Sub-3 nm pores in two-dimensional nanomesh promoting the generation of electroactive phase for robust water oxidation

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ABSTRACT

Herein, abundant and uniform nanopores with sub-3-nm sizes are introduced to 1.5 nm-thick nickel-iron layered double hydroxide (NiFe LDH) ultrathin nanosheets via an etching-aging process, realizing remarkable enhancement in oxygen evolution reaction (OER) performance. Detailed analyses revealed that the NiFe LDH phase around the nanopores can be preferentially oxidized into electroactive Fe:NiOOH phase. In addition, the buffering space provided by the nanopores can effectively avoid structural deformation during repeated redox cycling, leading to better electrochemical stability, which synergistically make the catalyst a promising candidate for commercial water splitting. This work highlights the positive role of porous structure in accelerating the formation of active phases beyond just increment of surface area, which can provide insight in designing advanced catalysts.

1. Introduction

Aiming at scalable hydrogen production, electrochemical water splitting has received substantial attention owing to its high energy conversion efficiency and environmentally benign morality [1,2]. Unfortunately, as a half reaction, the sluggish OER severely hampers the overall efficiency of water splitting for its complex four-electron redox processes [3]. Up to date, intensive research passion has been devoted focused on exploring earth-abundant alternatives for the highly efficient but expensive noble metal-based catalysts, such as the oxides of ruthenium and iridium, and enormous progresses on this topic have been developed accordingly [4–13].

During past decade, NiFe-based catalysts, including doped or mixed oxides [14,15], oxhydroxides [16–19] and layered double hydroxides (LDH) [20,21], hold broad interests owing to their low cost, easy availability and relatively high efficiency for OER. Both theoretical and experimental results have proved that Fe plays a crucial role in improving the OER activity of Ni-based host material [14–21], but overloading of Fe(III) ions can induce the formation of FeOxH2O due to the presence of Fe-Fe neighboring atoms and cause dramatic degradation of activity [22]. Therefore, realizing highly dispersed Fe(III) ions in Ni-based catalysts is urgently demanded. Bearing this in mind, NiFe LDH with randomly dispersed Fe(III) ions and tunable Ni:Fe ratio offers a promising platform to compensate this drawback. As a typical two-dimensional (2D) material, NiFe LDH holds large surface area with high percentage of exposed atoms which are beneficial to electrocatalysis [23]. Briefly, NiFe LDH can be regarded as Fe(III)-incorporated Ni(OH)2 layers in which the extra positive charges brought by high-valence Fe(III) ions are compensated by anion intercalation between layers, while the close-packed basal planes terminated by hydroxyl group unfortunately hinder the fast electrochemical conversion to generate high-valence phases, thus limiting the oxygen-evolving activity [16,24]. As well accepted, the catalytically active phases in NiFe-based catalysts are the electrochemically oxidized high-valence species, commonly in the form of Fe3O4, where the chemical state of Ni is +3 ~ +4 [25–27]. Therefore, enriching the high-valence phases [27–29] or constructing microstructures that can boost the generation of active species [30-33] have been regarded as effective routes to optimize OER performance, and for NiFe LDH, constructing ion/gas permeable nanopores would be an effective but challenging strategy in leaping over this obstacle [34]. Recently, catalysts with highly porous structure have attracted intensive attention due to their large surface area [32–37]. For
example, Zhang et al. developed porous NiFe oxide as an efficient OER catalyst, which achieves high activity as well as superior stability [32].

Up to date, most of currently explored catalysts with high porosity are polycrystalline, for which the poor inter-grain conductivity is a main limiting factor that impedes the OER activity. Recently, the authors proposed an etching-intralayered Ostwald ripening process to construct nanopore structure in α-NiOOH [31], signifi-

cantly promoting, endowing it with excellent OER activity. By means of structural characterizations combined with elec-

trochemical normalization analyses, the role that nanopores play in OER was confirmed. That is, the material around the nanopores is more active in undergoing electro-oxidation to generate catalytically active phase, therefore subsequently achieve higher OER performance than the nonporous counterpart where only edges are electroactive. Besides, for the porous catalyst, ample buffering space can be provided by the nanopores, which can effectively avoid structural deformation caused by the volume change during repeated redox reactions, thus guar-

anteeing superior electrochemical stability, making the NiFe LDH nano-

mesh catalyst a promising candidate for commercial water splitting.

