Boosting oxygen evolution activity of nickel iron hydroxide by iron hydroxide colloidal particles

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Graphical Abstract

Adsorption of Fe(OH)₃ colloids onto NiFeOH significantly enhances the OER activity, likely as a result of charge transfer from Ni²⁺ to Fe³⁺ that facilitates the adsorption of key oxygen intermediates.

Abstract

Nickel iron hydroxides (NiFeOH) have been drawing enormous attention as effective catalysts for oxygen evolution reaction (OER), a key process in water splitting. Herein, we report that negatively charged iron (III) hydroxide colloidal particles, can significantly enhance the OER activity of NiFeOH in alkaline media. NiFeOH is grown on nickel foam in a supersaturated iron(III) salt solution, which also contains a high content of Fe(OH)₃ colloidal nanoparticles, forming free-standing NiFeOH@Cₓ electrodes (with x being the Fe(OH)₃ concentration). The interface between NiFeOH and Fe(OH)₃ colloidal particles, as manifested by the unique volcano-like holes on the NiFeOH@Cₓ surface, is likely the OER active sites. In comparison to Fe(OH)₃-free NiFeOH, NiFeOH@C₁₀₀₀ exhibits a 40-fold enhancement of the OER activity, confirming the significant effect of Fe(OH)₃ colloidal nanoparticles in boosting the OER activity, likely as a result of enhanced charge transfer from Ni²⁺ to Fe³⁺ that facilitates the adsorption of key reaction intermediates. Furthermore, by coupling the free-standing NiFeOH@C₁₀₀₀ electrode with commercial Pt/C, full water splitting can occur and reach a current density of 10 mA cm⁻² under a cell voltage of 1.51 V, which is lower than that (1.59 V) based on noble metal catalysts of RuO₂ + Pt/C.

Keywords:
Oxygen evolution reaction
Electrodeposition
Nickel iron hydroxide
Iron hydroxide colloidal particle
Electron-transfer

1. Introduction

Water splitting has emerged as an effective technology in producing sustainable and clean energy by transforming intermittent...
energies (e.g., solar and wind) into hydrogen fuel [1–7]; yet the efficiency is largely limited by the sluggish electron-transfer kinetics of oxygen evolution reaction (OER) at the anode [8,9]. Currently, leading OER catalysts are based on noble metals, such as Ir and Ru, and first-row transition metals (e.g., Ni, Fe, and Co) have been attracting enormous interest as viable alternatives, thanks mostly to their low costs, high abundance and competitive electrocatalytic activity [10–17]. Among these, nickel iron hydroxide (NiFeOH) catalysts have been found to display the highest activity in alkaline electrolysis [24]. This can be impacted by “iron impurities” in the electrolytes in the form of free ions (within the concentration range of ppb to ppm). Another form of surface Fe species may arise from Fe(OH)3 colloids, which can co-adsorb with metal ions onto the hydroxide surface; however the contribution of such adsorption to the OER activity has remained mostly unexplored thus far. Notably, theoretical calculations have confirmed that electronegative substrates [25], N sites [4], and phosphate groups [26] can promote the OER activity, because of partial withdrawal of electrons from the active centers. Within this context, Fe(OH)3 colloids are anticipated to provide a large amount of electronegative surface Fe3+ and boost the OER activity of NiFe-based catalysts by a similar electron-transfer effect. This is the primary motivation of the present works.

In this study, for the first time ever, it is demonstrated that the OER activity of NiFeOH can be markedly enhanced by the adsorption of negatively charged Fe(OH)3 colloidal particles. Experimentally, a series of free-standing electrodes were fabricated in an alkaline electrolyte, whereby Fe3+ was in situ electrodeposited onto nickel foam (NF) in a 1 M KOH solution containing FeCl3 at varied concentrations (x, μM), and denoted as NiFeOH@Cx (Scheme 1). Among the series, the NiFeOH@C1000 electrode displayed the highest Fe content and the best OER performance with an overpotential (η10) of only +238 mV to reach the current density of 10 mA cm⁻². The impact of Fe(OH)3 colloids was further confirmed by comparing the OER activity of NiFeOH before and after modification with Fe(OH)3 colloids, where the latter exhibited an OER activity about 40 times better than the former. X-ray photoelectron spectroscopic (XPS) studies indicate that the remarkable activity most probably arose from charge transfer from Ni²⁺ to Fe³⁺, leading to an increase of the valence state of the Ni centers and hence enhanced adsorption of key oxygen intermediates. With the free-standing NiFeOH@C1000 electrode coupled with commercial Pt/C for water electrolysis, a cell voltage of 1.51 V was needed to reach the current density of 10 mA cm⁻², a performance better than that with commercial Pt/C + RuO2 catalysts. This fundamental insight may be exploited for the design and engineering of efficient NiFe-based OER catalysts.

