**Introduction**

Water splitting to produce hydrogen fuels represents one of the most appealing strategies to obtain clean and sustainable energy.\(^1\)\(^-\)\(^4\) The water splitting reaction can be classified into two half cell reactions: the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER).\(^3\)\(^-\)\(^4\) As one of the half reactions, OER has more sluggish kinetics and requires higher overpotentials than the relatively simple HER, since it involves the removal of 4e\(^-\) and 4H\(^+\) from two water molecules to generate one oxygen molecule.\(^3\) As a result, the large overpotential of the OER greatly increases the overall energy input of the water splitting.\(^3\) To reduce the overpotential loss of the OER, the development of cost-effective, high-performance OER electrocatalysts is urgently required.

Over the past decade, extensive efforts have been devoted to develop OER catalysts based on the first-row transition non-precious metals.\(^7\)\(^-\)\(^10\) Among these Earth-abundant materials, nickel-iron-based electrocatalysts have attracted much attention owing to their high OER activity.\(^11\)\(^-\)\(^13\) It has now been well-established that incorporation of Fe into Ni composite can significantly enhance the catalytic activity for water oxidation, since the conductivity and charge transfer of NiFe-based electrocatalyst can be dramatically increased by taking the advantage of synergistic metal–metal interactions.\(^14\)\(^-\)\(^16\) In earlier studies, these catalyst materials are usually prepared by electrodeposition or hydrothermal reaction methods followed by casting onto the electrode substrate surface.\(^17\)\(^-\)\(^21\) These strategies however may result in several problems, such as high energy input during the catalyst preparation, slow charge transfer between catalyst and electrode substrate and poor stability under vigorous O\(_2\) evolution conditions.\(^22\)\(^-\)\(^24\)

To overcome these obstacles, some integrated electrodes prepared by in situ self-growth method were reported recently.\(^22\)\(^-\)\(^26\) For example, Cao et al. reported an integrated NiFe-based electrode by a surface oxidation method, and Zheng et al. developed a combinatorial self-regulated acidic etching and topotactic selenization method for preparation of electrocatalysts.\(^22\)\(^,\(^25\)\(^-\)\(^26\) Recently, the Chen group and the Zou group reported respectively NiFe-based integrated electrodes by the spontaneous galvanic replacement reaction with an iron foam in Ni(II) solution, which show excellent catalytic activity for OER.\(^23\)\(^,\(^24\)\(^†\) These in situ self-growth strategies can simplify the fabrication procedures, lower the production costs and enhance catalytic activities and stabilities of NiFe-based electrocatalysts.

Herein, we report a NiFe-based OER electrocatalyst prepared by oxidative deposition of nickel foam in a chemical bath solution followed by an ion-exchange treatment. The fabrication procedure is simple and cost-effective without complex instrumentation, predesigned templates and extraneous nickel source. The fabrication process of the NiFe-based electrode...
Preparation of Ni(OH)$_2$–Fe/NF electrodes

The nickel foam (1 × 3 cm$^2$) was firstly cleaned by ultrasonication in 1 M HCl solution for 2 h to remove the organic impurities and oxides on the surface, and then cleaned in ethanol (5 min) and deionized water (5 min) in sequence by ultrasonication, respectively. The nickel foam was stored in a glass bottle for 24 h at room temperature. Then, the nickel foam was taken out and immersed in mixed solution of (NH$_4$)$_2$SO$_4$ (5 mL, 1 M) and KOH (10 mL, 3 M) in a 20 mL transparent bottle for 8 h under the ambient temperature. The resultant electrode was washed with deionized water thoroughly and named as Ni(OH)$_2$/NF electrode. The as-prepared Ni(OH)$_2$/NF electrode was then placed in a solution containing 20 mM Fe$_2$(SO$_4$)$_3$ aqueous solution. The Ni(OH)$_2$/NF electrode had an exposure geometric surface area of 2 cm$^2$ in the solution. The reaction between Fe(III) and Ni(OH)$_2$ was processed under the ambient temperature. The resultant electrode was washed with deionized water thoroughly and named as Ni(OH)$_2$–Fe/NF electrode.

