Analytical Chemistry: A Journal (2025)
Clausius Scientific Press, Canada

DOI: 10.23977/analc.2025.040104
ISSN 2616-1958 Vol. 4 Num. 1

Evaluation on the Potentials of Non-Nobel Metal Electrocatalyst in the Electrolysis of Water

Yunming Long[1,a], Xiaomi Wang[2,b], Yucheng Zhang[3,c]

[1]Han Academy, Aberdeen, Wong Chuk Hang Rd, Genesis, Basement 21, Hong Kong, China
[2]RDFZ Xishan School, No. 9, South Malianwa Road, Haidian District, Beijing, China
[3]St. George's International School, Chem. de Saint-Georges 19, 1815, Montreux, Switzerland
[a]me@achan.me, [b]15600619176@163.com, [c]yuchengz418@gmail.com

Keywords: ZIF-67, Non-Noble-Metal Electrocatalyst, Water Splitting, Trifunctional Catalyst

Abstract: Growing global awareness of environmental protection and sustainable development has positioned renewable resources, such as hydrogen, at the forefront of future energy solutions. Advancing the industrial and practical application of water electrolysis hinges on the development of efficient and cost-effective electrocatalysts. This research focuses on the synthesis and evaluation of several non-noble-metal electrocatalysts derived from zeolitic imidazolate framework-67 (ZIF-67). The catalytic performance of these materials was assessed through a series of electrochemical tests. We successfully verified that the synthesized NiSA@ACNTF catalyst exhibits prominent trifunctional activity for the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and oxygen reduction reaction (ORR). Among the materials tested, NiSA@ACNTF demonstrated the highest catalytic activity and maintained exceptional stability throughout a 10-hour chronoamperometry test. These findings highlight NiSA@ACNTF as a promising, low-cost alternative to precious-metal catalysts for water splitting. The development of this affordable and efficient catalyst offers new opportunities in the renewable energy sector and paves the way for a more prosperous future for hydrogen energy.

1. Introduction

Driven by the growing demand for renewable energy and the urgent need to reduce greenhouse gas emissions, hydrogen has been identified as a clean and sustainable energy carrier. Among various production methods, water electrolysis is considered one of the most promising technologies because it generates high-purity hydrogen using only water and electricity [1]. However, the efficiency of water electrolysis relies heavily on the performance of electrocatalysts that facilitate the HER and the OER.

Currently, the most efficient electrocatalysts are noble-metal-based materials, such as platinum (Pt) for the HER and iridium oxide (IrO_2) or ruthenium oxide (RuO_2) for the OER [2]. Although these catalysts exhibit excellent activity and stability, their high cost and scarcity render large-scale commercial applications economically unsustainable [3]. This reliance on precious metals poses a significant barrier to the widespread adoption of water electrolysis for global hydrogen production.

To address this challenge, researchers have focused on developing non-noble-metal electrocatalysts. Materials based on transition metals such as Ni, Co, and Fe—especially when combined with carbon-based supports or doped with heteroatoms—have shown great potential as cost-effective alternatives [4, 5]. Some studies have demonstrated that these catalysts can approach or even match the activity of noble metals under certain conditions, offering advantages in abundance and affordability [6]. Therefore, developing non-noble-metal catalysts with higher efficiency and greater economic viability has become a key objective for both academia and industry.

ZIF-67 is a prime example of such a precursor material. As a cobalt-based metal-organic framework (MOF), ZIF-67 is formed by the coordination of cobalt ions with 2-methylimidazole ligands. Its key advantages include ease of synthesis, scalability, and a uniform distribution of cobalt, nitrogen, and carbon elements. As a precursor for electrocatalysts, ZIF-67 offers a large specific surface area (1254 m^2/g) and abundant porosity, which provide numerous active sites and facilitate mass transfer. Through thermal decomposition, ZIF-67 can be converted into derivatives with a conductive carbon skeleton, enhancing both electrical conductivity and stability.

