ni(Fe)OOH-Fe2O3 hybrid electrode to adsorb the oxygenate intermediates. This work demonstrates a facile corrosion strategy to construct efficient electrodes for the OER, which may stimulate extensive interest in the multidisciplinary integration of traditional corrosion engineering, innovative nanomaterials preparation, and emerging energy and sustainable environment technologies.

Fig. 1A presents the schematic formation and phase transformation of the IOB corrosion-induced composite (SI Appendix, Fig. S1), and this IOB-assisted strategy can be adopted to successfully construct electrodes with different sizes (1 × 1 cm², 4 × 7 cm², and 15 × 15 cm²) (SI Appendix, Fig. S1B). Generally, IOB oxidizes Fe(II) into Fe(III) to obtain energy and uses O as the final electron acceptor. The formation process includes the dissolution of Ni foam (NF) to Ni ions and the generation of Fe biominerals (2H2O + O2 + 4 e− → 4 OH−; Fe3+ + e− → Fe2+; 2Fe2+ + 2OH− + O2 + 2e− → Fe2O3 + H2O), followed by their integration into Ni(Fe)(OH)2-Fe2O3 composites (Ni2+ + Fe3+ + O2 + 2OH− + Fe2O3 → Ni(Fe)(OH)2-Fe2O3). In this system, the adsorption film on the surface of NF changes the physical and chemical properties of NF, which can be used as the active site to promote the adsorption of IOB on the surface of the NF (35). Therefore, the oxidation of Fe(II) may happen right on the surface of IOB biofilm. As a result, IOB acts as the nucleation site for mineral precipitation and contributes to the formation of Fe2O3. Scanning electron microscopy (SEM) observations show that the uniform and highly rippled nanosheets grow uniformly on the NF substrate (Fig. 1B). Transmission electron microscopy (TEM) images further confirm the layered nanosheets of Ni(Fe)(OH)2-Fe2O3 with some amorphous structure (SI Appendix, Fig. S2A and B). High-resolution (HR) TEM observations show the characteristic interplanar spacing of 0.25 nm for the (111) plane of α-Ni(OH)2 (Fig. 1C). Typically, abundant α-Fe2O3 clusters (2–5 nm) are found on nanosheet substrates (Fig. 1D). Compared with the corrosion products obtained in the absence of IOB, the similar Ni(Fe)(OH)2 nanosheets are observed while no Fe2O3 particles appear (SI Appendix, Fig. S3), identifying IOB can induce the generation of α-Fe2O3 particles anchored on or embedded in the Ni(Fe)(OH)2 nanosheets to form Ni(Fe)(OH)2-Fe2O3. The elemental distribution confirms that Ni, O and Fe are uniformly presented in both corrosion products (SI Appendix, Figs. S2C and S3E) with a corresponding atomic ratio of 17:79:4 (Ni(Fe)(OH)2) and 16: 76:8 (Ni(Fe)(OH)2-Fe2O3) (SI Appendix, Table S1). Furthermore,
the Fe content in Ni(Fe)(OH)₂-Fe₂O₃ is higher than that in Ni(Fe)(OH)₂, (SI Appendix, Table S2), and the increase of Fe content in Ni(Fe)(OH)₂-Fe₂O₃ is induced by the IOB corrosion. After a short electrochemical activation, electron microscopy observations still show the maintained nanosheet arrays of Ni(Fe)(OH)₂ and Ni(Fe)OOH-Fe₂O₃ (Fig. 1E and SI Appendix, Figs. S2D and S4 A–C). However, the phase transformation from hydroxides to oxyhydroxides has obviously occurred, which is proven by the appearance of α-Ni(Fe)OOH (Fig. 1F and SI Appendix, Fig. S4D). At the same time, the Fe₂O₃ clusters keep the initial tight connection with Ni(Fe)OOH nanosheets in these heterojunction structures (Fig. 1G). The phase transformation is mainly related to the electrochemical Ni(II)/Ni(III) redox, which induces the subtraction of protons from hydroxides and the formation of oxyhydroxide (Fig. 1A). Furthermore, no obvious change in the Ni, O, and Fe of Ni(Fe)(OH)₂ (18:78:4) and Ni(Fe)OOH-Fe₂O₃ (13:81:6) is observed in the activated oxyhydroxide sample (SI Appendix, Figs. S2F and S4E and Table S1).