2. Experimental section

2.1. Materials

Ruthenium oxide (RuO2, 99.9%) and 5 wt% Nafion solution were purchased from Sigma Aldrich (Shanghai, China). Potassium hydroxide (KOH), ferric chloride (FeCl3), and nickel(II) chloride hexahydrate (NiCl2·6H2O) were of analytical grade and purchased from Aladdin Reagents (Shanghai, China). Deionized water (18.2 MΩ cm) was supplied with a Barnstead water purification system. Beakers made of standard polystyrene (PE) were used instead of glass beakers during the tests unless otherwise specified.

2.2. Preparation of free-standing NiFeOH@Cx electrodes on nickel foam

Nickel foam (NF, 1 cm × 5 cm × 1.5 mm, bulk density 0.25 g cm⁻³) was first sealed with an electronic sealant (displaying a working area of 1 cm²), sonicated in 0.5 M H2SO4 for 10 min to remove the NiO2 layer on the surface, and then rinsed with water and ethanol. NiFeOH@Cx electrodes were then prepared by electrochemical deposition in a standard three-electrode set-up (Scheme 1), where the NF piece was used as the working electrode, a platinum plate as the counter electrode and Ag/AgCl (in saturated KCl) as the reference electrode. The electrolyte consisted of 1 M KOH, along with FeCl3 at varying concentrations (e.g., x = 10, 100, and 1000 μM). The electrodeposition was carried out chronopotentiometrically at the current density of 10 mA cm⁻² for 600 s, with the corresponding potential much higher than 1.23 V vs reversible hydrogen electrode (RHE), and the as-prepared electrodes were denoted as NiFeOH@C10, NiFeOH@C100, NiFeOH@C1000, respectively.

2.3. Preparation of catalysts on a glassy carbon substrate

Experimentally, a glassy carbon (GC) electrode was sonicated in 0.5 M H2SO4 and rinsed with deionized water several times before use. NiO2 was then electrodeposited onto the GC surface (NiO2/GC) from a 3 mM Ni(NO3)2 solution at a constant current of 0.02 mA for 300 s, corresponding to a thickness of about 20 nm [27]. NiFeOH/GC was then prepared by immersing the resultant NiO2/GC into a 40 mM FeCl3 water solution for 5 min, where the solution showed no Tyndall effect. The obtained NiFeOH/GC electrode was rinsed with deionized water several times to remove residual iron ions, and immersed for 5 min in the Fe(OH)3 colloidal solution that contained 1 mM FeCl3 in 1 M KOH, such that sufficient Fe(OH)3 colloids were adsorbed onto the NiFeOH/GC electrode, producing NiFeOH@C1000/GC.

For comparison, Fe(OH)3 Colloid/GC (denoted as C1000/GC) was prepared at a Fe mass loading (12 μg/cm²) equal to that of NiFeOH@C1000 by dropcasting a calculated amount of a solution.

Scheme 1. Schematic illustration of the preparation of NiFeOH@Cx electrodes. The adsorption of negatively charged Fe(OH)3 colloids onto the electropositive Ni/Fe centers is driven by electrostatic interaction.
containing 1 mL of 1 mM FeCl₃ in 1 M KOH and 50 μL of 5 wt% nafion onto the GC surface.

2.4. Structural characterizations

Scanning electron microscopic (SEM) images were acquired on MIRA3 (LMH/LMU). X-ray powder diffraction (XRD) studies were carried out with an ADVANCE DB diffractometer (Japan) using a graphite-filtered Cu Kα radiation at 40 kV. X-ray photoelectron spectra (XPS) were obtained with an ESCALAB 250Xi spectrometer (USA). Inductively coupled plasma mass spectrometry (ICP-MS) data were collected with an Agilent ICPMS 7700 instrument.

2.5. Electrochemistry

Voltammetric tests were performed on an RST 5200F electrochemical workstation (China). All electrochemical tests were carried out in a conventional three-electrode electrochemical cell. Oxygen-saturated 1 M KOH was used as the electrolyte solution. The NiFeOH@C, supported on NF or GC prepared above were used as the working electrode, and a Pt plate as the counter electrode. The Ag/AgCl (in saturated KCl) reference electrode was calibrated against an RHE, and all potentials in the present study were referenced to this RHE [28]. Linear sweep voltammetry (LSV) was performed in 1 M KOH at the scan rate of 10 mV s⁻¹. The OER current density was obtained by normalizing the voltammetric current to the geometric area of the electrode, unless otherwise specified.

