



CORPUS PUBLISHERS

# Advance Research in Organic and Inorganic Chemistry (AROIC)

ISSN: 2833-3594

Volume 4 Issue 1, 2023

## Article Information

Received date : February 04, 2023

Published date: February 13, 2023

## \*Corresponding author

Wan-Xin Feng, Key Laboratory of Chemical Additives for China National Light Industry, College of Chemistry and Chemical Engineering, Shaanxi University of Science and Technology, Xi'an, 710021, China

DOI: 10.54026/AROIC/1014

## Keywords

Oxygen Evolution Reaction (OER); Co-Doping; Electrocatalysis; Nitrides; Water Splitting

Distributed under Creative Commons CC-BY 4.0

Short Communication

# Iron and Hafnium Co-Doped Ni<sub>3</sub>N Nanostructures as An Active Catalyst for Alkaline Water Oxidation

Wan-Xin Feng\*, Yang Yang

College of Chemistry and Chemistry Engineering, Shaanxi Key Laboratory of Chemistry Additives for Industry, Shaanxi University of Science & Technology, Xi'an 710021, China

## Abstract

The exploration of highly efficient electrocatalysts is critical to the oxygen evolution reaction (OER). Here, we synthesized iron and hafnium co-doped Ni<sub>3</sub>N (Fe, Hf-Ni<sub>3</sub>N) nanostructure and grew on nickel foam substrate to fabricate a three-dimensional (3D) electrode. The Fe, Hf-Ni<sub>3</sub>N catalyst exhibits an excellent OER performance with a small overpotential of only 198 mV at 10 mA cm<sup>-2</sup> and a lower Tafel slope of 89 mV dec<sup>-1</sup> in basic electrolyte. This may be due to the fact that the doping of Fe and Hf modulate the electronic interactions of Ni<sub>3</sub>N, thus increasing the OER activity. In addition, the Fe, Hf-Ni<sub>3</sub>N shows a considerable electrochemical stability, which has not weakened after 105 h operation. This work provides a useful approach to improve the OER performance of catalysts in the future.

## Introduction

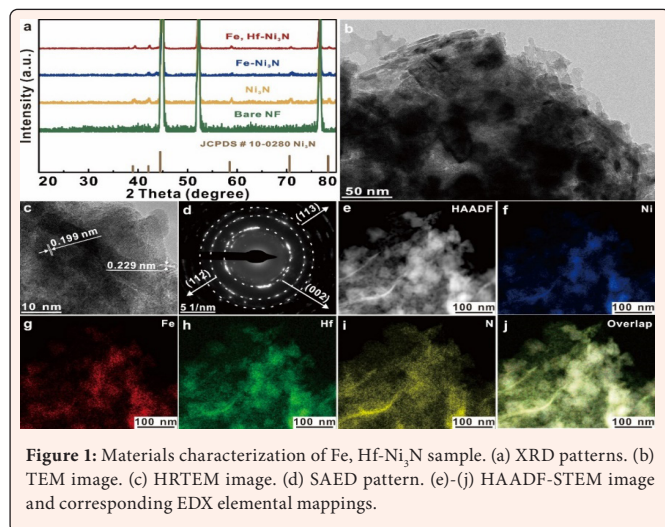
With the growing severity of energy crisis and environmental problem, green, clean, and sustainable energy sources are getting more and more valued [1-3]. While solar, wind and tidal energy are intermittent, hydrogen does not have this problem and is therefore considered one of the most promising clean energy sources [4]. Hydrogen production from water splitting, with water as the unique raw material, is regarded as the most clean and sustainable method [5]. However, the slow kinetics of oxygen evolution reaction (OER) affects the efficiency of water splitting [6]. Thus, it is essential that exploring a highly efficient electrocatalyst to increase the OER efficiency [7, 8]. At present, noble metal catalysts, such as iridium and ruthenium oxides, are regarded as the most effective electrocatalysts, but their large-scale applications are hampered by their high cost and scarcity [9]. Therefore, development of highly active catalysts contained transition-metal elements is extremely urgent.