X-ray diffraction (XRD) patterns also verify the existence of α-Fe₂O₃ (Powder Diffraction File #33-0644) by the emerging peaks located at 23°, 41°, and 76° in the IOB corrosion products (SI Appendix, Fig. S5). Moreover, Raman signals at 650 cm⁻¹, 510 cm⁻¹, and 460 cm⁻¹ are related to Fe–O, Ni–O, and Ni–OH, respectively, in Ni(Fe)(OH)₂ (Fig. 2A) (36). After being corroded in the IOB system, the characteristics of Ni-OH show profiles similar to those of Ni(Fe)₃(OH)₂, while the vibrations assigned to Ni–O and Fe–O vibration shift positively for Ni(Fe)(OH)₂-Fe₂O₃, implying that the local environment around Ni/Fe has changed after the incorporation of Fe₂O₃ (36). After a short activation, the emerging peaks located at 36°, 44°, 57°, and 62° for Ni(Fe)OOH are related to α-NiOOH (Powder Diffraction File #27-0956), which are further evidence of the phase conversion of hydroxides to oxyhydroxides (SI Appendix, Fig. S6A). Furthermore, XRD patterns of Ni(Fe)OOH-Fe₂O₃ still show the presence of α-NiOOH (34°, 37°, and 60°) and Fe₂O₃ (23° and 76°) (SI Appendix, Fig. S7), which is consistent with the TEM structural characteristics (Fig. 1F and G). Raman peaks of Ni–OH and Ni–O vibrations positively shift to 476 cm⁻¹ and 540 cm⁻¹. Furthermore, the decreased relative intensities (I₄76/I₅40) suggest the enhanced Ni–O bonds in the activated sample, indicating the phase conversion of hydroxides to oxyhydroxide (22). X-ray photoelectron spectroscopy (XPS) verifies that Ni, Fe, and O exist in the corrosion samples, the XPS spectrum contains sharp peak at ~531, ~713, and ~855 to 875 eV corresponding to O 1s, Fe 2p, and Ni 2p, respectively (SI Appendix, Figs. S6C and S8). The peaks at 529, 531, and 532 eV of O 1s spectrum is assigned to metal (M, Fe/Ni)–O, M–O–H, and H₂O, respectively (Fig. 2B, SI Appendix, Fig. S6D) (37). Compared with Ni(Fe)(OH)₂, the M–OH peak of Ni(Fe)(OH)₂-Fe₂O₃ shifts negatively while the M–O peak shifts positively, which indicates that Fe₂O₃ can induce more electrons to be attracted by the Ni-O-Fe bonds in the coupling interfaces (38). Compared with the initial Ni(Fe)(OH)₂ and Ni(Fe)(OH)₂-Fe₂O₃, the area ratio of M–O and M–OH increases after a short activation (Fig. 2B and SI Appendix, Fig. S6D). The Fe 2p spectra show both characteristic peaks for Fe(III) species (39). The Fe 2p₁/₂ peaks of both Fe₂O₃-integrated electrodes show a negative shift in comparison with hydroxides and oxyhydroxides (Fig. 2C, SI Appendix, Fig. S6E), which indicates that a strong electronic interaction exists between Fe₂O₃ and hydroxides or oxyhydroxides (40). The Ni 2p spectrum exhibits two peaks, which respectively correspond to Ni 2p₁/₂ (871 eV) and 2p₃/₂ (853 eV). In addition, the other two peaks (878 and 859 eV) are assigned to two satellites (Fig. 2D), which show both characteristic peaks for the Ni(II) species (41). The Ni 2p₃/₂ peaks move to higher values after the incorporation of Fe₂O₃ (Fig. 2D), illustrating that the incorporation of Fe₂O₃ can introduce
a partial electron of the Ni transfer to Fe in the corrosion electrodes by O bridges among the Ni/Fe ions (42). Moreover, the emerged peaks at 873 eV and 855 eV are the characteristics related to the Ni(III) species (Fig. 2D and SI Appendix, Fig. S6P) (43). All the above results suggest that the oxidative activation will induce the reconstruction and transformation of hydroxides into oxyhydroxides (Fig. 1 and SI Appendix, Fig. S4), which should be the active phase for electrocatalysis (28, 29).