Before OER tests, cyclic voltammetry (CV) activation was conducted within the potential range of 1.0 to 1.6 V. Tafel slopes were measured from the OER polarization curves obtained at 0.1 mV s⁻¹ in the KOH solution with 95% IR correction unless otherwise specified. Chronopotentiometry (CP) was used to investigate the stability of the NiFeOH@C₁₀₀₀ on NF at 10 mA cm⁻² for OER, and the corresponding LSV curves were obtained before and after an aging test for 20 h. Electrochemical impedance spectroscopy (EIS) was tested at 1.5 V within the frequency range of 0.1 to 100 kHz.

Purification of KOH was prepared by following the Boettcher’s method [27]. First, 2 g of Ni(NO₃)₂·6H₂O, 4 mL of ultrapure H₂O, and 20 mL of 1 M KOH were added into a clean polypropylene centrifuge tube (50 mL). The tube was shaken and centrifuged, and the supernatant was carefully decanted. The washing cycle was repeated for at least 10 min, followed by at least 3 h of resting. The supernatant in the tube was the purified KOH and collected by centrifugation at 10,000 RPM for 5 min.

For the estimation of the electrochemical surface area (ECSA), the electrochemical double-layer capacitance (Cdl) of the catalysts was measured by CV measurements at a series of scan rates in the non-Faradaic potential range, and ECSA = Cdl/Cₙ with Cₙ being the specific capacitance of 0.040 mF cm⁻² [29].

3. Result and discussion

Ni(OH)₂ can be readily generated by immersing a freshly polished NF in a KOH solution, and Fe³⁺ ions may react with local OH⁻ to form bimetallic hydroxide and deposit on the electrode surface [27,30]. Because of the ultraw high solubility product of Fe(OH)₃ (Ksp = 2.8 × 10⁻³⁸, 25 °C), only a trace concentration of free Fe³⁺ can be found in 1 M KOH. This suggests that iron impurities in alkaline solutions mainly exist in the form of colloidal particles rather than free ions.

Experimentally, an anodic current density of 10 mA cm⁻² was applied to the NF electrode, corresponding to an initial potential of over 1.6 V vs RHE, to oxidize the Ni metal. Fe(OH)₃ colloids became visibly present when FeCl₃ was added into 1 M KOH at concentrations higher than 10 μM (Fig. 1b), and exhibited a zeta potential (ξ) of ca. –24 mV (100 μM FeCl₃), suggesting that the Fe(OH)₃ colloids were negatively charged (Fig. 1a and inset). This led to the co-adsorption of the colloidal nanoparticles onto the surface of positively charged NiFeOH to form NiFeOH@C. Meanwhile, negatively charged Fe(OH)₃ colloids might facilitate the adsorption of free Fe³⁺ residue in the electrolyte via electrostatic interaction, leading to enriched Fe³⁺ on the NiFeOH@C surface. In fact, the surface of the NiFeOH@C electrode can be seen to display a brown thin film after deposition (Fig. S2). SEM measurements show that the NiFeOH@C₁₀₀₀ electrode displays a rough surface with a rather even distribution of nanoparticles (Fig. 1e and inset), in contrast to the smooth surface of bare NF (Fig. S3a and S3b) and NiFeOH@C₀ (Fig. S3c), suggesting the adsorption of Fe(OH)₃ colloidal particles from the electrolyte. For NiFeOH@C₁₀₀₀ that was prepared with a high FeCl₃ concentration, the number of colloidal particles significantly increased, along with the emergence of “volcano-like cavities”, as highlighted by the red and white circles in Fig. 1f and inset. Note that the layer of Fe(OH)₃ colloids is not completely contiguous, likely due to the disruption of oxygen bubbles generated during continuous oxygen evolution. TEM measurements of the electrodeposited film scratched off from NF confirmed the formation of circular nanoparticles (Fig. 1g), which showed an average core diameter of about 3.2 nm (inset to Fig. 1g). Moreover, energy-dispersive X-ray spectroscopic (EDS) analysis confirmed that the nanoparticles are primarily composed of iron and oxygen (Fig. 1h), and the distributions of Fe and O are consistent with the dispersion of the nanoparticles. A trace amount of nickel was also found, due to electrostatic adsorption of nickel (from the NF) on the surface of the colloidal particles during ultrasonication. Taken together, these results suggest that Fe(OH)₃ colloidal particles were indeed formed on the NF surface. The nanoparticles displayed mostly amorphous structure (Fig. 1i), and XRD measurements show only the patterns of the nickel substrate, owing to the relatively low content of the active composites (details below) (Fig. S4).