2. Experimental section

2.1. Materials

All the reagents for synthesis were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received.

2.2. Preparation of ZnNiFe LDH bulk material

Typically, 0.15 mmol Ni(NO₃)₂·6H₂O, 0.05 mmol Fe(NO₃)₃·9H₂O and 0.05 mmol Zn(NO₃)₂·6H₂O were dissolved in 80 mL deionized water, then 0.66 mmol urea was added to form a homogeneous solution under vigorous stirring. After stirring for 20 min, the transparent solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, sealed and maintained at 120 °C for 24 h. Then the reaction system was allowed to cool down to room temperature naturally. The obtained products were collected by centrifugation, washed with deionized water and ethanol, and dried at 60 °C under vacuum.

2.3. Liquid exfoliation to fabricate ZnNiFe LDH nanosheets

To obtain the ternary ZnNiFe LDH nanosheets, liquid exfoliation process was conducted under ultrasonication [38]. Generally, 300 mg ZnNiFe LDH bulk material was dispersed in 100 mL formamide for several times and dried at 60 °C under vacuum. Subsequently, 300 mg as-synthesized NiFe LDH nanoplates were dispersed in 100 mL formamide and sonicated for 6 h. After that, the dispersion was centrifugated at 4000 rpm to remove the un-
exfoliated bulk species, and then centrifugated at 12,000 rpm to obtain the exfoliated nanosheets. The exfoliated NiFe LDH nanosheets were washed with deionized water and ethanol, and then dried at 60 °C under vacuum.

2.4. Synthesis of the NiFe LDH ultrathin nanomeshes

The single-crystalline NiFe LDH ultrathin nanomeshes were fabricated via a consequent hydrothermal alkali-etching treatment of the exfoliated ternary ZnNiFe LDH nanosheets. Typically, 150 mg exfoliated ZnNiFe LDH nanosheets were dispersed in 10 mL deionized water under vigorous sonication, then 30 mL 1 M NaOH solution was added to form a homogeneous dispersion under subsequent ultrasonication for 15 min. The as-formed dispersion was then transferred into a 50 mL Teflon-lined stainless steel autoclave and maintained at 140 °C for 12 h. After cooling down to room temperature, the as-obtained product was collected by centrifugation at 12,000 rpm, washed with deionized water and ethanol, and dried at 60 °C under vacuum.

2.5. Fabrication of the nonporous NiFe LDH nanosheets

The nonporous NiFe LDH nanosheets were fabricated by exfoliating the corresponding binary LDH nanoplates synthesized according to a modified method reported in a previous literature [39]. Typically, 0.9 mmol Ni(NO₃)₂·6H₂O, 0.3 mmol Fe(NO₃)₃·9H₂O and 6 mmol urea were dissolved in 40 mL of distilled water and stirred to form a homogeneous solution. Then the aqueous solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave, sealed, and maintained at 120 °C for 12 h, after which the reaction system was allowed to cool to room temperature. The as-obtained product was washed by deio-

nized water and ethanol for several times and dried at 60 °C under vacuum. Subsequently, 300 mg as-synthesized NiFe LDH nanoplates were dispersed in 100 mL formamide and sonicated for 6 h. After that, the dispersion was centrifugated at 4000 rpm to remove the un-
exfoliated bulk species, and then centrifugated at 12,000 rpm to obtain the exfoliated nanosheets. The exfoliated NiFe LDH nanosheets were washed with deionized water and ethanol, and then dried at 60 °C under vacuum.