X-ray absorption spectroscopy is employed to further analyze the local coordination structures of corrosion electrodes. The Fe/Ni K-edge normalized X-ray absorption near edge structure (XANES) spectra display the electronic transition from the Fe/Ni 1s to 4p states. The Fe K-edge XANES reveal the existence of Fe(III) species in all samples. Compared to Ni(Fe)(OH)2, the main absorption peak intensity (~7133.3 eV) for Ni(Fe)(OH)2-Fe2O3 is decreased (Fig. 3A), implying that the local electronic structure around the Fe site is altered. Furthermore, the reduction of absorption peak intensity that accompanies the absorption edge is shifted ~0.4 eV to a lower energy (Fig. 3A), the reduced Fe 4p unoccupied states is originated from the gain of charges at the Fe site in Ni(Fe)(OH)2-Fe2O3 in comparison with Ni(Fe)(OH)2. According to Fermi’s golden rule, the electronic transition of the transition metal K-edge probes its unoccupied 3d orbital, which is directly associated with the valence orbital. Thus, the Fe L-edge is also presented to verify the change of the charge state (SI Appendix, Fig. S9A). The Fe L-edge energy position of Ni(Fe)(OH)2-Fe2O3 shifts to a lower energy as compared to Ni(Fe)(OH)2, which is consistent with the Fe K-edge (SI Appendix, Fig. S9A). Compared to Ni(Fe) (OH)2, the Ni K-edge XANES shows an edge shift (~0.2 eV) to a higher energy for Ni(Fe)(OH)2-Fe2O3 (Fig. 3B), reflecting the increased valence state of Ni after the incorporation of Fe2O3 (44, 45). Likewise, this observation is in accordance with the result of the Ni L-edge, the first derivative of the Fe K-edge and Ni K-edge, which shows a shift of the absorption edge to a higher energy in Ni(Fe)(OH)2-Fe2O3 in comparison with Ni(Fe)(OH)2 (SI Appendix, Fig. S9 B–D). These results show that the incorporation of Fe2O3 can induce the transformation of a Ni species to a higher valence, which confirms that the decrease of the unoccupied states of Fe 4p originates from the redistribution of charge between Fe and Ni. After the activation, the increased peaks intensity and a distinct positive edge-shifting occur at the Fe/Ni K-edge of oxyhydroxides than at that of the initial hydroxides (Fig. 3 A and B and SI Appendix, Fig. S9D), suggesting that the oxidation process induces a higher valence and the highly ordered local structure of Ni species (29, 46). The increased Ni valence can be ascribed to the deprotonation process during the oxidative reconstruction from hydroxide to oxyhydroxide (47). Moreover, the incorporation of Fe2O3 also leads to the further increased peak intensity and edge shift of Ni(Fe)OOH-Fe2O3 at the Ni K-edge (48). The Fourier-transformed extended X-ray absorption fine structure (EXAFS) of the Fe K-edge can verify the local atomic structure of the Fe species. Both the Fe–Fe/Ni and Fe–O bonds are observed in all samples (Fig. 3C). Two main EXAFS features in the Ni K-edge are associated with the Ni–O and Ni–Ni/Fe bonds (Fig. 3D) (49, 50). The wavelet transforms of Fe/Ni K-edge affirm the existence of these bonds in all samples (Fig. 3 E and F). The corresponding peak intensities, edge-shifting, and Fe/Ni–O shifting in the wavelet transforms further verify the higher valence of the Ni species and ordered local structure. Moreover, it is worth noting that Fe2O3 shows a lower coordination number. Compared to hydroxides and oxyhydroxides, the lower coordination numbers of the Fe–O and Fe–Fe/Ni shell in Ni(Fe)OOH-Fe2O3 and Ni(Fe)(OH)2-Fe2O3 suggest the existence of Fe2O3. These electronic interactions and oxidation of Ni species to a higher valence are synergistically beneficial to promote the OER process (46, 51).