Characterizations

Scanning electron microscope (SEM) images, energy dispersive X-ray spectroscopy analysis (EDX) data and EDX mapping images were obtained at Hitachi S-4800 (Hitachi, Japan) equipped with a Horiba EDX system. Transmission electron microscopy (TEM) images, high resolution TEM (HRTEM) images and selected area electron diffraction (SAED) image were obtained using JEM-2100, JEOL. The NiFe-based nanosheets catalyst was removed from the Ni(OH)$_2$–Fe/NF electrode substrate by sonication in the absolute ethanol, and a drop of the mixture was dried on a the micro grid copper network for analysis. Powder X-ray diffraction (XRD) was measured by Bruker D8 Focus via ceramic monochromatized Cu K$_\alpha$ radiation of 1.54178 Å, operating at 40 kV and 40 mA. Raman spectra were recorded on a confocal microscope laser Raman spectrometer (Reinshaw invia). X-ray photoelectron spectroscopy (XPS) for elemental analysis was conducted on a Kratos Axis Ultra DLD X-ray Photoelectron Spectrometer using 60 W monochromated Mg K$_\alpha$ radiation as the X-ray source for excitation. The carbon 1s peak (284.6 eV) was used for internal calibration. The peak resolution and fitting were processed by XPS Peak 41 software.

Electrochemical measurements

Electrochemical measurements were performed on a CHI 660E electrochemical workstation (Chenhua Corp., Shanghai, China). The three-electrode system consisted of a working electrode, a platinum plate counter electrode, and a saturated calomel reference electrode (SCE, −0.244 V vs. NHE). Unless stated otherwise, all potentials in cyclic voltammetry were reported vs. RHE with 80% iR compensation and all controlled potential electrolysis and chronopotentiometry experiments were conducted without iR compensation. All experiments were performed at 22 ± 2 °C.

Results and discussion

Characterizations of Ni(OH)$_2$–Fe/NF electrodes

As illustrated in Scheme 1, the Ni(OH)$_2$ nanosheets electrode is firstly prepared by oxidation of a fresh nickel foam in a mixed solution containing (NH$_4$)$_2$SO$_4$ and NaOH. In the second step, the as-prepared Ni(OH)$_2$ nanosheet electrode is immersed into a solution containing Fe(III) ions for different times at room temperature. Due to the different water solubility of Ni(OH)$_2$ and Fe(OH)$_3$, Ni(OH)$_2$ was removed by sonication for different immersion times. As shown in Fig. 1A and B show that a uniform film of Ni(OH)$_2$ nanosheets is formed on the electrode substrate after the oxidative deposition treatment. After immersion in 20 mM Fe(III) solution for 5 min, Fig. 1C displays that the resultant Ni(OH)$_2$–Fe/NF electrode maintains the uniform morphology of nanosheet structure. The SEM images of the Ni(OH)$_2$–Fe/NF electrodes prepared by different immersion times are also provided.
Fig. S1† the nanosheet structure of the electrode is destroyed after immersion in Fe(III) solution for a prolonged time of 10 min, indicating an important effect of the immersion time on the structure of the prepared electrode. The SEM-energy dispersive X-ray spectroscopy (EDX) measurement was conducted to probe the elemental composition and distribution in the Ni(OH)2–Fe/NF electrode. In Fig. S2,† the elemental analysis reveals that the nanosheet material is composed of Ni, Fe and O elements. Moreover, the elemental mapping images show that these elements are distributed uniformly within the nanosheets, as shown in Fig. 1D.

To further investigate the morphology structure of the Ni(OH)2–Fe/NF electrode, the transmission electron microscopy (TEM) test was also conducted. As shown in Fig. S3,† the nanosheet structure could be clearly observed. The selected-area electron diffraction (SAED) pattern in Fig. S3A† inset indicates the amorphous or low-crystallinity structure of the nanosheet material. Accordingly, the high-resolution TEM (HRTEM) image in Fig. S3B† also presents the amorphous structure with no visible lattice fringes in the nanosheet, consistent with the SAED pattern.