2.6. Electrocatalytic study

All the electrochemical measurements were performed in a three-
electrode system on an electrochemical workstation (CHI660d) at room temperature, and all the potentials were calibrated to a reversible hydrogen electrode (RHE). Typically, 4 mg of catalyst and 40 μL Nafion solution (Sigma Aldrich, 5 wt%) were dispersed in 1 mL water-isopropanol mixed solution (volume ratio of 3:1) by sonication for at least 30 min to form a homogeneous ink. Then 5 μL of the dispersion (con-
taining 20 μg of catalyst) was loaded onto an L-shaped glassy carbon electrode with 3 mm diameter, leading to a catalyst loading of 0.285 mg cm⁻². The as-prepared catalyst film was allowed to be dried at room temperature. Linear sweep voltammetry with a scan rate of 5 mVs⁻¹ was conducted in 1 M KOH aqueous solution (pH = 14, satu-
rated with pure O₂) using a Ag/AgCl (in saturated KCl solution) electrode as the reference electrode, a platinum gauze electrode (2 cm x 2 cm, 60 mesh) as the counter electrode, and the glassy carbon electrode loaded with various catalysts as the working electrode. Cyclic voltammetry (CV) was conducted at 5 mVs⁻¹ to survey the electro-
chemical reactions and operated at 50 mVs⁻² to investigate the cycling stability. Chronoamperometry data were recorded for the NiFe LDH ultrathin nanomesh catalyst at a static overpotential of 300 mV. The mass activity curves for various catalysts were calculated from the catalyst loading and the as-measured linear sweep voltammetry curves. In order to estimate the TOF value of the NiFe LDH nanomesh and its counterparts, the total amount of Ni and Fe in mole are identified by ICP analysis, and we assume that both Ni and Fe atoms are active sites for OER. Hence, the TOF values can be calculated as follows, which represents the lowest limits of the model:

\[
\text{TOF} = \frac{j}{S_{geo} \times 4F \times n}
\]

where \(j\) (mA cm⁻²) is the as-measured current density at various potentials, \(S_{geo}\) (0.0707 cm²) represents the surface area of the glassy carbon disk, the number 4 means a four-electron transfer during the formation of one mole of \(O_2\), \(F\) is the Faraday’s constant (96,485.3 C mol⁻¹), and \(n\) is the moles of Ni and Fe atoms on the elec-
trode which can be calculated by the loading weight of the metal atoms in the coated catalysts. The Faraday efficiency were calculated from the quantity of oxygen generated at various constant potentials by means of
mass spectroscopy [40].

3. Characterization

X-ray diffraction (XRD) was performed on a Philips X’Pert Pro Super diffractometer with Cu Kα radiation (λ = 1.54178 Å). The transmission electron microscopy (TEM) was carried out on a JEM-2100F field emission electron microscope and a JEOL JEM-ARF200F TEM/STEM at an acceleration voltage of 200 kV, respectively. The high-resolution TEM (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and corresponding electron energy loss spectroscopy (EELS) mapping analyses were performed on a JEOL JEM-ARF200F TEM/STEM with a spherical aberration corrector. Atomic force microscopy (AFM) was performed using a Veeco DI NanoScope MultiMode V system. Nitrogen adsorption-desorption isotherms were carried out by using a Micromeritics ASAP 2000 system, and all the gas adsorption experiments were performed at liquid-nitrogen temperature (77 K) after degassed at 200 °C for 6 h. X-ray photoelectron spectroscopy (XPS) analyses were performed on a VGESCALAB MKII X-ray photoelectron spectrometer with an excitation source of Mg Kα = 1253.6 eV, and the resolution level was lower than 1 atom%.

The inductively coupled plasma (ICP) emission spectrum was conducted on a Perkin Elmer Optima 7300DV ICP emission spectroscopy.

4. Results and discussion

Typically, ternary ZnNiFe LDH ultrathin nanosheets are firstly prepared as precursor via liquid exfoliation, and a following hydrothermal alkaline treatment is conducted to etch the amphoteric Zn ions, leading to the formation of NiFe LDH primary porous nanosheets. Since Zn ions are randomly distributed in the ternary LDH host layer, irregular primary nanopores with uneven size are resulted in the primary porous nanosheets, in which the protruding edges around the primary nanopores endow thermodynamically unfavorable feature according to Kelvin equation (see Supporting information S1 for details) [30]. Hence, the Ni or Fe atoms on protruding edges will tend to detach from the porous LDH matrix. Subsequently, the dissolved species will bond with the low-coordinated sites, i.e., the concaved edges or pore fringes, thereby reducing the pore size, smoothing edges and the pore fringes, and finally resulting in NiFe LDH ultrathin nanomesh with uniform nanopores (Scheme S1).