The OER performances of different corroded electrodes are conducted in 1.0 M KOH electrolyte. Prior to the collection, electrodes are usually cleaned and activated by cyclic voltammetry (CV). The peak pair at 1.32 to 1.42 V is related to the Ni(II)/Ni(III) redox (SI Appendix, Fig. S10). The CV curves clearly show the enhanced electrochemical performance of the IOB–corrosion electrode (Fig. 4A). The linear scan polarization curves (LSV) are collected to further evaluate their OER activities (Fig. 4B). Combined with their Tafel slopes (Fig. 4C), the blank NF at 10 mA cm−2 shows a similar potential of ~1.65 V vs. reversible...
hydrogen electrode (RHE), while the corrosion electrode of Ni(Fe)OOH presents a lower overpotential (270 mV). In particular, the IOB corrosion-induced Ni(Fe)OOH-Fe2O3 electrode displays a further decreased overpotential of only 230 mV. Compared to some reported Ni(Fe)-based electrocatalysts, this Ni(Fe)OOH-Fe2O3 electrode also presents considerable OER activity (SI Appendix, Table S3). Moreover, the Ni(Fe)OOH-Fe2O3 electrode demonstrates a much lower Tafel slope (41 mV dec⁻¹) than Ni(Fe)OOH (56 mV dec⁻¹) and the Ni substrate (95 mV dec⁻¹) (Fig. 4C), illustrating the favorable kinetics of Ni(Fe)OOH-Fe2O3. The formed nanosheet morphology is helpful for increasing the electrochemical active surface area (ECSA), as evidenced by the increased double-layer capacitance of both corroded electrodes (Fig. 4D). Even so, the Ni(Fe)OOH-Fe2O3 composite still exhibits better OER activity than Ni(Fe)OOH and blank NF after the normalization by ECSA (SI Appendix, Fig. S11), indicating that the incorporation of Fe2O3 in the Ni(Fe)OOH-Fe2O3 composite induces the enhanced intrinsic activity of the Ni(Fe) corroded electrode. The increase of ECSA also improves the interfacial charge transfer ability. As shown in Fig. 4E, the Ni(Fe)OOH-Fe2O3 electrode shows a lower charge–transfer resistance (Rct; 1.1 Ω) than Ni(Fe)OOH (2.0 Ω) and the initial NF (30 Ω), which would contribute to the accelerated activities (Fig. 4E). In addition, a high Faradaic efficiency of 98% suggests a close 4-electron pathway and high conversion efficiency for O production over the Ni(Fe)OOH-Fe2O3 electrode (SI Appendix, Fig. S12). Meanwhile, the retained microstructure and OER activity after 16 h operation also accounts for the stable current density for such a robust Ni(Fe)OOH-Fe2O3 electrode (Fig. 4F and SI Appendix, Figs. S13–S16).