The bulk crystallinity and surface composition of the hierarchical electrodes were characterized by X-ray diffraction (XRD). In Fig. S4,† the XRD patterns of the Ni(OH)2/NF and Ni(OH)2–Fe/NF electrodes exhibit three diffraction peaks located at 44.5°, 51.8°, and 76.4°, respectively, which can be assigned to the (111), (200) and (220) planes of cubic Ni (PDF# 04-0850).† No other diffraction peaks are observed in the XRD patterns, indicating the amorphous or low-crystallinity structure of the both Ni(OH)2 and Ni(OH)2–Fe nanosheet materials, which is consistent with TEM results.†

Fig. 2A shows Raman spectra of the Ni(OH)2/NF and Ni(OH)2–Fe/NF electrodes. As the electrode background, no Raman signal is detected for the bare nickel foam. At the Ni(OH)2/NF electrode, the Raman spectrum exhibits a pair of broad peaks located at 469 and 543 cm−1, which are attributed to Ni–O vibrations in NiOOH.14–16 At the Ni(OH)2–Fe/NF electrode, these two peaks shift to 477 and 552 cm−1, which is consistent with the incorporation of the Fe3+ cations into the Ni(OH)2 nanosheets.14–16

Fig. S5† shows the survey X-ray photoelectron spectroscopy (XPS) of the Ni(OH)2–Fe/NF electrode, revealing the Fe, Ni and O elements on the electrode surface with an atomic ratio of ∼2 : 1 for Ni : Fe. Fig. 2B–D show the high-resolution XPS of Ni 2p, Fe 2p, and O 1s, respectively. In Ni 2p XPS, two dominant peaks are observed at binding energies of 855.5 and 873.1 eV for Ni 2p1/2 and Ni 2p3/2, which are accompanied by two less intense satellite peaks, consistent with the presence of divalent Ni.12,24 In Fe 2p XPS, two dominant peaks are located at 710.9 and 725.0 eV, indicating the presence of trivalent Fe.22,27,28 The high-resolution XPS of O 1s exhibits the existence of three oxygen contributions, which are denoted as O1, O2, and O3, respectively. Specifically, the fitting peak of O1 at 529.7 eV is typical of metal–oxygen bonds.27,29,30 The O2 located at 531.1 eV is usually associated with oxygen in hydroxyl groups.27,29,30 The O3 appeared at 532.6 eV can be assigned to oxygen species in the surface-adsorbed H2O molecule.24,27 All the analysis results indicate that the NiFe co-doping double-hydroxide material has been successfully prepared.

**Electrocatalytic OER performance**

The electrocatalytic activity of the electrodes toward water oxidation were evaluated in a typical three-electrode setup in 1.0 M KOH with Pt-plate as the counter electrode and saturated calomel electrode as the reference electrode. Fig. 3A shows cyclic voltammetry (CV) plots of the bare nickel foam, Ni(OH)2/NF and Ni(OH)2–Fe/NF electrodes toward water oxidation. Obviously, in comparison with bare NF and Ni(OH)2/NF
electrodes, the Ni(OH)$_2$-Fe/NF electrode displays a significantly enhanced OER catalytic activity with an onset overpotential of 210 mV and an overpotential of 330 mV to deliver an extremely large current density of 1000 mA cm$^{-2}$. This excellent OER performance with large catalytic current density at small overpotential outperforms most reported state-of-the-art OER electrocatalysts, as shown in Table 1. It is noting that CVs of the Ni(OH)$_2$/NF and Ni(OH)$_2$-Fe/NF electrodes feature an apparent prewave before the catalytic OER onset, consistent with conversion of divalent Ni to trivalent Ni. The decreased intensity of this prewave and the enhanced catalytic activity of the Ni(OH)$_2$-Fe/NF electrode indicates that the Fe-doped Ni(OH)$_2$ nanosheet electrode has been successfully fabricated by this strategy. The catalytic activities of the Ni(OH)$_2$-Fe/NF electrodes prepared by varying the immersion time are shown in Fig. S6.$^\dagger$ The catalytic current density increases rapidly at the initial time, and then decreases by further extending the immersion time. With an optimized immersion time of 5 min, it reaches the maximum value. In contrast, the redox prewave is decreased monotonously along with the immersion time. These observations are consistent with the transformation of Ni(OH)$_2$ to Fe(OH)$_3$ on the electrode surface.

