Rapid large-scale synthesis of ultrathin NiFe-layered double hydroxide nanosheets with tunable structures as robust oxygen evolution electrocatalysts†

Changmin Hou, Zhao Cui, Sai Zhang, Wenlong Yang, * Hongtao Gao and Xiliang Luo†*

Introduction

Electrocatalytic water splitting has received considerable research interest owing to its renewable and high-efficiency hydrogen production for mitigating the growing energy demands and worsening environment issues. However, the electrochemical energy conversion efficiency has been largely restricted by the oxygen evolution reaction (OER) because of its sluggish anode kinetics. To date, although noble-metal-based materials including RuO₂ and IrO₂ have emerged as the most efficient catalysts to drive the complex OER process, the high cost and extreme scarcity largely limit their extensive usage in the field of energy conversion. Until now, continuous efforts have been made to develop cost-effective 3d transition metals and derivatives as promising alternatives to noble metals. Among these catalysts, layered double hydroxides (LDHs) based on transition metals (Fe, Co, Ni) have drawn plenty of attention due to their easy availability, novel electrical property and high catalytic activity. Of note, their intrinsic layered structure renders the production of ultrathin two-dimensional (2D) nanosheets feasible, which could endow them with highly exposed active sites and modified electronic structures for optimizing the electrocatalytic OER performance. In general, there are two main strategies for synthesizing ultrathin LDHs nanosheets: top-down and bottom-up approaches. Even though the top-down synthesis is the most widely used approach, its synthetic procedures usually involve complicated ion-exchange treatment or prolonged exfoliation times in appropriate solvents, and the as-exfoliated LDHs nanosheets show a wide size or thickness distribution, these shortcomings unfortunately block the practical application of this synthetic strategy. By contrast, the bottom-up synthesis requires fewer synthetic procedures, is considered comparatively simple and convenient. However, organic solvents or surfactants applied in the synthetic process are usually absorbed on the nanosheets surface and hard to be removed, which would inevitably impede the contact between active sites and the electrolyte, thus suppressing the overall electrochemical performance. Of particular note is that, the production yield of LDHs nanosheets obtained by above-mentioned methods is still relatively low and needs to be further boosted for large-scale applications. Therefore, it is highly imperative but challenging to develop a simple and time-saving method for synthesizing high-efficiency ultrathin LDHs nanosheets electrocatalysts on a large scale to meet the requirement of commercial development. On the other hand, from a componental manipulation point of view, the modulation of metal ratios in LDHs nanosheets could exert a significant...
influence on their electronic structures and physicochemical properties, thus offering the opportunity to optimize the overall electrochemical performance of LDHs catalysts. Unfortunately, due to the lack of ideal catalytic model for investigating the underlying effect of metal atom ratios on the OER activity, the fundamental understanding of the related mechanism for efficient water oxidation is still under debate.

 Bearing these considerations in mind, herein, we present an effective room-temperature co-precipitation route to achieve a series of ultrathin and tunable composition of NiFe-LDH samples, as well as the utilization of these obtained LDHs nanosheets as highly efficient electrocatalysts toward water oxidation. Most interestingly, the formation of precipitation in a liquid-phase reaction was quickly accomplished by the addition of ammonium hydroxide into an aqueous solution containing ammonium persulfate, Ni\(^{2+}\) and Fe\(^{3+}\) ions under ambient atmospheric conditions (see details in the ESI†), which can be available scaled up to gram-level yield just by increasing the size of vessel at low cost. Moreover, taking NiFe-LDHs nanosheets with different metal ratios as the proof-of-concept prototype, we highlight the crucial role of metal atom ratios during the electrocatalytic OER process in virtue of a combination of theoretical calculations and experimental investigations. In terms of electrochemical results, the obtained LDHs samples show robust electrocatalytic activity for OER. In particular, ultrathin Ni\(_2\)Fe\(_1\)-LDHs nanosheets exhibit a small overpotential of 263 mV (\(j = 10\) mA cm\(^{-2}\)) and a quite high current density of 349.1 mA cm\(^{-2}\) at a potential of 1.8 V vs. RHE, which are demonstrated as high-efficiency non-precious-metal electrocatalysts toward water oxidation.

**Experimental**

**Materials**

All reagents in this study were of analytical reagent grade, which were purchased from Sinopharm Chemical Reagent Co., Ltd., and utilized as received without any purification.