In the process of sample preparation (Scheme 1), Fe(OH)₃ colloids were generated when FeCl₃ was added into the alkaline solution, and immediately deposited on the electrode surface. As the initial potential was over 1.6 V during the electrodeposition of Fe(OH)₃ colloids (Fig. S5), O₂ bubbles were produced at the interface between NiFeOH and Fe(OH)₃ colloidal particles, and led to partial removal of the colloidal particles and hence the generation of “volcano-like cavities” (Fig. 1j). Similar “volcano-like cavities” were also formed during the cooking of millet gruel (Video S1).

Notably, the surface morphologies varied significantly with the current density used in electrodeposition. For instance, when the current density was reduced to 2 mA cm⁻² (NiFeOH@C₁₀₀₀/2, vs NiFeOH@C₁₀₀₀ at 10 mA cm⁻²), the production of oxygen bubbles was markedly diminished, and nanosheets were formed instead (Fig. 1k and inset), within which nanoparticles can be readily identified with a diameter almost the same as that of NiFeOH@C₁₀₀₀ (Fig. S6 and S7) and show an amorphous phase without lattice fringes.

The OER activity of the NiFeOH@C electrodes was then evaluated via LSV measurements (Fig. 2a). One can see that the activity varied markedly among the series of samples, with η₁₀ = +424 mV for NiFeOH@C₀, +296 mV for NiFeOH@C₁₀, +267 mV for NiFeOH@C₁₀₀, and only +238 mV for NiFeOH@C₁₀₀₀. That is, the OER activity increases markedly with the addition of an increasing concentration of FeCl₃. Notably, the NiFeOH@C₁₀₀₀ sample (+238 mV) even outperformed commercial RuO₂ (η₁₀ = +309 mV) and was comparable to state-of-the-art Ni-e based catalysts (Fig. 2e, Table S1). The LSV curve of NiFeOH@C₁₀₀₀ was also
recorded at a slow scan rate of 1 mV s\(^{-1}\) to diminish the influence of nickel oxidation on the determination of \(\eta_{10}\). As shown in Fig. S8a, the Ni oxidation peak is significantly reduced, and there is only a negligible positive shift (4 mV) of \(\eta_{10}\). Moreover, the NiFeOH@C\(_{1000}/2\) electrode exhibited an \(\eta_{10}\) of 241 mV, very close to that of NiFeOH@C\(_{1000}\) (+238 mV), indicating minimal impacts of the electrodeposition current density in electrode preparation on the eventual OER performance (Fig. S8b). In addition, the OER overpotentials of NiFeOH@C\(_{1000}\) at select current densities (i.e., 10, 50 and 100 mA cm\(^{-2}\)) estimated from the v-t curves (Fig. S8d) are very close to those from LSV measurements (Fig. 2a). Further experiments were conducted with electrodes prepared at the Fe\(^{3+}\) concentrations of 500 and 1500 \(\mu\)M. As displayed in Fig. S8c, the \(\eta_{10}\) value was essentially unchanged among the NiFeOH@C\(_{500}\), NiFeOH@C\(_{1000}\) and NiFeOH@C\(_{1500}\) samples; yet, NiFeOH@C\(_{1000}\) can be seen to exhibit a somewhat better activity...
at high current density than the other electrodes, suggesting that 1000 \( \mu \text{M} \) Fe\(^{3+}\) represented the optimal concentration for electrode preparation.

In addition, the ECSA of the NiFeOH@C\(_x\) electrodes displayed only a slight increase with increasing \( \frac{C}{C_0} \) (Fig. S9), suggesting that the enhanced OER performance of NiFeOH@C\(_{1000}\) arose from an improved intrinsic activity rather than an increase of the number of active sites. Notably, although the surface morphology of NiFeOH@C\(_{1000}\) is much rougher, it does not display a much larger ECSA, because the Fe(OH)\(_3\) colloids is insulating under the measured potentials\(^{[31]}\). This also suggests that the actual active sites most likely resided at the interface between NiFeOH and Fe(OH)\(_3\) colloids. The electrocatalytic activity of NiFeOH@C\(_x\) was also evaluated by normalizing the OER current to ECSA and compared to results of relevant transition metal-based catalysts reported recently (Table S2). It can be seen that NiFeOH@C\(_{1000}\) exhibited the highest current density (at 1.5 V vs RHE) among the NiFeOH@C\(_x\) catalysts, which was also over an order of magnitude higher than those of a number of catalysts reported earlier. This suggests that the intrinsic activity of NiFeOH@C\(_{1000}\) was enhanced by Fe(OH)\(_3\) colloids through interfacial interactions.

