In Situ Exfoliated, N-Doped, and Edge-Rich Ultrathin Layered Double Hydroxides Nanosheets for Oxygen Evolution Reaction

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The number of catalytically reactive sites and their intrinsic electrocatalytic activity strongly affect the performance of electrocatalysts. Recently, there are growing concerns about layered double hydroxides (LDHs) for oxygen evolution reaction (OER). Exfoliating LDHs is an effective method to increase the reactive sites, however, a traditional liquid phase exfoliation method is usually very labor-intensive and time-consuming. On the other hand, proper heteroelement doping and edge engineering are helpful to tune the intrinsic activity of reactive sites. In this work, bulk CoFe LDHs are successfully exfoliated into ultrathin CoFe LDHs nanosheets by nitrogen plasma. Meanwhile, nitrogen doping and defects are introduced into exfoliated ultrathin CoFe LDHs nanosheets. The number of reactive sites can be increased efficiently by the formation of ultrathin CoFe LDHs nanosheets, the nitrogen dopant alters the surrounding electronic arrangement of reactive site facilitating the adsorption of OER intermediates, and the electrocatalytic activity of reactive sites can be further tuned efficiently by introducing defects which increase the number of dangling bonds neighboring reactive sites and decrease the coordination number of reactive sites. With these advantages, this electrocatalyst shows excellent OER activity with an ultralow overpotential of 233 mV at 10 mA cm$^{-2}$.

1. Introduction

With the aggravation of energy crisis and environmental deterioration, hydrogen ($H_2$) energy as an alternative of fossil fuels has attracted more attention due to its highest energy density and renewability.$^{[1-3]}$ Electrolysis of water is a clean, renewable, and affordable method for hydrogen production. Oxygen evolution reaction (OER) is a major half-reaction limiting water splitting because it is a four-electron and uphill reaction, resulting in a large overpotential and sluggish kinetics for OER.$^{[4]}$ Therefore, designing highly efficient OER catalysts are extremely crucial to accelerate kinetics and largely reduce the overpotential.

IrO$_2$ and RuO$_2$ are considered as the most efficient OER catalysts for water splitting.$^{[5,6]}$ However, high cost, low durability, and limited resource impede their large-scale application.

Among various nonprecious metal compounds including metal oxides,$^{[7,8]}$ phosphides,$^{[9-11]}$ nitrides,$^{[12-14]}$ selenide,$^{[15]}$ and hydroxides, transition metal hydroxides such as Co(OH)$_2$,$^{[16]}$ NiFe(OH)$_x$,$^{[17]}$ and CoFe(OH)$_x$,$^{[18]}$ have been emphasized as promising candidates of OER electrocatalysts. Especially, layered double hydroxides (LDHs) are highly advantageous for large-scale production of $O_2$ because of their earth abundant and low cost.$^{[19]}$ Currently, LDHs show excellent OER activity owing to their unique 2D structure and tunable chemical compositions.$^{[19]}$ In addition, the strong anisotropic properties affect the basal and edge planes for layered materials endowing these materials with novel chemical and physical properties.$^{[20]}$ For bulk LDHs, the large particle size and thickness usually limit the exposure of active sites and reduce their electrocatalytic activity.$^{[21]}$ As known, ultrathin nanosheets are more conducive to expose electrocatalytic active sites compared to bulk materials. Hence, it is an efficient strategy for exfoliating bulk LDHs into ultrathin nanosheets to further improve the electrocatalytic activity of materials. Another important strategy to enhance OER activities of LDHs is heteroatom doping because the doping could alter the electronic density of the adjacent active atoms and form well-defined electronic configurations for adsorption of intermediates.$^{[22]}$ For example, Shi and co-workers reported N-doped Co$_2$ as OER catalysts showing an excellent electrocatalytic activity and long-term durability.$^{[22]}$

Generally, the electrocatalytic reaction is a surface reaction process, and the catalytic reaction occurs on the “active sites” of catalysts on which the low coordinated step, edges, terraces, kinks, and/or corner atoms often exhibit a high catalytic activity.$^{[21,24]}$ Thus, introducing more edges and corner sites in catalysts was considered to be an extremely effective strategy to further boost OER performance since the presence of edges and corner sites not only helps decrease the coordination number...
of the neighboring reactive sites but also affects the electronic structure of catalysts that in turn tailors the activity of the reactive sites. For example, Lu et al. synthesized LiCoO nanosheets exposing more edge active sites showing higher electrocatalytic activities. Zhang and co-workers synthesized ultrafine NiO nanosheets stabilized by TiO2 exhibiting excellent OER performance owing to the highly exposed edge and corner sites.