**Synthesis of ultrathin NiFe-LDHs nanosheets**

In a typical procedure, a certain amount of NiCl\(_2\)-6H\(_2\)O and FeCl\(_3\)-6H\(_2\)O (with total quantity of 1 mmol) and ammonium persulfate aqueous solution (0.5 mmol) were dissolved in 200 mL water at room temperature under vigorous magnetic stirring for 5 minutes. Then, 1 mL of 28% ammonia solution was added into the above solution drop by drop with vigorous magnetic stirring. After a few minutes of sedimentation, the resulting precipitation was isolated by centrifugation and washed with distilled water and ethanol several times, then dried at 60 °C in air overnight for further characterization. The other NiFe-LDHs samples with different Ni/Fe atomic ratio were synthesized by changing the ratio of starting materials.

**Synthesis of ultrathin NiCo\(_x\), CoFe-based nanosheets**

The synthetic procedure for NiCo\(_x\), CoFe-based ultrathin nanosheets was similar to that for the ultrathin NiFe-LDHs nanosheets, except that tuning the collocation of starting materials of NiCl\(_2\)-6H\(_2\)O, CoCl\(_2\)-6H\(_2\)O and FeCl\(_3\)-6H\(_2\)O while keeping their total dose at 1 mmol.

**Characterization**

Powder X-ray diffraction patterns (XRD) were measured on Japan Rigaku D/max-rA equipped with graphite monochromized high-intensity Cu K\(_\alpha\) radiation (\(\lambda = 1.54178\) Å). The transmission electron microscopy (TEM) images were performed on a H-7650 (Hitachi, Japan) operated at an acceleration voltage of 100 kV. X-ray photoelectron spectroscopy (XPS) valence spectra were conducted on an ESCALAB MKII X-ray photoelectron spectrometer with an excitation source of Mg K\(_\alpha\) = 1253.6 eV. The Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet FT-IR spectrometer in KBr tablets, scanning from 4000 to 400 cm\(^{-1}\) at room temperature.

**Electrochemical measurements**

All electrochemical tests were performed in 1 M KOH solution on an electrochemical station (CHI660B) by using Ag/AgCl (3.3 M KCl) electrode as the reference electrode, a graphite electrode as the counter electrode, and a glassy carbon (3 mm in diameter) electrode with different catalysts as the working electrode. Typically, 4 mg of catalysts and 30 μL of 5 wt% Nafion solutions (Sigma-Aldrich) were dispersed in 1 mL of water-isopropanol solution with volume ratio of 3:1 by sonicating for 1 h to form a homogeneous ink. Then, 5 μL of the obtained dispersion (about 20 μg of catalyst) was loaded onto a GC electrode (loading 0.285 mg cm\(^{-2}\)). Linear sweep voltammetry curves was carried out at a scan rate of 5 mV s\(^{-1}\). Electrochemical impedance spectroscopy (EIS) measurements were recorded at 0.45 V vs. Ag/AgCl. The amplitude of the applied voltage was 5 mV, and the frequency range was 100 kHz to 1 Hz.

**Calculation method**

All calculations were performed within density functional theory (DFT) framework in the Vienna \textit{ab initio} simulation package (VASP) software packages.\(^{37-39}\) The exchange-correlation energy of electrons was described within the generalized gradient approximation (GGA) framework using the Perdew–Burke–Ernzerhof (PBE) functional.\(^{40}\) The strong-correlated correlation in NiO is considered by GGA + U method with a U-J value of 6 eV for Ni atom.\(^{41}\) The model of NiFe-LDHs was simulated by Fe replacing Ni atom in a 5 \times 6 \times 1 supercell containing 30 Ni atoms. The plane-wave cutoff energy of 350 eV and \(p \times q \times r (1 \times 1 \times 1)\) \(k\)-points were used for electronic calculations within the Monkhorst-Pack scheme. In view of the characteristics of layered accumulation in model, van der Waals correction is incorporated to further describe the weak interlayer interaction.\(^{42}\) All geometric structures were fully relaxed and optimized until the force on the atoms was less than 0.05 eV Å\(^{-1}\), and the convergence criterion for the electron self-consistency was set to 1.0 \times 10\(^{-4}\) eV.