Among the most candidates for catalyzing the OER, transition-metal nitrides have got lots of attention from researchers based on their unique electronic structure and sufficient reserves, especially nickel nitride (Ni<sub>3</sub>N) [10]. However, the further development of Ni<sub>3</sub>N was limited to low activity for the OER. Metal element doping is an effective way to improve the catalytic activity of Ni<sub>3</sub>N, which can optimize the electronic structure and lowers the reaction energy barrier. Previous work demonstrates that the doping of Fe can modulate the electronic structure of the catalyst and increase the OER and HER activities [11]. Furthermore, hafnium (Hf) is a transition metal with a silvery luster, which has several stable oxidation states (from 0 to +4) and exhibit considerable corrosion resistance [12]. However, up to now there is no study on the improvement of intrinsic activity of Ni<sub>3</sub>N toward the OER *via* co-doping of Fe and Hf.

Here, we prepared Fe and Hf co-doped Ni<sub>3</sub>N (denoted as Fe, Hf-Ni<sub>3</sub>N) grown on the nickel foam to form an efficient electrode for the OER using the hydrothermal and high-temperature nitridation processes. This electrode only requires an overpotential of 198 mV to achieve at a current density of 10 mA cm<sup>-2</sup> and a Tafel slope of 89 mV dec<sup>-1</sup> compared with the pure Ni<sub>3</sub>N. This indicates that dual-incorporation of Fe and Hf is indeed able to improve the intrinsic OER activity of Ni<sub>3</sub>N, which is mainly because the dual-doping of Fe and Hf promotes the electron interaction among the Ni, Fe, and Hf and accelerates the electron transfer efficiency. Notably, Fe, Hf-Ni<sub>3</sub>N also exhibits an outstanding electrochemical stability toward the OER.

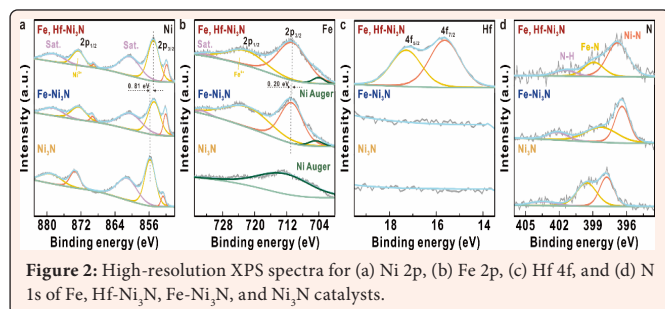
## Results and discussion

We firstly prepared NiFeHf layered double hydroxides (LDH) by a simple hydrothermal process using Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (98%, Macklin), FeCl<sub>2</sub>·4H<sub>2</sub>O (98%, Macklin), HfCl<sub>4</sub> (99.5%, Macklin), and urea (99%, Aladdin) precursors in the presence of nickel foam substrate at 120 °C for 6 h. And then the synthesized NiFeHf LDH was thermal azotized at 350 °C for 3 h under the NH<sub>3</sub> (99.999%) atmospheres. Figure 1a shows the XRD patterns of various nitrides, which indicates that Fe, Hf-Ni<sub>3</sub>N is match with Ni<sub>3</sub>N (JCPDS # 10-0280) with no impurity peaks [13]. TEM image (Figure 1b) shows that Fe, Hf-Ni<sub>3</sub>N sample is consistent of nanosheets. HRTEM image of Fe, Hf-Ni<sub>3</sub>N sample (Figure 1c) exhibits two sets of lattice stripes with 0.199 and 0.229 nm, which can be attributed to the (111) and (110) crystal planes, respectively. The SAED pattern (Figure 1d) displays three diffraction rings, which corresponded to the (113), (112), and (002) crystal planes, respectively. This result agrees with the diffraction peaks at 78.5, 58.8, and 42.4° in the XRD pattern of Fe, Hf-Ni<sub>3</sub>N sample. The HAADF-STEM and corresponding maps (Figure 1e-j) demonstrates the homogeneous distribution of Ni, Fe, Hf, and N elements on the surface of Fe, Hf-Ni<sub>3</sub>N sample.