X-ray diffraction (XRD) analysis was conducted to investigate the structural information of the samples at different stages in the synthesis procedure (Fig. 1A). As can be seen, the NiFe LDH ultrathin nanomesh exhibits only one weak and broadened diffraction peak, which can be attributed to the reduced layer thickness and subsequent structure relaxation along c-axis. Detailed analysis reveals that the exfoliation of ternary LDH can lead to a slight enlargement of interlayer spacing from 6.6 Å to 6.7 Å (Fig. 1B); while after removing Zn ions from the hydroxide layer, a dramatically increased interlayer spacing of 7.0 Å can be identified, which may arise from the weakened interaction between adjacent layers induced by the presence of abundant nanopores. Of note, the temperature for the etching-agining process is a crucial factor for preparing NiFe LDH ultrathin nanomesh, since lower temperature is not enough to remove Zn ions completely (Table S2), whereas temperature higher than 140 °C will trigger phase separation to generate β-Ni(OH)2 and FeOx (Fig. S2). Besides, the quantity of metal salt precursor is also crucial for the generation of NiFe LDH nanomesh. When the proportion of Fe reaches 40%, the product exhibits obvious phase separation (Fig. S3), indicating the severe damage of the LDH structure induced by the high component of M(III) ions [24]. When more Zn atoms were introduced into the ternary precursor, the 2D structure of the product after etching-aging process will be unstable rather than generating more nanopores. That is, the removal of high-ratio Zn component in the exfoliated ternary LDH nanosheets may lead to poor structural stability of the as-formed primary porous NiFe LDH nanosheets, which further cause the collapse of the 2D nanostructures rather than undergoing 2D-confined aging process to form ultrathin nanomeshes (Fig. S4).

Low-resolution transmission electron microscopy (TEM) images indicate that the product maintains sheet-like morphology with lateral size of several hundreds of nanometers, and the homogenous contrast suggests the uniform thickness (Fig. S5). As shown in Fig. 1C, abundant and uniformly distributed nanopores with size of approximately 2–3 nm can be clearly observed and the layer thickness is identified to be 1.5 nm from a curved edge, corresponding to two Fe-incorporated Ni(OH)2 layers in NiFe LDH. In addition, a piece of monolayered nanomesh overlapped on the bilayered nanomesh can also be revealed, indicating the ultrathin thickness and the strong tendency in forming layer-by-layer assemblies to minimize the surface energy [41]. In sharp contrast with the highly porous NiFe LDH nanomesh, the ZnNiFe LDH bulk precursor, the ZnNiFe LDH ultrathin nanosheets as well as the NiFe LDH ultrathin nanosheets exhibit nonporous nanosheet morphology with high crystallinity (Fig. S6–9). Atomic force microscopy (AFM) image further confirms the uniform thickness of 1.5 nm for the NiFe LDH nanomesh (Fig. S10). Of note, the nanopores cannot be detected since the size of AFM probe is larger than the nanopores [42]. Nitrogen adsorption-desorption isotherms were conducted to investigate the specific surface area as well as the pore size distribution. As can be seen from Fig. S11 and Table S1, the NiFe LDH nanomesh exhibits a high Brunauer-Emmett-Teller (BET) specific surface area of 57.7 m2 g−1, which is approximately 3.1, 4.0, and 52.5 times larger than that of the nonporous NiFe LDH nanosheets, ZnNiFe LDH nanosheets and the bulk ZnNiFe LDH. The corresponding Barrett-Joyner-Halenda (BJH) pore size distribution curve (Fig. S11B) derived from the N2 desorption branch further reveals the presence of nanopores with diameter of ~2.4 nm, which is consistent with the result from HRTEM analysis. Besides, a broad peak in the range of 3–5 nm can be observed for all the samples, which can be attributed to the stacking spacing of nanosheets or nanomeshes. This phenomenon matches well with the results from previous TEM and ICP analysis. High-resolution TEM (HRTEM) was applied to survey the crystal structure of the NiFe LDH ultrathin nanomesh, from which the hexagonal symmetry with interplaner spacing of 2.70 Å can be indexed (Fig. 1D), matching well with previous report on NiFe LDH [21]. Notably, although abundant nanopores exist in the basal plane, the nanodomains are interconnected and the crystal fringes are grown along the same orientation, indicating that the single-crystalline nature is retained, which may favor the electrocatalytic process owing to better intralayered conductivity when compared with the polycrystalline catalysts [43,44]. The corresponding selected area electron diffraction (SAED) pattern (Fig. 2D, inset) further confirms the single-crystalline nature of the nanomesh, from which the typical six-fold symmetry with six independent diffraction spots can be revealed, agreeing well with the hexagonal structure of NiFe LDH in the basal x-plane. Scanning transmission electron microscopy (STEM) under high-angle annular dark-field (HAADF) mode was conducted (Fig. 1E), from which the abundant nanopores can be further corroborated. Corresponding elemental mapping analyses were recorded under electron energy loss spectroscopy (EELS) mode (Fig. 1F), where nickel, iron and oxygen are homogenously distributed in the whole nanomesh. The atomic ratio of elements was analyzed by inductively coupled plasma (ICP) emission spectrum, and a Ni:Fe molar ratio of 3.20:1 can be identified without Zn residual, which is close to that of ZnNiFe LDH nanosheet precursor (Table S2). It is worth noting that, the Fe concentration in the NiFe LDH ultrathin nanomesh is in the range of broad maximum in activity, suggesting its high potential for OER [14].

