Nickel-Iron Layered Double Hydroxide for Highly Efficient Oxygen Evolution Reaction

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Abstract. It is extensively accepted that electrolysis of water producing regenerable energy is a crucial substitution of traditional fuel strategy. Herein, we report a wet-chemical route to Ni-Fe layered double hydroxide (LDH) interconnected nanosheets with large surface area with the support of vertically aligned ZnO microrods arrays on the nickel foam (Ni-Fe LDH@ZnO/NF) for oxygen evolution reaction. Owing to the 2D Ni-Fe LDH nanosheets distributed in 3D space, the Ni-Fe LDH@ZnO/NF demonstrates excellent OER performances with a reasonably low overpotential of 271 mV at a current density of 10 mA·cm⁻², and a long-term stability up to 29 hours. This work proposes a new strategy to prepare Ni-Fe LDH/NF as efficient OER catalyst.

1 Introduction

With the development of industry and increase of population, it is of great urgency to product clean regenerable energy to replace fossil fuels. Hydrogen is considered as one of the most promising candidates because of its environmental friendliness and recyclability [1, 2]. Among the various methods of hydrogen production, electrolysis of water can be coupled with the wind energy or photovoltaic system which has been considered as the main way of hydrogen production in the future [3]. However, the important half-reactions in the water electrolysis process—oxygen evolution reaction (OER)—involving a four-electron reaction is constrained a sluggish kinetics, which generally requires a high overpotential to drive the reaction [4, 5]. Currently, RuO₂ and IrO₂ have been demonstrated to be effective electrocatalysts for OER [6, 7], but high cost and resource scarcity hinder their practical applications [8, 9]. Consequently, it is of elementary significance to engineer competent, low-cost and stable OER catalysts [10, 11].

Up to now, the improvement of the performance of electrocatalytic catalysts contains three main approaches: (1) increasing the catalytic specific surface area of material to expose more catalytic active sites; (2) enhancing the stability through material structure design; (3) improving the catalyst’s electrical conductivity by integrating other components [12]. However, the mentioned enhancement strategies towards electrocatalytic materials still require numerous efforts to decrease the produced and maintained cost, prevent the secondary pollution, and promote the practical applications.

Among of Ni-Fe-based catalysts [13-17], particularly Ni-Fe layered double hydroxides (LDHs) have been extensively investigated, with a significant improvement of OER activity by structural design [18-22]. For example, Lou’s group synthesized Ni-Fe LDH double-shelled nanocages exhibited an overpotential of 246 mV in 1.0 M KOH, which is lower than 261 mV by conventional Ni-Fe LDH single-shelled nanocages at 20 mA·cm⁻² [18]. Shi et al. reported the immobilization of Ni-Fe LDH nanoplates reduced graphene oxide. Interestingly, the Ni-Fe LDH/3D-ErGO showed a higher OER activity with an overpotential of 259 mV than that of Ni-Fe LDH/2D-ErGO (278 mV) at 10 mA·cm⁻² because of the large electrochemically active surface area of Ni-Fe/3D-ErGO [19]. However, improvement of poor stability and low conductivity of Ni-Fe LDH [20, 21] is still challenging towards its practical application.

Herein, we reported a wet-chemical route to synthesis Ni-Fe LDH@ZnO on nickel foam (denoted as Ni-Fe LDH@ZnO/NF), and then we investigated their electrochemical properties via serial characterizations and experiments. The result illustrated that Ni-Fe LDH@ZnO/NF exhibited excellent oxygen evolution reaction (OER) activity and long-term stability, which was ascribed to the effective enhancement catalytic surface area after the introduction of Ni-Fe LDH onto ZnO microrods arrays.

2 Experimental section

Growth of ZnO microrods arrays on nickel foam (ZnO/NF): Commercial nickel foam (NF) was ultrasonically washed with concentrated HCl (~37 wt%), ethanol and ultrapure water for 10 min, successively. Treated NF was then dropped into Teflon-lined stainless reactors (50 mL) containing 40 mL ultrapure water, 0.030 M Zn(NO₃)₂·6H₂O, and 0.025 M C₆H₅N₂. After the
hydrothermal reaction conducting at 100 °C for 6 h, the uniform ZnO microrods were generated on NF.