**Results and discussion**

In this study, a series of high-quality ultrathin Ni\(_x\)Fe\(_{1-x}\)-LDH nanosheets with different components (Ni/Fe atomic ratio = x/)
troscopy (XPS) was used to characterize the surface composition of NiFe-LDHs. Moreover, X-ray photoelectron spectroscopy (XPS) was applied to detect the structural information of the presence of Ni2+ ions. As shown in Fig. 2C, the Fe 2p spectrum of Ni2Fe1-LDHs sample (Fig. 2B), pure NiFe-LDHs, consistent with the XRD analysis. In the high-resolution Ni 2p spectrum of Ni2Fe1-LDHs sample, the Ni 2p3/2 and Ni 2p1/2, respectively, ascribed to Ni 2p3/2 and Ni 2p1/2, which is indicative of the presence of Ni2+ ions. As shown in Fig. 2C, the Fe 2p spectrum of Ni2Fe1-LDHs was deconvoluted into four distinct peaks positioned at 711.7, 717.3 eV, 724.9 and 732.3 eV, which can be fairly assigned to Fe 2p3/2 and Fe 2p1/2, respectively, and their corresponding satellite peaks, verifying the presence of Fe3+ in the NiFe-LDHs sample. While the O 1s spectrum in Fig. 2D can be fitted into three legible peaks located at around 530.0, 531.2 and 532.0 eV, which agree well with the binding energies of O2−, OH− and adsorbed water, respectively. Especially, in comparison with the other two peaks, the prominent OH− peak confirms that hydroxide is the main existing form of O atoms in Ni2Fe1-LDHs sample. Next, inductively coupled plasma atomic emission spectrometry results in Table S1 reveal that the Ni/Fe atomic ratio for Ni9Fe1, Ni4Fe1, Ni2Fe1, Ni1Fe1 samples are about 8.81, 4.14, 2.03, 1.05, respectively, which are fairly coincided with the ratio values of their starting materials, implying the adjustable chemical compositions of NiFe-LDHs samples. Of note, TEM images in Fig. S4 confirm that this simple co-precipitation method can be employed as an effective strategy for synthesizing other transition-metal nanosheets with ultrathin thickness and tunable components, reflecting its impressive versatility for the fabrication of ultrathin 2D nanomaterials at room temperature. Especially, as illustrated by photographs in Fig. S5, the production yield of ultrathin Ni2Fe1-LDHs nanosheets can easily reach up to gram level with increasing the volume of container, demonstrating the mass production of ultrathin NiFe-LDHs nanosheets, which is in favor of the future commercial utilization.

To investigate the electrocatalytic activity of different NiFe-LDHs samples for water oxidation, a series of electrochemical tests were performed in a three-electrode system on a glassy carbon (GC) electrode. First, cyclic voltammetry (CV) curves were recorded at different potential sweep rates in 1 M KOH aqueous electrolyte are shown in Fig. S6, from which evident oxidation peaks ascribe to the oxidation reaction of Ni2+ to Ni3+ can be well observed between 1.4 and 1.6 V vs. RHE. Obviously, upon the increase in sweep rate (ν) from 10 to 150 mV s−1, the oxidation peaks demonstrate a corresponding increase in anodic current density (Ipa), which leads to a significant linear relationship between the peak current and the sweep rate.
correlation between the $I_{pa}$ and $v^{1/2}$ as shown in Fig. 3A. The calculated slope value for Ni$_2$Fe$_1$-LDHs is greater than that for Ni$_3$Fe$_2$-LDHs, Ni$_4$Fe$_2$-LDHs and Ni$_8$Fe$_2$-LDHs, suggesting a better diffusion capacity of OH$^-$ on the Ni$_2$Fe$_1$-LDHs sample in comparison with others, which is more favorable for the formation of electroactive high-valence species on catalyst surface to drive the water oxidation process.$^{27,28}$ Furthermore, the linear sweep voltammetry (LSV) curves (Fig. 3B) show that the anodic current density of NiFe-LDHs increases sharply with the linear sweep voltage (LSV) curves. Fig. 3C reveals that the Ni$_2$Fe$_1$-LDHs sample gives a small overpotential ($\eta$) of 283 mV at a current density of 20 mA cm$^{-2}$, which is obviously lower than that of other NiFe-LDHs samples, signifying the less energy required to achieve a rapid OER rate. Notably, the Ni$_2$Fe$_1$-LDHs sample affords the highest water oxidation activity among these tested NiFe-LDHs samples, with a considerable anodic current density of up to 349.1 mA cm$^{-2}$ at 1.8 V vs. RHE, much higher than that of reported IrO$_2$ and RuO$_2$ electrodes,$^{29}$ and even comparable to that of the best NiFe-based and perovskite-type electrocatalysts$^{30-32}$ under the similar condition (Table S4†). Moreover, the overpotential plotted against log(current density) in accordance with the Tafel equation was applied to study the catalytic kinetics for the OER. The corresponding Tafel plots in Fig. 3D show that the Tafel slope of Ni$_2$Fe$_1$-LDHs is calculated to be 60.0 mV per decade, marginally lower than that of Ni$_4$Fe$_2$-LDHs (88.5 mV per decade) and much smaller than that of Ni$_8$Fe$_2$-LDHs (126.5 mV per decade) and Ni$_3$Fe$_2$-LDHs (135.5 mV per decade), which is indicative of the largely accelerated OER rate with a facile increase in applied voltage by using the Ni$_2$Fe$_1$-LDHs electrode. Moreover, the electrochemical impedance spectroscopy (EIS) is carried out to gain insights into the electrode kinetics toward OER. Clearly, the Nyquist plots in Fig. 4A uncover that the charge-transfer resistance of Ni$_2$Fe$_1$-LDHs sample demonstrates a noticeable decrease in comparison to other NiFe-LDHs samples, undoubtedly confirming its more favourable charge transfer kinetics for the OER. In addition, the electrocatalytic OER activities of obtained CoFe- and NiCo-based ultrathin nanosheets were also measured and the collected LSV curves are present in Fig. S7.† As can be seen, some of the tested samples show impressive OER activity, with low overpotentials, large anodic current densities and small Tafel slopes. In comparison, Ni$_2$Fe$_1$-LDHs gives the highest OER activity among these catalysts, distinctly embodying its superiority in electrochemical water oxidation.