Electrochemical measurements were carried out to verify the structural benefits of the NiFe LDH ultrathin nanomesh catalyst. As shown in Fig. 2A, the polarization curve of NiFe LDH ultrathin nanomesh shows an early oxidation peak for Ni(II)-to-Ni(III) conversion located at 1.44 V vs. RHE, which is ~120 mV lower than that of the nonporous nanosheet. This phenomenon can be attributed to the highly
porous structure which can offer more reactive edge sites for oxidation reactions [34,45]. The early phase conversion can bring in more catalytically active high-valence species at a certain overpotential, realizing higher OER activity. For instance, a high current density of 234.5 mA cm\(^{-2}\) can be achieved at \(\eta = 500\) mV for the NiFe LDH ultrathin nanomesh catalyst, which is 6.5-, 93.8- and 156.3-folds larger than those of the nonporous NiFe LDH nanosheet, ZnNiFe LDH nanosheet and the bulk ZnNiFe LDH. Moreover, the overpotential required to drive an obvious water splitting, i.e., \(\eta\) for \(j_{\text{geo}} = 50\) mA cm\(^{-2}\) with elimination of the interference of the Ni(II)-Ni(III) oxidation reaction, is as low as 268 mV for the nanomesh catalyst, which is among the lowest values for earth-abundant OER catalysts (Table S3) [16,45–47]. In addition, the commonly used parameter, \(\eta\) for \(j_{\text{geo}} = 10\) mA cm\(^{-2}\), is also roughly estimated to be 184 mV from the reverse scan of CV curves as a reference (Fig. S13), which inevitably contains non-negligible errors due to the existence of double-layer capacitance as well as pseudocapacitance brought by high surface area and the reversible Ni(II)-Ni(III) redox reactions.

Tafel plot of the NiFe LDH ultrathin nanomesh also shows predominance in kinetic aspect when compared with the other three references (Fig. 2B). A small Tafel slope of 30 mV decade\(^{-1}\) can be identified, suggesting the facile OER process for the nanomesh catalyst. The small Tafel slope will lead to a strongly enhanced OER rate at a moderate increase of overpotential [48]. The facile catalytic process could be attributed to the highly porous morphology which provides more ion-accessible and gas-permeable channels that are perpendicular to the ultrathin layers, thereby exposing more reactive edges, facilitating the generation of catalytically active species, and guaranteeing easy release of oxygen bubbles to offer empty sites for subsequent catalysis [34,45].

In order to further understand the influence of the KOH concentration to the OER performance, the LSV curves measured in O\(_2\)-saturated 0.1 M KOH solution were investigated. As shown in Fig. S14A, the NiFe LDH nanomesh catalyst exhibits excellent OER activity with a high current density of 96.1 mA cm\(^{-2}\) at \(\eta = 500\) mV and a low overpotential of 403 mV to drive a rapid water splitting rate with current density of 50 mA cm\(^{-2}\), demonstrating the high OER activity of the NiFe LDH nanomesh catalyst even in lower pH condition.