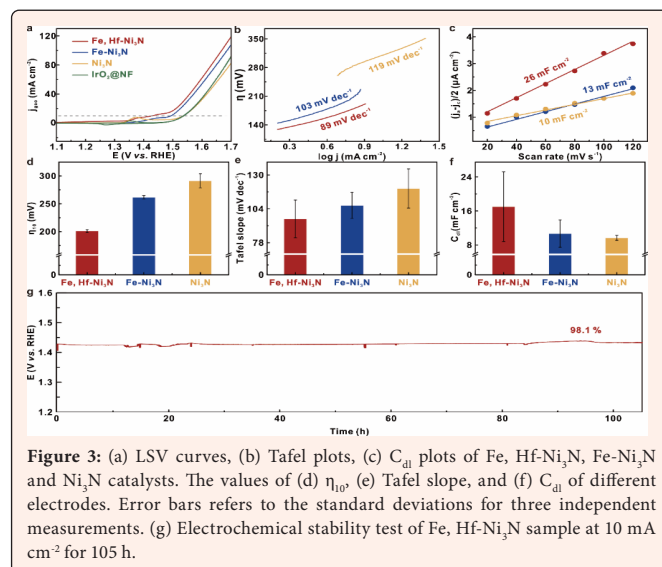
**Figure 1:** Materials characterization of Fe, Hf-Ni<sub>3</sub>N sample. (a) XRD patterns. (b) TEM image. (c) HRTEM image. (d) SAED pattern. (e)-(j) HAADF-STEM image and corresponding EDX elemental mappings.

Furthermore, high-resolution XPS was used to study the oxidation state and electron transfer of Fe, Hf-Ni<sub>3</sub>N, Fe-Ni<sub>3</sub>N, and Ni<sub>3</sub>N catalysts. As shown in the Ni 2p XPS spectra (Figure 2a), the Ni 2p<sub>3/2</sub> peaks at 854.95 eV and 851.86 eV in Fe, Hf-Ni<sub>3</sub>N samples can be attributed to Ni<sup>2+</sup> feature, which undergo a slightly negative shift compared to Ni<sub>3</sub>N [14-16]. This could be due to electrons transfer from Fe and Hf to Ni, which will accelerate the OER rate [17]. Peak fitting for Fe 2p of Fe, Hf-Ni<sub>3</sub>N sample (Figure 2b) reveals that the 2p<sub>3/2</sub> peak at 710.62 eV corresponded to the Fe<sup>3+</sup> [15]. Compared to Fe-Ni<sub>3</sub>N sample, we also see a slightly negative shift of Fe peak for Fe, Hf-Ni<sub>3</sub>N, which indicates that Fe attracts electrons from Hf, thus strengthening the electron interactions [18]. The Hf 4f spectra (Figure 2c) shows two peaks at 15.64 eV (4f<sub>7/2</sub>) and 17.28 eV (4f<sub>5/2</sub>), which can be assigned to Hf<sup>2+</sup> and Hf<sup>4+</sup> [19, 20], respectively. N 1s spectra of Fe, Hf-Ni<sub>3</sub>N (Figure 2d) exhibits three peaks at 396.78, 398.90, and 401.47 eV, which corresponds to Ni-N, Fe-N, and N-H species, respectively [21]. These results reveal that Fe and Hf have successfully been doped into Ni<sub>3</sub>N nanostructures.



**Figure 2:** High-resolution XPS spectra for (a) Ni 2p, (b) Fe 2p, (c) Hf 4f, and (d) N 1s of Fe, Hf-Ni<sub>3</sub>N, Fe-Ni<sub>3</sub>N, and Ni<sub>3</sub>N catalysts.