As well accepted, the electrochemical active surface area (ECSA) has been regarded as a key parameter for determining the electrocatalytic activity, which is positively associated with the double layer capacitance ($C_{dl}$).$^{33,34}$ As shown in Fig. 8B,† the $C_{dl}$ values of Ni$_2$Fe$_1$-LDHs and Ni$_4$Fe$_2$-LDHs are respectively estimated to be 950.4 µF cm$^{-2}$ and 729.7 µF cm$^{-2}$, larger than that of Ni$_3$Fe$_2$-LDHs (542.8 µF cm$^{-2}$) and Ni$_8$Fe$_2$-LDHs (703.1 µF cm$^{-2}$), which indeed demonstrates the higher electrochemical active surface areas of Ni$_2$Fe$_1$-LDHs and Ni$_4$Fe$_2$-LDHs related to the more exposed active sites. Especially, the LSV curves were normalized by the corresponding $C_{dl}$ values to gain more insights into the electrocatalytic OER activity. As can be seen from Fig. 4C, the normalized anodic current density of

Fig. 3 Electrochemical tests for the OER performance of various NiFe-LDHs samples in 1 M KOH solution. (A) Linear correlation between the $I_{pa}$ and $v^{1/2}$, (B) Polarization curves and (C) the overpotentials required for different current densities and (D) corresponding Tafel plots.

Fig. 4 (A) Nyquist impedance plots, (B) current density plotted versus scan rate for the estimation of $C_{dl}$ values and (C) the normalized LSV curves of various NiFe-LDHs samples. (D) Chronopotentiometric measurement of Ni$_2$Fe$_1$-LDHs sample at a constant current density of 10 mA cm$^{-2}$ for 12 h. The inset in (D) shows the TEM image of Ni$_2$Fe$_1$-LDHs sample after the long-term stability test. (E) Illustration of the adsorption of water molecule on the Ni$_2$Fe$_1$-LDHs and the corresponding differential charge density. (F) The calculated formation energies of electroactive NiOOH species and adsorption energies of water molecules onto the surface of different NiFe-LDHs samples.
Ni$_2$Fe$_1$-LDHs (5.6 mA cm$^{-2}$) is roughly 1.3, 1.7 and 2.3 times larger than that of Ni$_8$Fe$_1$-LDHs (4.4 mA cm$^{-2}$), Ni$_4$Fe$_1$-LDHs (3.3 mA cm$^{-2}$) and Ni$_2$Fe$_1$-LDHs (2.4 mA cm$^{-2}$) at the overpotential of 592 mV, respectively, indicating the superior intrinsic catalytic activity of every reactive center in the Ni$_2$Fe$_1$-LDHs sample. Apart from the catalytic activity, long-term stability is another vital criterion for the assessment of advanced electrocatalysts for the OER. Fig. 4D shows the chronopotentiometric test at an invariant current density ($J = 10$ mA cm$^{-2}$) for Ni$_2$Fe$_1$-LDHs, from which negligible changes in potential can be identified even after continuous 12 h operation in 1 M KOH solution, revealing its excellent catalytic stability. Besides, TEM image (inset of Fig. 4D) demonstrates slight variations in morphology of Ni$_2$Fe$_1$-LDHs sample after the long-term stability measurement, verifying its impressive structural durability. On the basis of above results, the Ni$_2$Fe$_1$-LDHs sample gives prominent electrocatalytic OER activity and robust stability, which is in favour of potential practical applications for electrocatalytic water splitting.