Based on the above discussions, it is of essential significance to develop a strategy to simultaneously realize the exfoliation, heteroatom doping, and creating more edges on LDHs. Fortunately, plasma technology has been verified as a very facile and efficient approach to exfoliate 2D nanomaterials. Plasma was defined as the fourth state of matter which may produce highly reactive species on the surface of catalysts. It could be used extensively for the surface modification of catalyst such as surface etching and nitrogen doping. Thus, N-doping can be carried out using plasma containing nitrogen source such as N2 and NH3 plasma. Meanwhile, plasma can also etch the surface of catalysts leading to the formation of more edges and defects.

Herein, we have successfully realized the exfoliation of bulk CoFe LDHs into edge-rich ultrathin LDHs nanosheets with nitrogen doping by N2 plasma. The exfoliated ultrathin CoFe LDHs nanosheets produce numerous atomic-sized holes and expose more edges sites, as shown in Scheme 1. The bulk CoFe LDHs (denoted as CoFe LDHs) were synthesized by a typical hydrothermal reaction. Furthermore, the bulk CoFe LDHs were treated by the N2 plasma for 60 min (denoted as N-CoFe LDHs). After N2 plasma treatment, bulk CoFe LDHs were exfoliated to ultrathin CoFe LDHs nanosheets with nitrogen doping, higher surface area, and producing numerous atomic-sized pores and edges sites in the basal planes of the 2D crystal. This unique ultrathin CoFe LDHs nanosheet structure with more reactive sites, atomic-sized pores, and edges sites significantly improves the catalytic activity and enhances ultimately the OER performance.

2. Results and Discussion

The scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atom force microscopy (AFM) were used to observe the microstructure of the bulk CoFe LDHs and the as-exfoliated N-CoFe LDHs nanosheets. Figure 1A and Figure S1A (Supporting Information) showed that bulk CoFe LDHs were composed of numerous nanosheets with a typical thickness of ≈20.01 nm (Figure 2A and Figure S2A, Supporting Information). In addition, the TEM images further suggested a structure of the hexagonal multilayer nanosheets of bulk CoFe LDHs (Figure S1B, Supporting Information). The high-resolution TEM (HRTEM) could observe obviously that bulk CoFe LDHs have very smooth lattice fringes (Figure 1C). In contrast, after the exfoliation by N2 plasma, the lattice orders were severely damaged with atomic defects formed (Figure 1D) demonstrating the existence of defects on the surface of ultrathin N-CoFe LDHs nanosheets. The as-observed atom-sized pores in HRTEM (Figure 1D) indicate that the brucite-like metal host layers of the bulk CoFe LDHs were etched by N2 plasma.

After the exfoliation assisted by N2 plasma, the microscopy of N-CoFe LDHs nanosheets was observed by SEM, TEM, and AFM. The morphology of N-CoFe LDHs nanosheets was basically maintained a hexagonal nanosheet structure (Figure 1B and Figure S3, Supporting Information). Obviously, the N-CoFe LDHs nanosheets are much thinner than bulk CoFe LDHs, indicating the successful exfoliation by N2 plasma. The CoFe LDHs were subjected to different treatment time by N2 plasma (Figures S4–S6, Supporting Information), and all the obtained products own thinner nanosheets, proving the exfoliation efficiency of N2 plasma. Surprisingly, the thickness of the as-exfoliated N-CoFe LDHs nanosheets is only 1.6 nm (two atomic layer thick), as evidenced by the AFM images (Figure 2B,C and Figure S2B,C, Supporting Information). The ultrathin structure of N-CoFe LDHs nanosheets reveal that bulk CoFe LDHs were successfully exfoliated into ultrathin nanosheets after N2 plasma treatment owing to that N2 plasma can etch efficiently the anion...
within the potential of 1.1–1.6 V. As expected, the ultrathin N-CoFe LDHs nanosheets exhibit much better OER performance with lower onset potential of 1.470 V compared with bulk CoFe LDHs (1.496 V) (Figure 3A). In addition, the ultrathin N-CoFe LDHs nanosheets can achieve a geometric current density of 10 mA cm⁻² at an overpotential of 281 mV which is much lower than the bulk CoFe LDHs (324 mV). At overpotential of 341 mV, the current density of ultrathin N-CoFe LDHs nanosheets can reach 50 mA cm⁻² which is 3.125 times as much as the bulk CoFe LDHs (16 mA cm⁻²).