To study the effect of OER performance of Ni<sub>3</sub>N *via* Fe and Hf co-doping, we make a series of electrochemical measurements in a typical three-electrode configuration in an O<sub>2</sub>-saturated 1.0 M KOH solution. The LSV curves (Figure 3a) shows that the Fe, Hf-Ni<sub>3</sub>N electrode has the smallest overpotential (198 mV) at 10 mA cm<sup>-2</sup> compare with those of Fe-Ni<sub>3</sub>N (265 mV), Ni<sub>3</sub>N (305 mV), and commercial IrO<sub>2</sub> (308 mV), indicating the better catalytic performance of Fe, Hf-Ni<sub>3</sub>N electrode. Similarly, as shown in Figure 3b, Fe, Hf-Ni<sub>3</sub>N electrode exhibits the lowest Tafel slope among various electrodes, suggesting the faster reaction kinetics. To probe the effect of electrochemical surface area (ECSA) on the OER performance, we measured the double-layer capacitance (C<sub>dl</sub>) of all electrodes that is half of the ECSA. Figure 3c displays the C<sub>dl</sub> of various electrodes, which indicates that Fe, Hf-Ni<sub>3</sub>N electrode possess the largest C<sub>dl</sub> than other reference electrodes. This reveals that Fe, Hf-Ni<sub>3</sub>N electrode exposed the more active sites. Additionally, the reproducibility of OER performance indicators is essential for the fairly evaluation of catalytic performance. Figure 3d-f demonstrates that the overpotential, Tafel slope, and C<sub>dl</sub> are highly accurate and repeatable. The electrochemical stability of Fe, Hf-Ni<sub>3</sub>N electrode was evaluated at a constant current density of 10 mA cm<sup>-2</sup>. Figure 3g indicates a slight decrease after 105 h operation and maintain potential of 98.1%, suggesting an excellent stability. These results demonstrate that Fe and Hf co-doping are favorable to improve the OER performance of Ni<sub>3</sub>N.



**Figure 3:** (a) LSV curves, (b) Tafel plots, (c) C<sub>dl</sub> plots of Fe, Hf-Ni<sub>3</sub>N, Fe-Ni<sub>3</sub>N and Ni<sub>3</sub>N catalysts. The values of (d) η<sub>10</sub>, (e) Tafel slope, and (f) C<sub>dl</sub> of different electrodes. Error bars refers to the standard deviations for three independent measurements. (g) Electrochemical stability test of Fe, Hf-Ni<sub>3</sub>N sample at 10 mA cm<sup>-2</sup> for 105 h.

## Conclusion

In summary, we have successfully doped Fe and Hf into Ni<sub>3</sub>N (Fe, Hf-Ni<sub>3</sub>N) *via* hydrothermal and thermal nitridation processes. The Fe, Hf-Ni<sub>3</sub>N@NF electrode only requires 198 mV to reach at 10 mA cm<sup>-2</sup> and a low Tafel slope of 89 mV dec<sup>-1</sup>. The excellent OER performance are mainly attributed to the strong electronic interaction among Ni, Fe, and Hf in Fe, Hf-Ni<sub>3</sub>N@NF electrode. Furthermore, this three-dimensional electrode exhibits the outstanding electrochemical stability in alkaline electrolyte. This work also provides a useful avenue to enhance the OER performance of transition-metal based nitrides.

## Acknowledgements

This work was supported by Scientific Research Foundation for Ph.D. of Shaanxi University of Science and Technology (Grant No.2019QNBj-04).

## References

- Chu S, Majumdar A (2012) Opportunities and challenges for a sustainable energy future. *Nature* 488(7411): 294-303.
- Lems S, Kooi HJV, Arons JS (2002) The sustainability of resource utilization. *Green Chem* 4(4): 308-313.
- Lewis NS, Nocera DG (2006) Powering the planet: Chemical challenges in solar energy utilization. *Proc Natl Acad Sci U S A* 103(43): 15729-15735.
- Chow J, Kopp RJ, Portney PR (2003) Energy resources and global development. *Science* 302(5650): 1528-1531.
- Turner J, Sverdrup G, Mann MK, Maness PC, Kroposki B, et al. (2008) Renewable hydrogen production. *Int J Energy Res* 32(5): 379-407.
- Zhou DJ, Li PS, Lin X, McKinley A, Kuang Y, et al. (2021) Layered double hydroxide-based electrocatalysts for the oxygen evolution reaction: identification and tailoring of active sites, and superaerophobic nanoarray electrode assembly. *Chem Soc Rev* 50(15): 8790-8817.
- Du K, Zhang LF, Shan JQ, Guo JX, Mao J, et al. (2022) Interface engineering breaks both stability and activity limits of RuO<sub>2</sub> for sustainable water oxidation. *Nat Commun* 13(1): 5448.
- Ge K, Sun SJ, Zhao Y, Yang K, Wang S, et al. (2021) Facile synthesis of two-dimensional iron/cobalt metal-organic framework for efficient oxygen evolution electrocatalysis. *Angew Chem Int Ed* 60(21): 12097-12102.
- Reier T, Oezaslan M, Strasser P (2012) Electrocatalytic oxygen evolution reaction (OER) on Ru, Ir, and Pt catalysts: a comparative study of nanoparticles and bulk materials. *ACS Catal* 2(8): 1765-1772.



