

Metal-organic frameworks Derived NiFe-hydroxides for efficient Electrocatalytic hydrogen evolution

Huihua Luo¹, Chong Liu¹, Nannan Chen,¹ Kehui Xue¹, Lianqing Yu^{*1}, Haifeng Zhu², Yaping Zhang²

¹ School of materials science and engineering, China University of Petroleum, QingDao 266580 China.

² College of Science, China University of Petroleum, QingDao 266580 China.

* Corresponding author: Lianqing Yu

lyy2000@163.com

Abstract. Ni-based layered double hydroxides (Ni-LDH) is regarded as one of the most promising electrocatalyst for hydrogen evolution reaction (HER). To further improve the HER performance of Ni-LDH, it is important to provide more active sites and decrease reaction energy. Herein, bimetal NiFe-LDH derived from NiFe-MIL was constructed by two-steps hydrothermal strategy. NiFe-LDH-0.3 displays the excellent HER activity, which achieves a low overpotential of 148 mV at 10 mA • cm⁻². This work offers a novel strategy to design and develop highly efficient electrocatalyst via for HER activity and other energy conversion application.

Keywords: hydrogen evolution reaction, bimetallic hydroxides, Metal - organic frameworks

1. Introduction

Electrocatalytic water splitting have attracted a great deal of concerns due to its low-cost, large-scale, sustainable hydrogen products, facile and controllable process.[1] However, most of electrocatalysts are faced with severe challenges that lack of highly active and high stability for hydrogen evolution reaction (HER). Therefore, a great deal of efforts should be devoted to the development of electrocatalytic water splitting of electrocatalysts.

Recently, layered double hydroxides (LDHs) have employed as electrocatalysts for HER activity. Specially, the Ni(Fe)-based hydroxide has increasing attention as promising electrocatalysts due to their low-cost, excellent electrical conductivity and exhibits outstanding electrochemical activity than Pt/IrO₂ in alkaline solution.[2] For example, Li and co-workers reported have designed and developed an efficient bifunctional catalyst for hydrogen and oxygen evolution reactions, and bifunctional Fe-Ni⁵P⁴/NiFeOH-350 displayed a remarkable overpotentials of 197 and 221 mV for HER and OER, respectively. [3] However, so far few catalysts with favorable and efficient electrocatalytic performance have been employed for HER due to their complex and harsh design and synthesis approach. In order to overcome those challenges, tremendous efforts have been focused on Metal-organic frameworks (MOFs) derived layered double hydroxides for electrocatalytic water splitting.[4]

In this work, bimetal NiFe-LDH derived from NiFe-MIL was obtained by using two-steps hydrothermal method. The NiFe-LDH electrocatalyst exhibits a better HER activity than that of Ni-LDH and Fe-LDH. NiFe-LDH-0.3 achieves a low overpotential of 148 mV at 10 mA • cm⁻². The enhanced electrocatalytic activity can be assigned to the active area, unique structural stability and optimized electronic structures.

2. Experimental Section

2.1 Synthesis of NiFe-MIL

The NiFe-MIL was obtained by a facile hydrothermal method. 0.432 g $\text{Fe}(\text{Cl})_3 \cdot 6\text{H}_2\text{O}$, 0.114 g $\text{Ni}(\text{Cl})_2 \cdot 6\text{H}_2\text{O}$ and 0.465 g terephthalic acid were added into 27 mL N,N-Dimethylformamide (DMF). The mixed solution was magnetically stirred for 15 min. And then 3 ml NaOH (0.4 M) was added into above solution, continually stirred for 15 min. The solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave for a hydrothermal reaction maintained at 130 °C for 12 h. The obtained products were washed with ethanol and dried at 60 °C in a vacuum oven.