Turnover frequency (TOF) is a key parameter to evaluate an advanced OER catalyst. Unfortunately, the determination of the TOF per active sites for NiFe-based catalysts is still controversial, mainly owing to the ambiguous nature of the active sites (i.e., Ni or Fe, bridge \(\mu_2\)-OH or on top \(\mu_1\)-OH) and lack of reliable methods to identify them [16]. In order to estimate the TOF value of the NiFe LDH nanomesh and its counterparts, the total amount of Ni and Fe in mole are measured by ICP analysis, and we assume that both Ni and Fe atoms are active sites for OER, which can derive the lowest limits of TOF for various catalysts. As shown in Fig. 2C, the TOF values of the NiFe LDH nanomesh catalyst are calculated to be 1.49 s\(^{-1}\) and 4.74 s\(^{-1}\) at \(\eta = 300\) mV and 500 mV, respectively, which show significant superiority to those of the NiFe LDH nanosheets, ZnNiFe LDH nanosheets and bulk ZnNiFe LDH material. The value of 1.49 s\(^{-1}\) at \(\eta = 300\) mV has surpasses that of the NiFeO\(_x\) film (TOF = 0.21 s\(^{-1}\); on Au/Ti, in 1 M KOH) [26], bulk and exfoliated NiFe LDH (TOF = 0.01 s\(^{-1}\) and 0.05 s\(^{-1}\), respectively; loaded on glassy carbon (GC) electrode, in 1 M KOH) [45], the NiFe LDH/CNT...
hybrid catalyst (TOF = 0.56 s⁻¹; loaded on carbon fiber paper, in 1 M KOH) [21], and even the state-of-the-art gelled FeCoW oxyhydroxide at the same conditions (0.46 s⁻¹ in 1 M KOH, loaded on GC electrode) (Table S3) [47], confirming the excellent OER activity of the NiFe LDH nanomesh catalyst.

When measured in 0.1 M KOH electrolyte, the TOF of the NiFe LDH nanomesh catalyst is also sound (Fig. S14B). The TOF value in 0.1 M KOH solution reaches 0.99 s⁻¹ at \( \eta = 400 \) mV, showing 9.3 times enhancement than the nonporous NiFe LDH nanosheets. This value is also larger than some previously developed earth-abundant OER catalysts [33,49,50].

Faraday efficiency is another important parameter to investigate the conversion efficiency from electric energy to chemical energy. The Faraday efficiency of the NiFe LDH nanomesh catalyst for OER in 1 M and 0.1 M KOH electrolyte at various constant potentials was determined by using mass spectroscopy, respectively [40]. As can be seen from Fig. 2D, the Faraday efficiency for oxygen evolution is measured to be ~ 95% at an applied potential of 1.50 V vs. RHE in 1 M KOH electrolyte, and further reaches ~ 98% at higher potentials. The lower Faraday efficiency at 1.50 V may arise from the incomplete oxidation reaction that consumes charges for Ni(II)-Ni(III) phase conversion, while at higher potentials, OER becomes the predominant reaction, which displays high Faraday efficiency for the NiFe LDH nanomesh catalyst. Of note, the Faraday efficiency of ~ 98% is comparable to many earth-abundant OER catalysts, demonstrating the high activity of the NiFe LDH nanomesh catalyst [40,51–53]. Furthermore, the Faraday efficiency of the NiFe LDH nanomesh catalyst in 0.1 M KOH solution was also investigated, which reaches ~ 96% at potentials higher than 1.6 V vs. RHE where OER process is predominant, revealing the high conversion efficiency.
efficiency for OER even at lower pH conditions. The high Faraday efficiency and the high TOF value further confirm the excellent OER activity of the NiFe LDH nanomesh catalyst.