Several studies have built upon these properties. For instance, modifying ZIF-67 with dicyandiamide (DCD) has led to the synthesis of carbon nanotubes embedded with cobalt atoms, which exhibit unique morphology and excellent electrochemical performance, particularly for the OER. This approach has provided new directions for fuel cell technology. More recently, Dilpazir et al. synthesized an efficient tetra-functional electrocatalyst, denoted as NiSAs@ACNTF, by encapsulating CoNi nanoalloys within N-doped carbon nanotubes (NCNTs) and immobilizing single Ni atoms on the surface [7]. This material features uniformly dispersed active sites, well-defined porosity, and a high specific surface area. It has demonstrated significant potential for the ORR, OER, CO_2 reduction reaction (CO_2RR), and hydrogen evolution reaction (HER) by achieving synergistic catalysis across these key energy conversion reactions. The high electrical conductivity of the N-doped CNTs, combined with the catalytic effects of CoNi and N-doping, effectively reduces the free energy required for proton adsorption in the HER.

In this study, we synthesized the target catalyst, NiSAs@ACNTF, along with two other ZIF-67-based variants. Following synthesis, we evaluated their electrocatalytic performance using methods such as cyclic voltammetry (CV), linear sweep voltammetry (LSV), and Faradaic efficiency tests. The research goal was to demonstrate the effectiveness of this non-noble-metal catalyst. Our results successfully verify the superior performance of NiSAs@ACNTF in catalyzing the HER. Its high efficiency and stability highlight its great potential for application in rechargeable metal-air batteries, fuel cells, and other renewable energy technologies.

2. Materials and Methods

2.1 Materials

All chemical reagents were of analytical grade and used as received without further purification. The chemicals included cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), dicyandiamide (DCD), 2-methylimidazole, anhydrous methanol, isopropanol, and a 5 wt% Nafion solution.

2.2 Synthesis of Electrocatalysts

Three distinct electrocatalysts were synthesized and evaluated in this study. The first was derived from a pure ZIF-67.The second was derived from ZIF-67 modified with dicyandiamide (ZIF-67@DCD). The third, the target material NiSAs@ACNTF, was synthesized by incorporating nickel atoms into the ZIF-67@DCD framework.

Synthesis of ZIF-67: ZIF-67 was synthesized via a co-precipitation method. In a typical procedure, 0.55 mmol of $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in 10 mL of anhydrous methanol and stirred for 30 minutes. Subsequently, a solution of 1.0 mmol of 2-methylimidazole in 15 mL of methanol was added dropwise to the cobalt solution under continuous stirring. The reaction mixture was stirred at room temperature for 4 hours, during which a purple turbid suspension formed. The resulting product was collected by centrifugation, washed twice with methanol, and dried overnight in a vacuum oven at 60 ℃.

Synthesis of ZIF-67@DCD: To prepare the ZIF-67@DCD composite, 0.3 mmol of dicyandiamide (DCD) was first dissolved in the cobalt(II) nitrate methanol solution described above. The 2-methylimidazole solution was then added dropwise under vigorous stirring. The mixture was stirred for 4 hours at room temperature. The final solid was collected by centrifugation, washed multiple times with methanol, and dried under vacuum at 60 ℃ for 4 hours.

Synthesis of NiSAs@ACNTFs: The synthesis of NiSAs@ACNTFs followed a similar procedure. First, $Co(NO_3)_2 \cdot 6H_2O$ and dicyandiamide were dissolved in methanol. Nickel(II) nitrate was then added to this mixed solution. Subsequently, the 2-methylimidazole solution was added dropwise, and the reaction was stirred for 4 hours. The precipitate was collected, washed, and dried overnight in a vacuum oven at 60 ℃.

Pyrolysis: All three dried precursors (ZIF-67, ZIF-67@DCD, and the Ni-containing precursor) were pyrolyzed to obtain the final catalysts. Each material was heated to 750 ℃ in a tube furnace under a continuous argon flow at a controlled ramping rate. This process carbonized the organic ligands to form a nitrogen-doped carbon matrix.