In addition, the OER activity of the exfoliated CoFe LDHs by N₂ plasma for different time showed that the optimal etching time was 60 min (Figure S8, Supporting Information). Surprisingly, the ultrathin N-CoFe LDHs nanosheets exhibited higher OER activity than RuO₂ (Figure S9, Supporting Information). The OER activity of ultrathin N-CoFe LDHs nanosheets was also compared with previously reported electrocatalysts and is better than most electrocatalysts (Table S1, Supporting Information). The outstanding OER activity of the ultrathin N-CoFe LDHs nanosheets was attributed to the following three aspects: (1) the efficient exfoliation increased the specific surface area facilitating to expose more catalytically reactive sites and the exfoliated ultrathin CoFe LDHs was similar to an open structure which enables intimate and large area contact with both current collector (glassy carbon or Ni foam) and the electrolyte guaranteeing faster interfacial charge transfer for electrocatalytic reaction; (2) Recent studies demonstrate that N-doping into CoS₂ can tune efficiently the electronic density of the adjacent Co atoms and thus form well-defined electronic configurations for adsorption of OER intermediates according to theoretical density functional theory (DFT) calculations.[22] Thus, it can be concluded that the nitrogen doping can also alter efficiently the electronic density of the adjacent Co or Fe atoms which facilitate the adsorption of OER intermediates leading to the enhancement of OER activity on ultrathin N-CoFe LDHs nanosheets. (3) Finally and most importantly, the as-exfoliated ultrathin CoFe LDHs nanosheets would increase the quantity of catalytically reactive sites in edge sites (holes) with more dangling bonds and lower coordination numbers which have a higher electrocatalytic activity compared with the bulk CoFe LDHs.[18,25] Therefore, the increasing of reactive sites from higher specific surface area, the rearrangement of the electronic configurations from the dopant of nitrogen, and the enhancement of the intrinsic electrocatalytic activity from the edge and corner reactive sites played a synergistic role in enhancing the OER performance.

To evaluate the kinetics of the OER, the Tafel slope of CoFe LDHs and N-CoFe LDHs was calculated, as shown in Figure 3B. The Tafel slope value of N-CoFe LDHs is 40.03 mV dec⁻¹ which is lower than 57.37 mV dec⁻¹ of CoFe...
LDHs, representing N-CoFe LDHs with a rapid kinetic OER process and further explaining the improvement of OER performance. The electrochemical impedance spectroscopy (EIS) was used to further evaluate the electrode reaction kinetic of OER, as shown in Figure 3C and Figure S10 (Supporting Information). The N-CoFe LDHs exhibited a smaller charge transfer resistance \((21.4 \ \Omega)\) than the CoFe LDHs \((94.9 \ \Omega)\), confirming that the N-CoFe LDHs have a faster charge transfer than the CoFe LDHs in the OER process.

Another vital factor for influencing the OER performance is the intrinsically poor electrical conductivity of ultrathin N-CoFe LDHs nanosheets. To further improve the OER properties of ultrathin N-CoFe LDHs nanosheets, we would distribute the electrocatalysts uniformly on nickel foam (denoted as N-CoFe LDHs/NF) with a loading of \(0.2 \ \text{mg cm}^{-2}\). To get a geometric catalytic density of \(10 \ \text{mA cm}^{-2}\), the N-CoFe LDHs/NF only needs an ultralow overpotential of \(233 \ \text{mV}\) (Figure 3D). In addition, there was almost no decay of the LSV curves of N-CoFe LDHs/NF after 2000 CV cycles exhibiting a superior stability (Figure 3D). In sum, the low overpotential, small Tafel slope, small charge transfer resistance, and outstanding durability indicate that the ultrathin N-CoFe LDHs nanosheets could serve as an excellent OER electrocatalyst for water splitting or metal air batteries.