To get insights into the impact of Ni/Fe atomic ratios on the electronic structures of NiFe-LDHs samples, density functional theory (DFT) calculations were carried out by using NiFe-LDHs with different Ni/Fe ratios as applicable models. As well accepted, water molecules should be proactively adsorbed on the surface of catalysts, which means that the adsorption of H$_2$O molecules plays a decisive role in determining the OER performance. From the differential charge density in Fig. 4E, a notable charge transfer between water molecule and Ni$_2$Fe$_1$-LDHs can be well observed, reflecting its famous electrocatalytic reactivity toward water oxidation. Furthermore, as shown in Fig. 4F and Table S2, the adsorption energies of H$_2$O molecules on the NiFe-LDHs surface are calculated to be about $-2.71$, $-2.92$, $-3.29$ and $-2.63$ eV for Ni$_8$Fe$_1$-, Ni$_4$Fe$_1$-, Ni$_4$Fe$_1$- and Ni$_2$Fe$_1$-LDHs sample, respectively. The smallest adsorption energy for Ni$_2$Fe$_1$-LDHs means that the water molecule is more easily adsorbed on the surface of Ni$_2$Fe$_1$-LDHs with respect to the other three samples, thus achieving optimized OER kinetics to promote the catalytic process. Besides, for the NiFe-LDHs catalyst, the formation energy of NiOOH species is another important factor that influences the whole OER activity of catalyst, as the high-valence NiOOH phase has been deemed as electroactive species for the OER. As displayed in Fig. 4F and Table S3, the calculated formation energy of active NiOOH species for Ni$_8$Fe$_1$-LDHs sample is about 3.07 eV, obviously lower than that for Ni$_4$Fe$_1$-LDHs (4.66 eV), Ni$_4$Fe$_1$-LDHs (3.69 eV) and Ni$_2$Fe$_1$-LDHs (4.22 eV). This result demonstrates that the Ni$_2$Fe$_1$-LDHs sample is more favourable for the formation of electroactive NiOOH phase, thereby obtaining accelerated electrochemical OER process. Based on the experimental and theoretical data, the Ni$_2$Fe$_1$-LDHs samples give prominent electrocatalytic OER activity and robust stability, which is mainly attributed to two aspects as follows: (1) the ultrathin 2D structure not only renders highly exposed metal atoms as active sites to promote the catalytic reaction, but also enables a better contact with the GC electrode and electrolyte as well as good electrical conductivity to accelerate electron transfer. (2) The tunable component with an optimal Ni/Fe ratio is beneficial to the synergistic optimization of the adsorption energy of H$_2$O molecules and formation energy of active NiOOH species as well as the charge transfer during the electrocatalytic process, thus realizing highly efficient OER.

Conclusions

In summary, ultrathin NiFe-LDHs nanosheets with adjustable components and mass production yield were synthesized at room temperature through a simple and fast co-precipitation route, which were further taken as examples to investigate the effect of Ni/Fe ratio on the OER activity through combining theoretical calculations and experimental measurements. Benefiting from plenty of catalytically active sites, efficient electron transport and optimal OER kinetics, the as-prepared ultrathin NiFe-LDHs nanosheets were proved as highly active electrocatalysts for water oxidation application. It was found that Ni$_2$Fe$_1$-LDHs exhibits a small overpotential of 263 mV to reach 10 mA cm$^{-2}$ and large current density of 349.1 mA cm$^{-2}$ at a potential of 1.8 V vs. RHE, as well as excellent long-term OER stability in strong alkaline solution. This work opens up a pathway for large-scale synthesis of efficient transition-metal-based LDHs catalysts for water oxidation at low cost.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21805149, 21675093), the Natural Science Foundation of Shandong Province of China (ZR2018BB012, 2015ZRB01A0D), the Taishan Scholar Program of Shandong Province of China (ts20110829).

Notes and references