2.2 Synthesis of NiFe-LDH

NiFe-OH was obtained by deriving from NiFe-MIL. 0.05 g NiFe-MIL was added into 25 ml KOH (1 M) solution, magnetically stirred for 15 min. The solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave for a hydrothermal reaction maintained at 120 °C for 5 h. The obtained products were washed with ethanol and dried at 60 °C in a vacuum oven. The Ni-LDH and Fe-LDH were prepared as the same conditions.

2.3 Materials Characterization

The morphology and microstructure of samples were tested by using an Emission scanning electron microscopy (Sigma300, U.K.). The X-ray powder diffraction (XRD) patterns were investigated via a DX-2700. The structural information of the samples was evaluated by Fourier transform-infrared spectroscopy (FT-IR, Perkin Elmer spectrum 100).

2.4 Electrochemical measurements

The electrocatalytic activity was investigated by a standard three-electrode system controlled by a CHI 760E electrochemistry workstation, where graphite rod and Hg/HgO were served as the counter and reference electrodes, respectively. For alkaline (1 M KOH), saturated Hg/HgO reference electrode was calibrated corresponding to the reversible hydrogen electrode (RHE) follow the formula: $\text{ERHE} = \text{EHg/HgO} + 0.098 + 0.059 \times \text{pH}$. The Ni foam with testing area of 1 cm^2 as the working electrode, which was uniformly covered by the electrocatalyst.

3. Results and Discussion

3.1 Morphology and structural characterization

The morphology of the as-prepared samples was investigated by scanning electron microscopic (SEM). As shown in Fig. 1, the Ni-LDH displayed a porous spindle skeleton. It was also noted that NiFe-LDH-0.3 demonstrated a rod-shaped morphology with many small particles were loaded on its surface. NiFe-LDH-0.3 perfectly preserves the skeleton of the MOF precursor and has many structural advantages including high active sites, larger specific surface area and excellent tailorability. Moreover, the large height aspect ratio is beneficial for hydrogen adsorption and desorption and provides sufficient reaction site for HER.

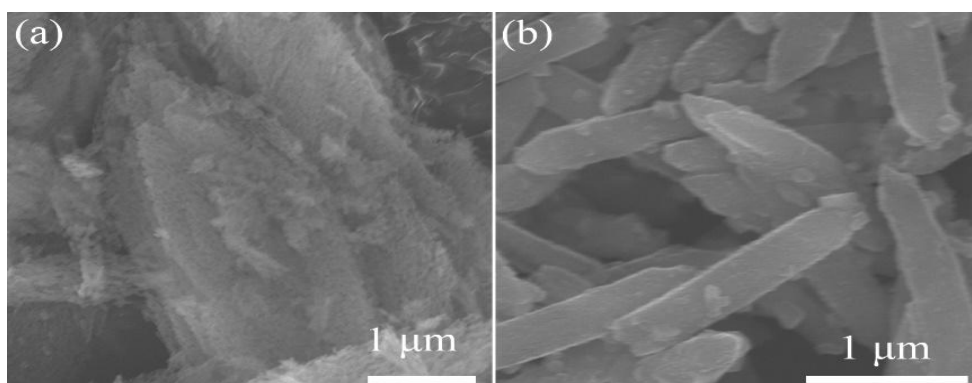


Fig. 1 The SEM images of (a) Ni-LDH, (b) NiFe-LDH-0.3.

Furthermore, XRD measurement were conducted to further investigate the crystal structure of Ni-LDH, Fe-LDH and NiFe-LDH-0.3. As shown in Fig. 2(a), the peaks appear at 33.06° , 38.54° , 52.10° , 59.05° , 62.73° , 70.48° and 72.74° are assigned to the (100), (101), (102), (110), (111), (103) and (201) planes of Ni-LDH (JCPDS Card No. 14-0117).[5] Meanwhile, the crystalline structures are in good agreement with the Fe-LDH (JCPDS Card No. 29-0713). It can be observed that the peaks of both Ni-LDH and Fe-LDH coexist in the NiFe-LDH-0.3 composites, indicating the successful preparation of NiFe-LDH electrocatalyst.