The OER is considered to be a surface reaction process, and the electrocatalytic activity and selectivity is determined by the surface properties of the catalyst.\(^{[10]}\) To gain further insight into the reaction mechanism, the chemical environment and valence states at the surface of CoFe LDHs and N-CoFe LDHs were further investigated by the X-ray photoelectron spectroscopy (XPS). For CoFe LDHs, the XPS spectrum of the Co 2p\(_{3/2}\) shows a peak at 781.2 eV which can be ascribed to Co\(^{2+}\)–OH bonds (Figure 4A); the XPS spectrum of the Fe 2p\(_{3/2}\) shows that the peak at 712.7 eV can be ascribed to the Fe\(^{3+}\)–OH bonds (Figure 4B); the XPS spectrum of O 1s is divided into three peaks: O1 (533.1 eV) adsorbed molecular water, O2 (532.2 eV) hydroxyl groups or surface-adsorbed oxygen, and O3 (531.5 eV) defects with a low oxygen coordination (Figure 4C).\(^{[8]}\) For N-CoFe LDHs, the peaks at 779.9 and 781.2 eV for Co 2p\(_{3/2}\) were ascribed to the Co\(^{3+}\)–OH bonds and Co\(^{2+}\)–OH bonds, respectively (Figure 4D). The presence of Co\(^{3+}\) was because N\(_{2}\) plasma etched the 2D basal planes of CoFe LDHs leading to the formation of atomic-sized holes, namely, defects, which would prompt the neighboring Co\(^{2+}\) to have a transformation toward the Co\(^{3+}\) once exposed to air. The peaks for Fe 2p\(_{3/2}\) at 710.6 and 712.5 eV were attributed to the Fe\(^{2+}\)–OH bonds and Fe\(^{3+}\)–OH bonds, respectively (Figure 4E).\(^{[31]}\) The presence of Fe\(^{2+}\) was considered to be the reducing action of N\(_{2}\) plasma. The O 1s XPS spectrum of N-CoFe LDHs was divided into four peaks: O1, O2, O3, and O4 (Figure 4F). O1 (533.1 eV) is for the peak of adsorbed molecular water, O2 (532.2 eV) represented the peak of hydroxyl groups or surface-adsorbed oxygen, O3 (531.5 eV) could be considered to be defects with a low oxygen coordination, and O4 (529.8 eV) could be attributed to the peak of metal–oxygen bonds.\(^{[8]}\) The peaks at 399.7 eV for N 1s could be attributed to the Co/Fe–N bonds (Figure S11, Supporting Information) which demonstrated the existence of N. For ultrathin N-CoFe LDHs nanosheets, the presence of Co\(^{3+}\), the increasing of O3 (defects with a low oxygen coordination), and the dopant of nitrogen can further boost the improvement of electrocatalytic activity of reactive sites.

In an OER process, the adsorption capacity of reactive sites to OOH species is usually identified as the rate-determining factor.
Moreover, it was reported that the adsorbed OOH species interact with 3d orbital of transition metal-based materials.[33] Shao-Horn and co-workers have reported that 3d transition-metal-based electrocatalysts exhibit a higher electrocatalytic activity when the eg orbital occupancy of surface transition-metal cations is close to unity.[34] Therefore, for ultrathin N-CoFe LDHs nanosheets, Co^{2+} has a t_{2g}^{6}e_{g}^{1} electronic configuration representing a higher catalytic activity. Xie and co-workers also recently reported that the spin states of Co^{3+} octahedral self-adapt from low-spin (t_{2g}^{6}e_{g}^{0}) to high-spin states (t_{2g}^{4}e_{g}^{2}) in the atomically thin nanosheets and the exfoliation further induced high-spin Co^{3+} distort (Jahn–Teller effect) to remove the degeneracy and form a slightly distorted prism, which improves significantly the OER activity of Co^{3+}S_{4}.[26] Thus, we can conclude that the spin states of Co^{3+} have a similar transformation process in ultrathin N-CoFe LDHs nanosheets, which further boosts the electrocatalytic activity. Previous reported literatures have proved that the Co^{3+} site with oxygen vacancy could efficiently decrease the hindrance for the adsorption of H_{2}O and OER intermediates which improved the OER performance.[35] Moreover, on a surface with oxygen vacancies at Co^{3+} center, the electrons neighboring the oxygen vacancy at the O 2p orbital become delocalized, suggesting that a surface with oxygen vacancies is much more active and facilitate the adsorption of H_{2}O near an oxygen vacancy on the surface.[36] Previous DFT calculation also further demonstrated that the adsorption energy for a surface with one oxygen vacancy is lower than that of the perfect surface.[36] Therefore, we can deduce that the increase of O3 (oxygen vacancies) content further promote the adsorption of H_{2}O molecules and OER intermediates on the surface of the N-CoFe LDHs, which is valuable for increasing the reactivity of active sites and the OER performance. To exclude the contribution of the increased specific surface area, the LSV curves of CoFe LDHs and N-CoFe LDHs were normalized by Brunauer-Emmett-Teller (BET) specific surface area, as shown in Figure S12 (Supporting Information). The results further demonstrated that the enhancement of OER properties for N-CoFe LDHs was also attributed to the contribution of the dopant of nitrogen and the enhancement of the intrinsic electrocatalytic activity induced by edges/defects.