In order to monitor the influence of the IOB corrosive environment on the OER, the corrosion electrodes are synthesized under different concentrations of IOB (V(IOB; 0%, 17%, 33%, 55%, and 80%) and different corrosion times (3 to 10 d) (SI Appendix, Fig. S17). Compared with the blank NF, chemical corrosion electrodes demonstrate a much higher OER activity. In particular, the IOB corrosion-induced electrodes display further improved OER activity (SI Appendix, Fig. S17). With the same corrosion time, the IOB-assisted corrosion electrodes show an approximate OER performance with an increased concentration of IOB (SI Appendix, Fig. S17), implying that there is a certain amount of Fe2O3 with strong bonding strength between Ni(Fe)(OH)2 in the Ni(Fe)(OH)2-Fe2O3 and that the content of Fe2O3 in the Ni(Fe)(OH)2-Fe2O3 electrode can be controlled. Among the electrodes, the corrosion-induced electrode containing 55% IOB displays excellent OER activity and achieves the best activity within 7 d corrosion time. Specifically, SEM images show that the corrosion-formed biofilm becomes looser and presents obvious nanosheets when the corrosion time increases from 3 d to 7 d; then, the corrosion-formed biofilm becomes denser (SI Appendix, Fig. S18), which indicates a similar trend with the growth of IOB. Furthermore, this IOB corrosion-induced strategy can also be applied to other different commercial metal substrates (such as Fe foam, stainless steel, carbon steel, and carbon cloth), and all electrodes obtained by this IOB-assisted corrosion method show the improved OER activity (SI Appendix, Fig. S19). Finally, this IOB-assisted corrosion electrode presents the improved OER activity in alkaline media with a concentration of OH⁻ up to 0.01 mol L⁻¹ (SI Appendix, Fig. S20).

We then employ density functional theory (DFT) to further clarify the OER mechanism over different corrosion electrodes. The surface substitution of Fe into Ni(OH)2 forms Ni(Fe) (OH)2, while the Fe atoms at the (sub)surface of Ni(Fe)(OH)2 are constructed by Fe2O3 in Ni(Fe)(OH)2-Fe2O3. The short activation will lead to the subtraction of protons from hydroxides and the formation of oxyhydroxides (Fig. 5B). Adsorption geometries are applied to analyze the reaction kinetics on the proposed 4-step pathway. *OH, *O and *OOH represents chemisorbed OH, O, and OOH active site on the catalyst surface, respectively (Fig. 5B). Thermodynamic analyses illustrate that the rate-determining step (RDS) of the OER process is the formation of *O over hydroxide (SI Appendix, Fig. S21A). However, the lower free energy gap between *OH and *O will
lead to the lower overpotential of the oxihydroxide electrode (SI Appendix, Table S4). Meanwhile, the RDS for Fe$_2$O$_3$ is also the formation of *O, with an overpotential of 0.61 V (SI Appendix, Fig. S22 and Table S4). After the incorporation of Fe$_2$O$_3$, the formation of *O also turns out to be the RDS of the OER process, accompanied by a significantly reduced overpotential for Ni(Fe)(OH)$_2$-Fe$_2$O$_3$ (0.29 V) and Ni(Fe)OOH-Fe$_2$O$_3$ (0.24 V) (Fig. 5C and SI Appendix, Table S4). Compared with the density of states (DOS) of Ni(Fe)OOH, the incorporation of Fe$_2$O$_3$ demonstrates an obviously higher DOS around the Fermi level (Fig. 5D), which can induce the d-band center of Ni to move closer to the Fermi level, resulting in improved O intermediates to adsorb/desorb (28). Electron localization function (ELF) is applied to analyze the distribution of electrons on various surfaces, which can be used to describe the bonding type and the probability of spin parallel electrons. ELF analysis shows that the presence of Fe$_2$O$_3$ can induce a stronger Fe–O bond (0.50) than hydroxide (0.43) (SI Appendix, Fig. S21 B and C), indicating the generation of a more ionic Fe–O bond in the IOB corrosion-induced electrodes. After protons are subtracted, the formed Ni(Fe)OOH-Fe$_2$O$_3$ shows a higher ELF (0.55) for Fe–O bonds (Fig. 5D), which will further optimize the bonding between Fe and *O group, thereby improving the OER activity (43).

In summary, a microorganism corrosion method is introduced to construct the composite electrode of oxihydroxides integrated with Fe$_2$O$_3$ clusters to improve OER activity. The corroded electrode needs an overpotential of only 230 mV at 10 mA cm$^{-2}$. The incorporation of Fe$_2$O$_3$ from microorganism corrosion further optimizes the electronic structure of Ni species in the activated oxihydroxide electrodes, which explains the improved electrocatalytic performance. DFT calculations also verify that the incorporation of Fe$_2$O$_3$ would generate a more positive charge on Fe atoms, which helps strengthen the binding of active *O intermediates and promote the OER process over the Ni(Fe)OOH-Fe$_2$O$_3$ electrode. This work demonstrates a successful microorganism–corrosion-inspired preparation of efficient electrocatalysts, and it may stimulate broad interest in the multidisciplinary fields of traditional corrosion engineering, nanomaterials preparation innovations, and emerging energy and sustainable environment technologies.