2.3 Preparation of Catalyst Ink

For electrochemical testing, a catalyst ink was prepared for each pyrolyzed material. Typically, 5 mg of the catalyst powder was dispersed in a mixed solution containing 500 μL of deionized water, 480 μL of isopropanol, and 20 μL of 5 wt% Nafion solution. The mixture was then subjected to sonication for at least 4 hours to ensure the formation of a homogeneous black ink.

2.4 Electrochemical Performance Evaluation

All electrochemical measurements were performed at room temperature using a three-electrode setup connected to an electrochemical workstation. A Hg/HgO electrode served as the reference electrode, and a graphite rod was used as the counter electrode. The working electrode was prepared by drop-casting 150 μL of the catalyst ink onto a carbon cloth, achieving a mass loading of 0.3 $mg \cdot cm^{-2}$.

All potentials were calibrated to the reversible hydrogen electrode (RHE) scale using the Nernst equation. Linear sweep voltammetry (LSV) curves were recorded at scan rates of 20, 40, 60, 80, and 100 $mV \cdot s^{-1}$ and were iR-corrected. The long-term stability of the catalysts was evaluated using chronoamperometry.

3. Results

All three catalysts samples were tested by LSV, giving us the results shown in figure 1. In the diagram, the horizontal axis presents the potential vs Hg/HgO electrode, the vertical axis presents the current flow in the circuit. Significant section throughout whole tests were captured in the diagram, ranging from -1.0 V to 0.2 V, and -0.30 A to 0.10 A. Three curves in the diagram are the LSV curves of three tested catalysts. The diagram helps to obtain two insights. First, among the three catalyst materials, the NiSAs@ACNTF material, represented by the red curve, has the earliest turning point. It requires the least electrical potential to conduct 0.01 A current, while two other catalysts all need higher potential to achieve that. Second, after the turning point, three curves start to separate, having different gradients each, while the red curve representing NiSAs@ACNTF has the largest gradient, showing its high conductivity. Therefore, for NiSAs@ACNTF, the current flow increases much faster than two other catalysts. By recognizing the advantages of the catalyst, NiSAs@ACNTF, we suggest that the non-noble metal catalyst has shown high catalytic activities, showing excellent performance in water splitting, and setting it apart from two other catalyst materials. A major result that has been obtained is the capacity of NiSAs@CNTFs to reach HER performance with lower overpotentials versus other catalysts under study. The LSV results demonstrated that OER catalytic activity on NiSAs@CNTFs required a low overpotential for a current density compared to the others, which reflected its reduced driving potential and superior intrinsic catalytic efficiency. In chronoamperometric tests, this activity persisted over long periods, which indicates the stability of the material as well, an important requirement for future practical application in water electrolysis at industrial scale.

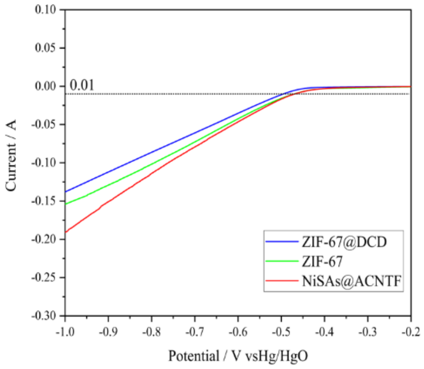

Figure 1 LSV curves of ZIF-67@DCD, ZIF-67 and NiSAs@ACNTF at a scan rate of 0.01 Vs^{-1}

As can be seen from the figure 2, the current shows almost no noticeable attenuation within ten hours, and the line is very stable, indicating that our catalyst can still maintain stable catalytic performance during long-term operation, proving its high stability and durability.