Furthermore, NiFeOH@C\(_{1000}\) shows a Tafel slope of 45 mV dec\(^{-1}\), which is much lower than other samples, indicating its fastest electron-transfer kinetics (Fig. 2\( b \)). Consistent results were obtained in EIS measurements, where the charge-transfer resistance (\( R_c \)) was estimated to be 9 \( \Omega \) for NiFeOH@C\(_{1000}\) as compared to 12 \( \Omega \) for NiFeOH@C\(_{100}\), 15 \( \Omega \) for NiFeOH@C\(_{10}\), 67 \( \Omega \) for NiFeOH@C\(_0\) and 22 \( \Omega \) for commercial RuO\(_2\) (Fig. S10). Indeed, as shown in Fig. 2\( c \), there is a positive correlation between the Fe content and OER activity of the NiFeOH@C\(_x\) samples. In addition, one can see a broad voltammetric peak within the range of 1.30 to 1.45 V, which is ascribed to Ni oxidation (Fig. 2\( a \)), and the NiFeOH@C\(_{1000}\) electrode displays a much more positive peak potential than other samples, likely due to enhanced adsorption of iron \(^{[27]}\). Remarkably, the OER polarization curves of NiFeOH@C\(_{1000}\) exhibited virtually no change after chronopotentiometric tests for 20 h, suggesting excellent stability (Fig. 2\( d \) and inset).

To unravel the significance of Fe additives in the OER electrocatalysis, a further control experiment was conducted. Experimentally, Fe impurity was removed from KOH\(^{[27]}\), and a GC electrode was used instead of NF as the supporting substrate to minimize the interference of Fe residuals. NiO\(_x\) was first electrodeposited onto the GC surface in a 3 mM Ni(NO\(_3\))\(_2\) solution (NiO\(_x\)/GC)\(^{[30]}\), and immersed into a FeCl\(_3\) solution to prepare NiFeOH/GC, while NiFeOH@C\(_{1000}\)/GC was obtained by the adsorption of Fe(OH)\(_3\) colloids onto NiFeOH/GC. From Fig. 2\( f \), one can see that the NiO\(_x\)/GC electrode displayed only a minimal activity towards OER, which was significantly improved with NiFeOH/GC, signifying the critical role of Fe additives in enhancing the OER activity, and even more so with NiFeOH@C\(_{1000}\)/GC, confirming the boosting effect of Fe(OH)\(_3\) colloids on the OER activity. In fact, one can see that NiFeOH@C\(_{1000}\)/GC exhibited a 40-fold increase of the OER activity at +1.55 V as compared to NiFeOH/GC. However, Fe(OH)\(_3\) colloids were unlikely the OER active sites, as the Fe(OH)\(_3\) colloid/GC electrode displayed only a minimal activity (Fig. S11), largely because of the poor electrical conductivity of Fe(OH)\(_3\) colloids\(^{[24,31]}\). Furthermore, the GC-supported electrodes exhibit an obvious change of the oxidation peak around 1.4 V, as compared to the NF-supported ones. Fig. S12a displays the zoom in of the polarization curves in this region (Fig. 2\( f \)). One can see that the oxidation peak disappeared with NiFeOH/GC, which could be accounted for by the extensive doping of iron into NiFeOH\(^{[27,32]}\). Note that Fe in NiFeOH can be leached into the alkaline electrolyte, converted into Fe(OH)\(_3\) colloids, and redeposited onto NiFeOH@C\(_{1000}\)/GC during the electrode preparation\(^{[24]}\).
XPS measurements were then carried out to analyze the chemical composition, valence states, and electronic interactions of the series of catalysts deposited on NF (Fig. 3). First of all, based on the integrated peak areas, the Fe content was found to increase significantly from 0.25 at% for NiFeOH@C_{10} to 0.68 at% for NiFeOH@C_{100} and 2.15 at% for NiFeOH@C_{1000}, in accord with results from ICP-MS measurements (Fig. 3c), confirming the adsorption of Fe-rich nanoparticles onto the electrode surface. In contrast, a much smaller change was observed with the content of Ni (Table S3).