To evaluate the intrinsic catalytic activity of the material electrodes, Tafel plots were obtained from the polarization curves recorded at an extremely slow scan rate of 0.1 mV s$^{-1}$ to minimize the influence of capacitive currents. According to the Tafel equation, the Tafel slope was calculated by using a linear fit applied to points in the Tafel region. As shown in Fig. 3B, the Ni(OH)$_2$-Fe/NF electrode displays a Tafel slope of 46 mV dec$^{-1}$ in 1 M KOH solution, which is lower than Ni(OH)$_2$/NF electrode. Compared to previously reported three-dimensional (3D) OER systems in Table 1, this hierarchically structured electrode exhibits competitive catalytic activity under similar experimental conditions.

The electrochemical impedance spectroscopy (EIS) measurement was conducted at various overpotentials to evaluate the catalytic activity of Ni(OH)$_2$-Fe/NF electrode in 1 M KOH. Fig. 3C and the inset display the Nyquist plots obtained from the Ni(OH)$_2$-Fe/NF electrode at different potentials. The charge transfer resistance decreased as the overpotential increased, which is consistent with the high catalytic activity of the NiFe-based electrocatalyst. In addition, all the EIS Nyquist plots exhibit two semicircles at all applied potentials, which correspond to a two-time-constant behavior of the materials. The first one at the high frequency is associated with the porous structure of the electrode surface, while the second one at the low frequency is ascribed to the charge transfer resistance during electrocatalytic reactions. The low charge transfer resistance of the Ni(OH)$_2$-Fe/NF electrode is attributed to intimate contact between NiFe-based catalyst and nickel foam substrate constructed by in situ autologous growth strategy.

The electrochemical surface area (ECSA) of the Ni(OH)$_2$-Fe/NF electrode is estimated by the charging currents recorded in cyclic voltammetry (CV) curves at 1.0 V vs. RHE at different scan rates in 1 M KOH, as shown in Fig. 3D. The double layer capacitance is calculated from the slope of the anodic charging currents against the scan rates and a capacitance of 640 μF is obtained. Based on the estimated specific capacitance (40 μF

### Table 1 Comparison of the electrocatalytic performance of the OER catalysts at 3D substrates in 1 M KOH solution

| Electroanlyst | Onset overpotential | $j$ (mA cm$^{-2}$) @ $\eta = 300$ mV | Tafel slope (mV dec$^{-1}$) | Ref. |
|---------------|---------------------|------------------------------------|-----------------------------|------|
| NiFe/NF       | 215 mV              | 300                                | 28                          | 17   |
| Fe: Ni(OH)$_2$/NF | 215 mV              | 750                                | 48.5                        | 22   |
| NiFe/IF       | 220 mV              | 500                                | 48.3                        | 23   |
| NiFeOx/IF     | 220 mV              | 1000                               | 34–36                       | 24   |
| NiFe LDH/IF   | 200 mV              | —                                  | 40.4                        | 25   |
| NiFe/NiCo$_2$O$_4$/NF | 240 mV              | 280                                | 39                          | 31   |
| NiFe foam     | 240 mV              | 80                                 | 56                          | 32   |
| Ni(OH)$_2$-Fe/NF | 210 mV              | 530                                | 46                          | This work |

*a* LDH: layered double hydroxide; NF: nickel foam; IF: iron foam.
excellent electrocatalytic activity and stability toward water oxidation. In 1 M KOH, the Ni(OH)$_2$–Fe/NF electrode can deliver a current density of 1000 mA cm$^{-2}$ at an overpotential of only 330 mV. The facile preparation approach with no energy input and the high performance of this Earth-abundant material electrode toward water oxidation are appealing for practical applications in large-scale water splitting.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

This work was supported by the National Natural Science Foundation of China (21573160, 21872105), the Natural Science Foundation of Jiangsu Province (BK20181211), and Science & Technology Commission of Shanghai Municipality (14DZ2261100).

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