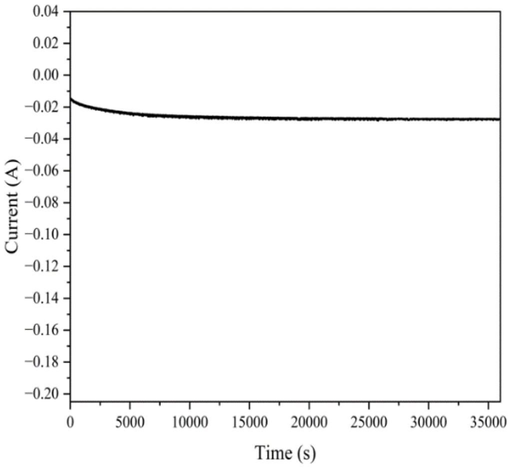

Figure 2 IT test curves of NiSAs@ACNTFs

Figure 3 plots the specific capacitance (or current density) versus scan rate for ZIF-67, ZIF-67@DCD, and NiSAs@ACNTFs, revealing distinct electrochemical behaviors. Among the three catalysts, ZIF-67 exhibits the highest specific capacitance at low scan rates. In contrast, ZIF-

67@DCD shows a much smaller reduction in capacitance with increasing scan rate. Its overall capacitance profile is closer to that of NiSAs@ACNTFs than to pristine ZIF-67. NiSAs@ACNTFs demonstrates the most stable performance, characterized by smallest change in capacitance across the tested scan rate range. This minimal variation signifies superior charge storage and favorable charge transfer kinetics during rapid cycling. Such stability implies excellent rate capability and robust structural integrity under dynamic electrochemical conditions, which is crucial for practical applications.

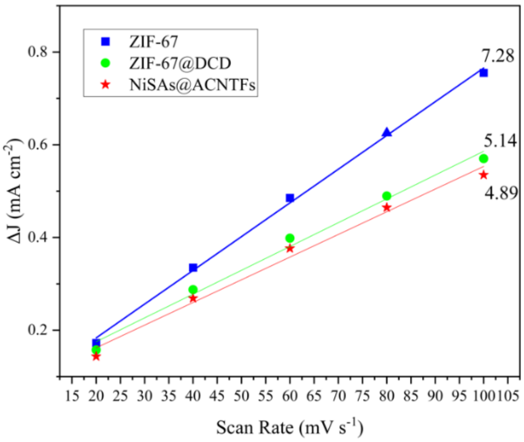

Figure 3 CV curves of ZIF-67, ZIF-67@DCD and NiSAs@ACNTFs

4. Conclusion

Herein, NiSAs acted as active sites for OER were successfully loaded on CNTFs to prepare the non-noble metal catalysts (NiSAs@CNTFs), which owns an excellent electrocatalytic activity and stability towards water electrolysis. By systematic synthesis and electrochemical evaluation, we demonstrate that NiSAs@CNTFs exhibit superior catalytic activity and stability compared to ZIF-67 and ZIF-67@DCD, underlying the synergetic effect of integrating single atom Ni with CoNi alloy/N-doped carbon nanotube framework. The uniformly dispersed single-atom Ni sites and the conductive N-doped carbon nanotube network cooperate to contribute greatly to this excellent performance.

The performance of NiSAs@CNTFs compares favorably with the conventional noble-metal-based electrocatalysts, such as Pt, RuO_2 and IrO_2. Noble metals are still the standard for catalytic activity, but their low abundance and high cost prohibit their use for widespread hydrogen production. On the contrary, NiSAs@CNTFs are made of earth-abundant materials and can be fabricated by relatively inexpensive methods, thereby having potential for a large-scale production. ZIF-67 as the precursor so as to combine a desired high porosity and functionality in terms of material tunability, while the introduction of Ni doping and addition of dicyandiamide supported facile synthesis and attain high-turnover active sites with optimal coordination environments. It could be inferred that these advantageous for its structure endow it with the high activity and outstanding durability as NiSAs@CNTFs.

In the more direct sense, this success with NiSAs@CNTFs for water splitting could be a major breakthrough in the field of renewable energy going forward. The hydrogen economy is often touted as a keystone of the clean-energy strategies that are part and parcel of the global transition away from fossil fuels. When generated from water by electrolysis using renewable electricity hydrogen is one of the cleanest available energy vectors, as it emits no GHGs at the point of use. They will be part of the arsenal we need in order to drive mankind into a sustainable hydrogen economy but also accessible and cost-effective rechargeable batteries. Apart from hydrogen production, such catalysts may have broader implications in fuel cells, metal-air batteries and carbon dioxide reduction systems owning to their multi-functional catalytic properties.