Mass activity is also crucial for commercial water splitting. As depicted in Fig. 2E, the mass activity of NiFe LDH ultrathin nanomesh reaches 257.8 A g⁻¹ and 818.6 A g⁻¹ at η = 300 mV and 500 mV, respectively, indicating the high OER activity (Table S3). In sharp contrast, nonporous NiFe LDH nanosheet only gains 32.0 A g⁻¹ and 125.3 A g⁻¹ at the same overpotentials, further confirming the structure-performance relationship of the nanomesh catalyst. Electrochemical double layer capacitance (Cdl) was measured to better understand the merits of the nanomesh morphology, which is linearly proportional to the electrochemically active surface area (ECSA) [34,44]. As shown in Fig. 2F, the NiFe LDH ultrathin nanomesh shows a Cdl of 8.3 μF, which is roughly 4.9, 3.2 and 27.7 times larger than the values of NiFe LDH nanosheet, ZnNiFe LDH nanosheet and the bulk ZnNiFe LDH, respectively, revealing the high exposure of electrochemically active and ion-accessible sites in the nanomesh catalyst, which is responsible for the enhanced OER activity. Interestingly, the increment of ECSA by forming nanospheres (4.9 times enlargement) is more obvious than that for the comparison in BET specific surface area (3.1 times enlargement). That is, both nanosheet and nanomesh catalysts have strong tendency in accumulating into layer-by-layer assemblies during the solution-processed preparation of catalyst-coated working electrode to lower their surface energy [41]. Under this circumstance, the basal surfaces of the nonporous nanosheets undergo severe overlapping, making the as-measured Cdl values underestimated. While for the NiFe LDH nanomesh catalyst, although the overlapping of individual nanomeshes is inevitable, the abundant nanopores can act as effective channels for vertical ion penetration, thus achieving a higher Cdl value and further resulting in significant enhancement in OER activity [30]. By means of normalization of the LSV curves by Cdl values (Fig. S16), the nanomesh catalyst exhibits the highest normalized current among all the tested samples, which confirms the increased intrinsic activity in OER catalysis. The high intrinsic activity of the nanomesh catalyst may arise from the highly porous structure, which can provide more reactive sites for electro-oxidation to generate active phases for OER [32,34,36,37].