Synthesis of Ni-Fe LDH@ZnO/NF: NiFeSx was grown on the surface of ZnO microrods by electrochemical cathode deposition at 70 °C in the 0.010 M NiCl\textsubscript{2} and 0.001 M FeCl\textsubscript{3} + 0.100 M Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} (10 mL) aqueous solution at 1.0 mA cm\textsuperscript{-2} for 600 seconds. After drying, the NiFeS\textsubscript{x} was soaked in a 2-methylimidazole aqueous solution (0.10 M, 20 mL) at 90 °C for 2 h to obtain Ni-Fe LDH@ZnO/NF. For comparison, Ni-Fe LDH on NF (Ni-Fe LDH/NF) was synthesized by using the same method without ZnO microrods arrays.

3 Results and discussion

The Ni-Fe LDH@ZnO/NF mesostructured microrods were synthesized via wet-chemical route. Firstly, Hexagonal prism ZnO microrods arrays with an average lateral length of 1.2 μm were in-situ grown on NF (ZnO/NF) by hydrothermal method. Secondly, a NiFeS\textsubscript{x} layer was electrodeposited on the surface of ZnO/NF (Figure. 1(a, b)). Finally, Ni-Fe LDH grew on the outside of ZnO via the reduction of NiFeS\textsubscript{x} by using 2-methylimidazole (Figure. 1(c, d)). As we can see, Ni-Fe LDH was uniformly distributed with a thickness of 2 nm with a distinct boundary between ZnO microrods arrays.

Figure 1. SEM images of NF (a) NiFeS\textsubscript{x}@ZnO/NF (b) and Ni-Fe LDH@ZnO/NF (c and d). TEM images of Ni-Fe LDH@ZnO (e) and HRTEM (f) images of Ni-Fe LDH. Element distribution of Ni-Fe LDH@ZnO (g).

TEM images of Ni-Fe LDH@ZnO and Ni-Fe LDH were shown as Figure. 1(e, f). The layered structure of Ni-Fe LDH was well maintained after decorated on the surface of ZnO microrods arrays. High-resolution image of TEM (HRTEM) revealed a lattice fringe distance of 0.26 nm, which corresponded to the spacing of (012) lattice plane of Ni-Fe LDH [22]. The image of TEM element mapping (Figure. 1(g)) indicated a homogeneous elemental distribution of Ni, Fe, Zn, and O, which further verified that the successful synthesis of Ni-Fe LDH/ZnO.

The X-ray diffraction (XRD) patterns of Ni-Fe LDH@ZnO/NF, Ni-Fe LDH/NF, ZnO/NF, and NF were displayed in Figure. 2(a). The peaks at 2θ =13.1 °, 19.5 ° and 33.7 ° can be attributed to (003), (006) and (009) planes of Ni-Fe LDH nanosheets (Figure. 2(b)) [23], indicating that LDH was successfully loaded on the ZnO (2θ = 32 °, 34.6 ° and 36.4 °) [24]. To investigate the electrocatalytic OER active sites, quasi real-time Raman spectra were obtained at different potential as shown in Figure. 2(c). The Raman bands at 484 cm\textsuperscript{-1} and 564 cm\textsuperscript{-1} correspond to γ-NiOOH (Ni\textsuperscript{3+}) [25]. The band intensities were changed with the increase of potential, indicating that the content of oxyhydroxides increased at the high potential. This revealed that oxyhydroxide was the active catalytic substance of OER. Thus, in line with the previous reports [23, 30], the oxyhydroxide was active for OER in our study. Besides, the peak at 1060 cm\textsuperscript{-1} was assigned to intercalated carbonate in Ni-Fe LDH.

Figure 2. (a) and (b) XRD patterns of Ni foam, ZnO/NF, Ni-Fe LDH/NF, and Ni-Fe LDH@ZnO/NF. (c) In-situ Raman spectra of Ni-Fe LDH@ZnO/NF recorded at varied potentials during OER process. (d) XPS survey spectrum of Ni-Fe LDH@ZnO/NF. (e) and (f) High-resolution Ni 2p spectrum and Fe 2p of Ni-Fe LDH@ZnO/NF, respectively.