Moreover, FT-IR spectra were carried out to evaluate the functional group bonding of the as-prepared samples. For the Ni-LDH, the peak appears at 617 cm^{-1} is attributed to the stretching vibration of Ni-O. The peaks at 887 cm^{-1} and 792 cm^{-1} are assigned to the stretching vibration and bending vibration of Fe-O-H. It is found that there two peaks at 3440 cm^{-1} and 1635 cm^{-1} belong to the tensile vibration and bending vibration of O-H, respectively.[6]

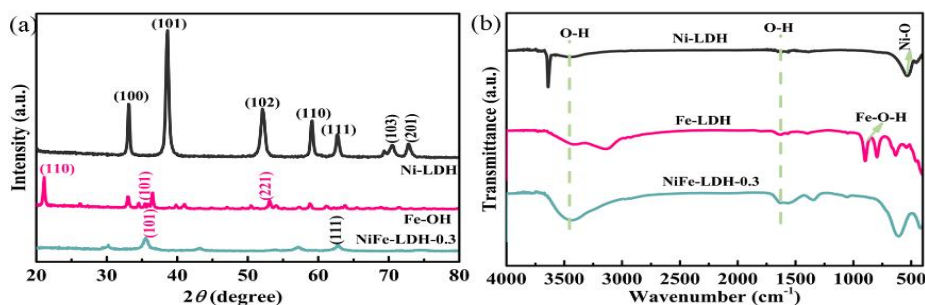


Fig. 2 (a) XRD patterns and (b) FT-IR of Ni-LDH, Fe-LDH and NiFe-LDH-0.3.

3.2 Electrochemical catalytic activity for HER

The electrochemical catalytic activity of Ni-LDH, Fe-LDH and NiFe-LDH-0.3 was investigated in 1 M KOH solution. The linear sweep voltammogram (LSV) of as-prepared samples was demonstrated in Fig. 3(a). To achieve $10\text{ mA}\cdot\text{cm}^{-2}$, the NiFe-LDH-0.3 displays the lowest overpotential of 148 mV than that of Ni-LDH (181 mV) and Fe-LDH (196 mV). Fig. 3(b) shows that the NiFe-LDH-0.3 exhibits a smaller Tafel ($90\text{ mV}\cdot\text{dec}^{-1}$) than that of Ni-LDH ($100\text{ mV}\cdot\text{dec}^{-1}$) and Fe-LDH ($119\text{ mV}\cdot\text{dec}^{-1}$), suggesting the Volmer step is the rate-limiting step for HER activity. The results of double-layer capacitance and electrochemical impedance spectroscopy (EIS) also confirm the NiFe-LDH-0.3 displays the excellent HER performance.