There are also some important caveats that help constrain the inferences we can draw from this study. Although NiSAs@CNTFs exhibited outstanding activity and stability in laboratory tests, their performance under industrially real conditions, including high current densities or continuous operation for hundreds or thousands of hours need to be further confirmed. In addition, it has to be confirmed whether the synthesis method can be scaled. Pyrolysis of ZIF-67 precursors is relatively tame compared with other pathogenic approaches, but it still faces issues such as batch-to-batch consistency and the exact reproduction of single-atom status. Future research should focus on perfecting the synthesis to make it reproducible, and on determining if these pincer structures degrade due to impurities in water sources (that are expected to deteriorate the durability of this type of catalyst in a real-world situation).

In addition, more mechanistic studies through the combination of DFT calculations on experimental data could offer more extensive insights into catalytic pathways promoted by NiSAs@CNTFs in future work. The electron interactions between the single Ni sites, CoNi alloy nanoparticles and N-doped carbon scaffold not only lead to the formation of the single Ni sites on CoNi/N-C catalyst but also facilitate the enhancement of electrocatalytic performance, thereby offering a deeper understanding for rational design of more efficient electrocatalyst. Studying such work could also inform us on the synergistic effects of different active sites in enhancing the overall catalytic performance, which is still an open question in electrocatalysis research.

To summarize, we have successfully developed NiSAs@CNTFs in a facile method and revealed that the as-prepared electrocatalysts exhibit impressive catalytic activity and stability for water splitting, with lower cost compared to noble metal-based catalysts. The results underscore the potential for transition-metal-based systems that are properly conceived to match or even exceed traditional noble-metal catalysts in some settings. In the end, further advancing these catalysts such as NiSAs@CNTFs will be crucial in helping to facilitate the broader uptake of hydrogen as a clean and renewable energy vector — part of a larger effort for countries around the world to transition toward a low-carbon future. This work makes a significant step forward in the field of non-noble metal electrocatalysis, which will advance downstream sustainable hydrogen production industries that are scalable, cost competitive and environmentally responsible.

References

[1] SEH Z W, KIBSGAARD J, DICKENS C, et al. Combining theory and experiment in electrocatalysis: insights into materials design[J]. Chemical Reviews, 2017, 117(7): 986-1114. DOI: 10.1021/acs.chemrev.6b00763.

[2] GONG M, DAI H. A mini review of NiFe-based materials as highly active oxygen evolution reaction electrocatalysts [J]. Nano Research, 2015, 8(1): 23-39. DOI: 10.1007/s12274-014-0591-z.

[3] ZHANG B, ZHENG X, VOZNYY O, et al. Homogeneously dispersed multimetal oxygen-evolving catalysts[J]. Science, 2016, 352(6283): 333-337. DOI: 10.1126/science.aaf1525.

[4] ZHUANG T, JIA H, CAO X, et al. Non-noble metal electrocatalysts for the hydrogen evolution reaction in water electrolysis[J]. Electrochemical Energy Reviews, 2021, 4: 1-36. DOI: 10.1007/s41918-020-00086-z.

[5] HAN J, LIU Q, YANG Y, et al. Noble-metal-free catalysts for the oxygen evolution reaction in acids [J]. Chemical Science, 2025, 16(9): 3788-3809. DOI: 10.1039/D4SC08400D.

[6] LI Y, WANG H, XIE L, et al. MoS_2 *nanoparticles grown on graphene: an advanced catalyst for the hydrogen evolution reaction[J]. Journal of the American Chemical Society, 2011, 133(19): 7296-7299. DOI: 10.1021/ja201269b.*

[7] WANG M, CHEN Y, HAN Y, et al. Efficient tetrafunctional electrocatalyst with synergetic effect of different active sites for multimodel energy conversion and storage[J]. ACS Applied Materials & Interfaces, 2020, 12(20): 23136-23146. DOI: 10.1021/acsami.0c05481.