The X-ray photoelectron spectroscopy (XPS) spectra recorded on the surface of Ni-Fe LDH@ZnO/NF revealed the presence of Ni 2p, Fe 2p, and O 1s (Figure. 2(d)). The high-resolution XPS spectrum of Ni 2p in Figure. 2(e) showed a binding energy difference between two spin-orbit peaks, which was related to Ni-O (Ni 2p\textsubscript{3/2} at 873.43 eV) and Ni-OH (Ni 2p\textsubscript{3/2} at 855.73 eV) [26]. Figure. 2(f) showed the divided Fe 2p\textsubscript{3/2} and Fe 2p\textsubscript{1/2} were affiliated with iron oxides or hydroxides such as Fe\textsubscript{3}O\textsubscript{4}, Fe\textsubscript{2}O\textsubscript{3}, and Fe\textsubscript{2}O\textsubscript{4}.
FeOOH. Though oxygen evolution reaction mechanisms demonstrated that the active variety was Ni\(^{2+}\) in the vicinity of Fe ions. With the Fe incorporation, overpotential of OER was significantly reduced, which was attributed to Ni\(^{3+}\) reduced to Ni\(^{2+}\) by H transfer around Fe\(^{2+}\). Both Ni 2p and Fe 2p exhibited same ingredient of Ni-Fe LDH, verifying the existence of LDH. Zn 2p was not detected by XPS and we believe that it is due to the dense coverage of Ni-Fe LDH nanosheets (~200 nm) on the surface of ZnO which can be seen from the TEM image.

The OER performances of Ni-Fe LDH@ZnO/NF was evaluated in 1.0 M KOH at the ambient condition. Figure 3(a) showed its linear sweep voltammetry (LSV) curves. Ni-Fe LDH@ZnO/NF exhibited the lowest overpotential of 271 mV at 10 mA·cm\(^{-2}\) (NF 419 mV, ZnO/NF 386 mV and Ni-Fe LDH/NF 303 mV). It was worth noting that, the overpotential of Ni-Fe LDH@ZnO/NF was reduced by 32 mV in comparison with Ni-Fe LDH/NF which resulted from the introduction of ZnO. The Tafel slope of Ni-Fe LDH@ZnO/NF was calculated to be 72 mV·dec\(^{-1}\) (Figure. 3(b)), which was lower than that of Ni-Fe LDH/NF (107 mV·dec\(^{-1}\)), ZnO/NF (143 mV·dec\(^{-1}\)), and NF (152 mV·dec\(^{-1}\)). This indicated that Ni-Fe LDH@ZnO/NF possessed a faster kinetics towards OER due to the increase of γ-NiOOH and 3D structure. The ECSA was studied through the double-layer capacitance (Cdl) (Figure. 3(c) and Figure. 4(a-d)). ECSA with values of 2.8 μF·cm\(^{-2}\), 1.2 μF·cm\(^{-2}\), 0.68 μF·cm\(^{-2}\), 0.35 μF·cm\(^{-2}\) were obtained for Ni-Fe LDH@ZnO/NF, Ni-Fe LDH/NF, ZnO/NF and NF, respectively. Ni-Fe LDH@ZnO (3D) had a larger ECSA than Ni-Fe LDH (2D) with the existence of ZnO. The best OER performance of Ni-Fe LDH@ZnO/NF results from the largest surface area of the materials. We also evaluated the stability of Ni-Fe LDH@ZnO/NF at 10 mA·cm\(^{-2}\) and it exhibited a long-term stability up to 29 h (with a potential increase of 1.6%) (Figure. 3(d)).
4 Conclusion

A novel wet-chemical method has been successfully developed for Ni-Fe LDH nanosheets on ZnO microrods. Multiple characteristic technologies such as SEM, TEM, XRD, and XPS were conducted to confirmed the accessibility of this method. The Ni-Fe LDH@ZnO/NF exhibited excellent OER catalytic ability with an overpotential of 271 mV at 10 mA·cm$^{-2}$ as well as long-term stability up to 29 h with potential increase of 1.6%. The excellent OER activities of LDH@ZnO/NF were owing to a larger catalytic surface area and more catalytically active sites.

Acknowledgments

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References