Except for the activity, electrochemical stability is another key criterion to evaluate an electrocatalyst. Long-term cyclic voltammetry (CV) was first applied to the NiFe LDH ultrathin nanomesh. As shown in Fig. 3A, the anodic current shows slight increment after 5 CV cycles, and reaches a maximum after 100 cycles, showing a 17.9% increment in catalytic current at η = 300 mV. This phenomenon is common for earth-abundant OER catalysts, which can be ascribed to the activation process with substantial accumulation of active high-valence species [54,55]. When applying further cycling, the current undergoes slight degradation, but is still higher than that of the initial cycle even after 3000 CV cycles, indicating the superior stability of the nanomesh catalyst. Of note, the onset overpotential exhibits negligible degradation during long-term CV cycling, revealing the high OER activity against performance fading. The high stability of the nanomesh catalyst may arise from the highly porous structure which offers ample space to buffer the volume change during repeated redox reactions [44]. In addition, the electrochemical stability was further evaluated by chronoamperometry under fixed overpotential. As shown in Fig. 3B, at η = 300 mV, the anodic current of the nanomesh catalyst exhibits considerable increment within first 36 h and shows only slight degradation until 48 h, confirming the superior electrochemical stability in long-term OER operation. In contrast, the nonporous NiFe LDH nanosheet catalyst undergoes a similar activation process but subsequently a severe performance fading, indicating its poor operational stability (Fig. S18). X-ray photoelectron spectroscopy (XPS) was applied to investigate the valence of nickel for the catalyst after OER operation. As can be seen from Fig. 3C, the Ni 2p spectrum of the catalyst after undergoing 100 CV cycles can be fitted as two spin-orbit doublets, characteristic of Ni(II) and Ni(III), and two shakeup satellites [56–58]. The binding energy of Ni 2p3/2 region can be deconvoluted into two peaks at 857.5 eV and 859.3 eV that match the oxidation states of Ni(II) and Ni(III), respectively; while the binding energy of Ni 2p1/2 region can be deconvoluted into two peaks centered at 875.0 eV and 876.5 eV, corresponding to Ni(II) and Ni(III), respectively [56–58]. Furthermore, two broad peaks at 863.0 eV and 881.2 eV can be indexed to the satellite peaks of 2p3/2 and 2p1/2 spin orbits. Therefore, the existence of catalytically active Ni(III) species can be confirmed for the post-OER nanomesh catalyst, which may be responsible for the enhanced activity during the initial cycling (from 1st cycle to 100th cycle, Fig. 3A). In order to verify the morphological benefits in fast generation of active high-valence species for the NiFe LDH ultrathin nanomesh catalyst, HRTEM was conducted to the nanomesh and nanosheet catalysts after repeated CV cycles. As shown in Fig. 3D, the hexagonal LDH structure of the nanomesh catalyst is generally maintained, and the original position of nanopores can be observed from the lower diffraction contrast, suggesting the high structural stability of the nanomesh. Of note, a new orthorhombic phase can be observed around the original position of nanopores, which can be indexed as α-NiOOH, indicating that the pore region are more active to undergo electro-oxidation from Ni(II) to Ni(III) [29]. In sharp contrast, the HRTEM image of the nonporous NiFe LDH nanosheet catalyst after continuous CV cycling can be seen from Fig. S20, where the hexagonal LDH structure is basically maintained in the internal area of the nanosheet, and the α-NiOOH phase can only be identified in the edge area. This phenomenon indicates that the edges of the nonporous nanosheets have a higher tendency in undergoing redox reactions than the close-packed internal basal planes of the LDH structure. For the NiFe LDH nanomesh catalyst, the fringes around the nanopores possess similar structure with the edges, which are rich in low-coordinated metal atoms and more active for the Ni(II)-Ni(III) redox reactions [37]. Therefore, the abundant sub-3 nm pores in the NiFe LDH nanomesh catalyst can effectively promote the generation of electroactive high-valence phase during the OER operation rather than just increase surface area. Therefore, the intrinsic electrochemical activity can be improved via introducing pore structure, in line with the result from Cdl normalization study of the OER activity (Fig. S16). Besides, the electroactive α-NiOOH phase accumulated in repeated CV operation may also contribute to the improved OER activity, which has been proved in Fe-incorporated Ni-based catalysts [27]. As indicated in HRTEM analysis (Fig. 3D), considerable α-NiOOH phase can only be observed after approximately 100 CV cycles. Interestingly, LSV curves indicate that the OER activity reaches a maximum after 100 CV cycles (Fig. 3A), which is coincident with the content trend of Ni(III) species. Therefore, the accumulation of Ni(III) species in the nanomesh catalyst may serve as the activation effect for OER catalysis, leading to the increased OER activity during repeated CV scanning.

A schematic illustration is depicted in Fig. 4 to intuitively highlight the structural benefits of the NiFe LDH ultrathin nanomesh catalyst. As illustrated, the active high-valence phases are mainly formed in the fringes of nanopores and the edges, which is benefited from the presence of abundant nanopores that ensures facile ion interaction and subsequently leads to fast phase conversion from LDH to the high-valence electroactive phase. This fast phase conversion is deemed to be responsible for the enhanced OER activity. Moreover, owing to the high porosity of the nanomesh catalyst, sufficient space could be offered to avoid the structural deformation induced by frequent redox phase conversion, which guarantees superb electrochemical stability in long-term OER operation.

5. Conclusions

In summary, highly porous NiFe LDH ultrathin nanomesh with uniformly distributed nanopores in size of sub-3 nm was synthesized via an etching-aging process by serving ZnNiFe LDH nanosheets as the precursor. The amphoteric Zn ions in the ternary precursor can be selectively etched by alkaline treatment, and a subsequent aging process

can result in the homogenization of nanopores. Benefited from the 2D highly porous morphology, the generation of catalytically active high-valence phase can be effectively promoted, realizing remarkably enhanced OER activity. Detailed structural analyses revealed that the pore region is more electroactive in undergoing the redox reaction to generate active α-NiOOH phase, which is responsible for the enhanced OER activity. In addition, the abundant nanopores in 2D layers can provide ample space for buffering the volume change in repeated redox reactions, which effectively avoids structural deformation and guarantees superior stability for OER. This work provides an efficient strategy on optimizing the OER performance, and may enlighten future designing of catalysts for energy-related applications.

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Appendix D. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2018.08.045.

References


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