3. Conclusion

In conclusion, we synthesized N-doped ultrathin CoFe LDHs nanosheets with edge-rich sites by etching bulk CoFe LDHs with N_{2} plasma. It is a very facile and effective strategy to exfoliate the bulk CoFe LDHs into ultrathin nanosheets, tuning the number of the edge and corner active sites in 2D basal plane and carrying out the nitrogen doping in the ultrathin CoFe LDHs nanosheets. The as-synthesized ultrathin N-CoFe LDHs nanosheets on Ni foam showed an excellent OER performance with an overpotential of 233 mV at the current density of 10 mA cm^{-2}. The outstanding OER performance of ultrathin N-doped CoFe LDHs nanosheets is mainly attributed to high surface area of ultrathin nanosheets exposing more reactive sites for OER, more edge and corner sites bringing more dangling bonds and unsaturated coordination atoms to ultrathin nanosheets with higher electrocatalytic activity and N-doping altering the electronic density of the adjacent metal atom and forming well-defined electronic congratulations for adsorption intermediates for OER. This strategy can also be further extended and applied to the surface modification of other layered materials.

Figure 4. The XPS spectrum. A) Co 2p_{1/2}, B) Fe 2p_{3/2}, and C) O 1s of the bulk CoFe LDHs. D) Co 2p_{3/2}, E) Fe 2p_{3/2}, and f) O 1s of the ultrathin CoFe LDHs nanosheets.
4. Experimental Section

Synthesis of the Bulk CoFe LDHs: The bulk CoFe LDHs were synthesized using a typical hydrothermal method. One solution contained 0.3 mM Fe(NO$_3$)$_3$·9H$_2$O and 0.6 mM Co(NO$_3$)$_2$·6H$_2$O (the molar ratio of Co/Fe is 2:1) and the other solution contained 1.92 mM NaOH and 0.8 mM Na$_2$CO$_3$. Equal volumes of two solutions were mixed and added simultaneously into a beaker under vigorous stirring. Finally, the mixed solution (60 ml) was transferred into a stainless-steel Teflon-lined autoclave (100 mL) followed by reacting in a preheated oven at 80 °C for 48 h. The obtained product was washed with water for three times and dried at 60 °C for 10 h.

Synthesis of Ultrathin CoFe LDHs Nanosheets by the N$_2$ Plasma: 20 mg bulk CoFe LDHs were spread on the quartz boat in a plasma reactor. At last, the bulk CoFe LDHs were treated using N$_2$ plasma with power of 100 W and the treatment time is 5, 15, 30, 60, and 90 min, respectively.

Electrochemical Characterization: The electrochemical performances of as-obtained materials were tested in a CHI 760D electrochemical workstation. The OER activity of the as-obtained materials was tested in a three-electrode configuration including working electrode (glassy carbon electrode), the reference electrode (saturated calomel electrode, SCE), and the counter electrode (platinum gauze). The LSV polarization curves for OER of as-obtained catalysts were studied by dropping a glassy carbon electrode (0.204 mg cm$^{-2}$) on the glassy carbon working electrode, and the other solution contained 1.92 mM NaOH and 0.8 mM Na$_2$CO$_3$. The CVs were recorded at a scan rate of 50 mV s$^{-1}$ until reaching a stable state. All the polarization curves were corrected by eliminating iR drop with respect to the ohmic resistance of the solution. The SCE reference electrodes were also calibrated by measuring the reversible hydrogen electrode (RHE) potential using a Pt electrode under a H$_2$ atmosphere. In addition, span life of as-obtained catalysts was also tested to assess the long-term stability. The impedance spectra of OER were investigated under 1.5 V versus RHE over the frequency range from 1 MHz to 0.1 Hz in 1 M KOH.

Characterization: SEM (Hitachi, S-4800) and TEM (FEI Tecnai G20) were used to observe the morphology of as-obtained catalysts. AFM (Bruker Bioscope system) was used to study the size and thickness of the as-obtained catalysts. AFM (Bruker D8 Advance diffractometer, Cu Kα1). XPS analysis was performed on an ESCALAB 250Xi X-ray photoelectron spectrometer using Mg as the excitation source. The nitrogen adsorption–desorption isotherms were measured at 77 K with a Quantachrom NOVA 1000e system.

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

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Conflict of Interest
The authors declare no conflict of interest.

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