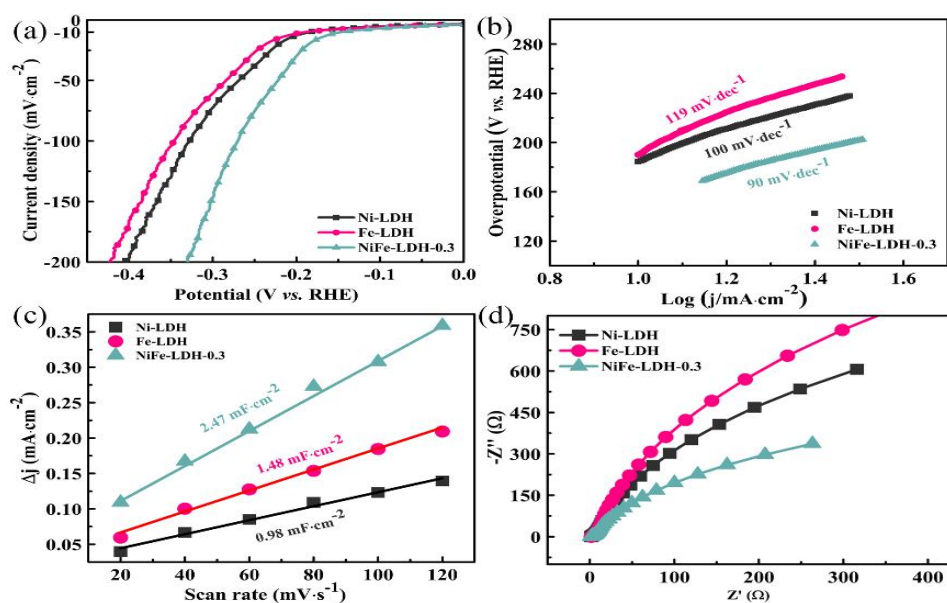


Fig. 3 HER activity in 1 M KOH: (a) LSV, (b) Tafel lobes, (c) double-layer capacitance, (d) EIS of Ni-LDH, Fe-LDH and NiFe-LDH-0.3.

4. Conclusions

In summary, we have developed a facile strategy to synthesis MOF-derived NiFe-LDH electrocatalyst. NiFe-LDH-0.3 shows an enhanced HER activity, which is required overpotential for 148 mV to achieve current density at $10 \text{ mA} \cdot \text{cm}^{-2}$. The outstanding HER activity can be attributed to the abundant active sites, unique structural stability and optimized electronic structures of NiFe-LDH-0.3. This work offers a new strategy for the rational design of cost-effective and high-performance electrocatalyst for HER.

Acknowledgements

This work was supported by the Technology Project of Qingdao (22-3-7-cspz-9-nsh), National Key Research and Development Program (2021YFB3500102) are gratefully acknowledged.

Reference

- [1] H. Feng, L. Tang, G. Zeng, J. Yu, Y. Deng, Y. Zhou, J. Wang, C. Feng, T. Luo, B. Shao, Electron density modulation of Fe_{1-x}CoxP nanosheet arrays by iron incorporation for highly efficient water splitting, *Nano Energy*, 67 (2020) 104174.
- [2] W. Chen, Y. Wang, B. Wu, J. Shi, Y. Li, L. Xu, C. Xie, W. Zhou, Y.C. Huang, T. Wang, S. Du, M. Song, D. Wang, C. Chen, J. Zheng, J. Liu, C.L. Dong, Y. Zou, J. Chen, S. Wang, Activated Ni-OH Bonds in a Catalyst Facilitates the Nucleophile Oxidation Reaction, *Advanced Materials*, 34 (2022) 2105320.

- [3] C.-F. Li, J.-W. Zhao, L.-J. Xie, J.-Q. Wu, G.-R. Li, Fe doping and oxygen vacancy modulated Fe-Ni₅P₄/NiFeOH nanosheets as bifunctional electrocatalysts for efficient overall water splitting, *Applied Catalysis B: Environmental*, 291 (2021) 119987.
- [4] Y. Xu, K. Ren, R. Xu, In situ formation of amorphous Fe-based bimetallic hydroxides from metal-organic frameworks as efficient oxygen evolution catalysts, *Chinese Journal of Catalysis*, 42 (2021) 1370-1378.
- [5] S. Yuan, J. Peng, B. Cai, Z. Huang, A.T. Garcia-Esparza, D. Sokaras, Y. Zhang, L. Giordano, K. Akkiraju, Y.G. Zhu, R. Hübner, X. Zou, Y. Román-Leshkov, Y. Shao-Horn, Tunable metal hydroxide–organic frameworks for catalysing oxygen evolution, *Nature Materials*, 21 (2022) 673-680.
- [6] H. Luo, L. Yu, K. Xue, C. Liu, R. Ding, H. Zhu, Y. Zhang, Multilevel hollow hierarchical heterostructure with DB-IEF and space-confined effect for enhanced bifunctional PHE/HER activity, *Separation and Purification Technology*, 330 (2024) 125373.