10. Zhou P, Zhai GY, Lv XS, Liu YY, Wang ZY, et al. (2021) Boosting the electrocatalytic HER performance of Ni<sub>3</sub>N-V<sub>2</sub>O<sub>3</sub> via the interface coupling effect. *Appl Catal B* 283(2021): 119590.
11. Mahala C, Sharma MD, Basu M (2019) Fe-doped nickel hydroxide/nickel oxyhydroxide function as an efficient catalyst for the oxygen evolution reaction. *ChemElectroChem* 6(13): 3488-3498.
12. Nielsen RH (2000) Hafnium and hafnium compounds. *Kirk-Othmer Encyclopedia of Chemical Technology*.
13. Chen XH, Li XL, Wu LL, Fu HC, Luo J, et al. (2021) Nb<sub>2</sub>O<sub>5</sub>-Ni<sub>3</sub>N heterojunction tuned by interface oxygen vacancy engineering for the enhancement of electrocatalytic hydrogen evolution activity. *J Mater Chem A* 9(19): 11563-11570.
14. Yang Y, Wang WJ, Yang YB, Guo PF, Zhu B, et al. (2022) Ru-doped NiFe layered double hydroxide as a highly active electrocatalyst for oxygen evolution reaction. *J Electrochem Soc* 169(2): 024503.
15. Yang Y, Zhu B, Guo PF, Ding TY, Yang QN, et al. (2022) In situ anodic oxidation tuning of NiFeV diselenide to the core-shell heterojunction for boosting oxygen evolution. *Inorg Chem* 61(42): 16805-16813.
16. Guo PF, Yang Y, Wang WJ, Zhu B, Wang WT, et al. (2021) Stable and active NiFeW layered double hydroxide for enhanced electrocatalytic oxygen evolution reaction. *Chem Eng J* 426(15): 130768.
17. Wang BR, Jiao SH, Wang ZS, Lu MJ, Chen D, et al. (2020) Rational design of NiFe LDH@Ni<sub>3</sub>N nano/microsheet arrays as a bifunctional electrocatalyst for overall water splitting. *J Mater Chem A* 8(33): 17202-17211.
18. Yang Y, Zhu B, Guo PF, Wang WJ, Wang WT, et al. (2022) Core-shell trimetallic NiFeV disulfides and amorphous high-valance NiFe hydroxide nanosheets enhancing oxygen evolution reaction. *Chem Eng J* 430(3): 133047.
19. Peighambaroust NS, Sadeghi E, Mete B, Yagci MB, Aydemir U, et al. (2022) Evaluating electrocatalytic activity of metal-substituted hafnium diboride (Hf<sub>1-x</sub>TM<sub>x</sub>B<sub>2</sub>; TM= Ni and Co) toward water splitting. *J Alloys Compd* 905(5): 164148.
20. Zhao F, Wen B, Niu WH, Chen Z, Yan C, et al. (2021) Increasing iridium oxide activity for the oxygen evolution reaction with hafnium modification. *J Am Chem Soc* 143(38): 15616-15623.
21. Wang YY, Liu DD, Liu ZJ, Xie C, Huo J, et al. (2016) Porous cobalt-iron nitride nanowires as excellent bifunctional electrocatalysts for overall water splitting. *Chem Commun* 52(85): 12614-12617.