Materials and Reagents

NF, Fe foam, stainless steel, carbon steel, and carbon cloth (Aldrich Chemical Co.) were used as the substrates. Other reagents, including K$_2$HPO$_4$, MgSO$_4$, 7H$_2$O, C$_6$H$_8$FeNO$_7$, NaNO$_3$, (NH$_4$)$_2$(SO$_4$)$_2$, CaCl$_2$, HCl, acetone, and absolute ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd.

Methods. First, IOB cultivation and inoculation was carried out; then, the pretreated NF was put into a reagent bottle containing different concentrations of un inoculated IOB (V$_{sub}$: 17%, 33%, 55%, and 80%) and kept in an aerobic environment for 3, 7, 10 days at 37 °C. For comparison, NF in the above corrosion environment without IOB was considered. The prepared corrosion electrodes were used for characterizations and electrochemical measurements. For more details, please refer to the experimental methods in the SI Appendix.

Data Availability. All study data are included in the article and/or SI Appendix.

ACKNOWLEDGMENTS. We acknowledge the support of the National Key Research and Development Program of China (2021YFA1600800), the National Natural Science Foundation of China (22102125), the Scientific Research Foundation of Wuhan Institute of Technology (K2021040), the Program for HUST Academic Frontier Youth Team (2018QYTD15), and the Innovation Foundation of the Key Laboratory of Green Chemical Engineering Process of Ministry of Education (GCX202108). The support of the Analytical and Testing Center of HUST are also acknowledged for structural characterization for SEM, TEM, XPS, Raman, and XRD.

Author affiliations: *Hubei Key Laboratory of Plasma Chemistry and Advanced Materials, Key Laboratory of Green Chemical Engineering Process of Ministry of Education, School of Materials Science and Engineering, Wuhan Institute of Technology, Wuhan 430205, China; **Key Laboratory of Material Chemistry for Energy Conversion and Storage (Ministry of Education), Hubei Key Laboratory of Material Chemistry and
1. D. Zhao et al., Atomic site electrocatalysts for water splitting, oxygen reduction and selective oxidation. Chem. Soc. Rev. 49, 2215-2264 (2020).

2. J. Kibsgaard, I. Chorkendorff, Considerations for the scaling-up of water splitting catalysts. Nat. Energy 4, 430-435 (2019).

3. Z. I. Wang, D. Xu, J. J. Xu, B. Z. Zhang, Oxygen electrocatalysts in metal-air batteries: From aqueous to nonaqueous electrolytes. Chem. Soc. Rev. 43, 7746-7786 (2014).

4. J. Song et al., A review on fundamentals for designing oxygen evolution electrocatalysts. Chem. Soc. Rev. 49, 2196-2214 (2020).

5. N. T. Suen et al., Electrocatalysis for the oxygen evolution reaction: Recent development and future perspectives. Chem. Soc. Rev. 46, 337-365 (2017).

6. H. Yang et al., Advanced oxygen electrocatalysis in energy conversion and storage. Adv. Funct. Mater. 31, 2007662 (2021).

7. Q. Shi, C. Zhu, D. Du, Y. Lin, Robust noble metal-based electrocatalysts for oxygen evolution reaction. Chem. Soc. Rev. 48, 3181-3192 (2019).

8. S. Wang, M. W. Urban, Self-healing polymers. Nat. Rev. Mater. 5, 562-583 (2020).

9. Z. P. Wu, X. F. Lu, S. D. Zeng, X. W. Lou, Non-noble-metal-based electrocatalysts toward the oxygen evolution reaction. Adv. Funct. Mater. 30, 1902740 (2020).