Fig. 3a shows the Ni 2p spectra of the three NiFeOH@C_{x} samples. For NiFeOH@C_{1000}, two peaks can be resolved at 855.6 and 873.3 eV, with a spin–orbit coupling of 17.7 eV, corresponding to the 2p_{3/2} and 2p_{1/2} electrons of Ni^{2+}, respectively [25]. In comparison, the Ni 2p binding energies for NiFeOH@C_{100} and NiFeOH@C_{10} are somewhat lower, at 855.3/872.8 eV, and 855.1/872.6 eV, respectively. This suggests increasingly electron-deficient nickel centers in the samples prepared at increasing FeCl_{3} feed.

The Fe 2p spectra are shown in Fig. 3b (note that the overlapping spectra of Ni LMN have been removed [23]), where an opposite feature was observed. Two peaks can be deconvoluted at 711.1 and 725.5 eV for NiFeOH@C_{1000}, due to the 2p_{3/2} and 2p_{1/2} electrons of Fe^{3+}, respectively [30,33]. For comparison, the Fe 2p peaks of NiFeOH@C_{100} and NiFeOH@C_{10} are somewhat higher at 711.5/725.9 and 712.0/726.4 eV, respectively. This suggests electron transfer from Ni^{2+} to Fe^{3+}, which became intensified with increasing Fe^{3+} content in the catalyst [34–36]. The formation of electron-deficient nickel centers facilitated the transformation of insulating Ni(OH)_{2} to conducting Ni(OOH)_{x} [36,37], a critical step in the production of key OER intermediates, such as O* and OO* [34,38]. In addition, as O* intermediates could be stabilized by the high-valence Fe^{3+} sites, which lowered the energy barrier of OH* oxidation to O*, a potential limiting step in OER [39]. It is such synergistic interactions between Fe^{3+} and Ni^{2+} that led to the markedly enhanced OER activity.

Given the outstanding electrocatalytic activity towards OER, commercial Pt/C catalyst and NiFeOH@C_{1000} were combined to construct an overall water splitting system. As displayed in Fig. 4a, a low cell voltage (E_{10}) of 1.51 V was needed to reach the current density of 10 mA cm^{-2}, which is much improved as compared to that based on commercial noble metal catalysts RuO_{2} + Pt/C (1.59 V) and leading transition metal-based catalysts, such as Co_{2}P@Co_{3}O_{4} (1.57 V) [40] and NiVB/rGO (1.56 V) [41]. One may also notice that the oxidation peaks of NiFeOH@C_{1000} + Pt/C and RuO_{2} + Pt/C for water splitting appear to be obviously weaker than those observed in OER electrocatalysis (Fig. 2a and Fig. S12b). This is because LSV measurements were conducted with a three-electrode setup (with a stable reference), whereas water splitting was carried out in a two-electrode mode without a well-defined reference. There is no simple correlation between the numerical
values in Fig. 2a and those in Fig. 4a. Such a behavior has been observed previously [42,43]. Fig. 4b and inset depict the digital photos of water splitting with one AA battery (1.5 V), and the formation of H2 and O2 bubbles can be clearly seen (Video S2). Moreover, the water splitting system can work continuously for over 20 h, and E10 remained virtually unchanged, demonstrating good stability and high potential of the NiFeOH@C1000 + Pt/C couple in overall water splitting (Fig. 4c and 4d).

4. Conclusion

In conclusion, the deposition of negatively charged Fe(OH)3 colloids onto NiFeOH has been found to significantly enhance the OER performance by approximately 40 times, with the intrinsic activity over an order of magnitude better than those of leading transition metal-based catalysts. With the NiFeOH@C1000 + Pt/C system, a low cell voltage of 1.51 V was needed to power full water splitting at the current density of 10 mA cm$^{-2}$ for 20 h. The remarkable performance was primarily accounted by the negatively charged Fe(OH)3 colloids that facilitated the adsorption and surface enrichment of Fe on the electrode as well as charge transfer from Ni$^{2+}$ to Fe$^{3+}$ that enhanced the adsorption of key oxygen intermediates and OER electron-transfer kinetics. Such a unique strategy is energy- and time-efficient, environmentally friendly, and may be exploited for the design and engineering of high-performance electrocatalysts based on transition metal hydroxides for a wide range of important reactions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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