10. X. Wang, A. Vaseifel, Y. Jiao, Y. Zheng, S. Z. Qiao, Electronic and structural engineering of carbon-based metal-free electrocatalysts for water splitting. Adv. Mater. 31, e1803625 (2019).

11. D. Diaz-Moniales et al., Iridium-based double peroxo catalysts for efficient water oxidation in acidic media. Nat. Commun. 7, 12563 (2016).

12. J. Yu et al., Recent advances and prospects in ruthenium-based materials for electrochemical water splitting. ACS Catal. 9, 9773-10011 (2019).

13. O. Karien, J. P. Gote, S. Geiger, S. Cherepea, K. J. J. Mayhoffer, The common intermediates of oxygen evolution and dissolution reactions during water electrolysis on iridium. Angew. Chem. Int. Ed. Engl. 57, 2488-2491 (2018).

14. L. Zhang, J. Xiao, H. Wang, M. Shao, Carbon-based electrocatalysts for hydrogen and oxygen evolution reactions. ACS Catal. 7, 7855-7865 (2017).

15. H. Sun et al., Self-supported transition-metal based catalysts for hydrogen and oxygen evolution. Adv. Mater. 32, e1806326 (2020).

16. P. Chen et al., Strong coupled cobalt borate nanosheets/graphene hybrid as electrocatalyst for water oxidation under both alkaline and neutral conditions. Angew. Chem. Int. Ed. Engl. 55, 488-4949 (2016).

17. B. Zhang et al., Homogeneously dispersed multimetal oxygen-evolving catalysts. Science 352, 333-337 (2016).

18. C. Walter et al., A molecular approach to manganese nitride acting as a high performance oxygen evolution catalyst in the oxygen evolution reaction. Angew. Chem. Int. Ed. Engl. 57, 698-702 (2018).

19. L. Trotschud, S. L. Young, J. K. Ranney, S. W. Boettcher, Nickel-iron oxyhydroxide electrocatalyst in the oxygen evolution reaction (OER) electrocatalysts. Angew. Chem. Int. Ed. Engl. 58, 1252-1265 (2019).

20. F. Dionigi et al., In situ structure and catalytic mechanism of NiFe and CoFe layered double hydroxides during oxygen evolution. Nat. Commun. 11, 2522 (2020).

21. Z. Qi, C. Zhao, Electrodeposition of hierarchically structured three-dimensional nickel-iron electrodes for efficient oxygen evolution at high current densities. Nat. Commun. 6, 6615 (2015).

22. C. Ellingford et al., Intrinsically tuned polythiophene-biadumene-styrene-based self-healing dielectric elastomer actuators with enhanced electromechanical properties. ACS Appl. Mater. Interfaces 10, 38438-38448 (2018).

23. Z. Gu, C. W. Tai, G. A. Niklasson, T. Edvinsson, Direct observation of active catalyst surface phases and the effect of dynamic self-optimization in NiFe-layered double hydroxides for alkaline water splitting. Energy Environ. Sci. 12, 572-581 (2019).

24. X. Lu, C. Zhao, Activity origins and design principles of nickel-based catalysts for nucleophile addition reactions. Chem. Rev. 116, 1986-1994 (2016).

25. F. Song et al., An unconventional iron nickel catalyst for the oxygen evolution reaction. ACS Cent. Sci. 5, 558-568 (2019).

26. V. Manoharapandian, M. Mathankumar, V. Saraswathy, B. Subramanian, S. Muraleedharan, Study of the oxygen evolution reaction catalytic behavior of Co3Ni05Fe2O9 in alkaline medium. ACS Appl. Mater. Interfaces 9, 13132-13141 (2017).

Author contributions: B.Y.X. conceived and guided the project; H.Y., L.G., J.Y., S.C., and C.H. performed the experimental parts; C.D. and Y.L. performed and discussed XAS characterizations; H.W. provided the DFT calculations; R.Q. provided the TEM observations; B.Y., H.L., X.J., and X.G. discussed the work and revised the manuscript; H.Y. and B.Y.X. discussed, wrote, and revised the manuscript; and all of the authors have commented on the manuscript.