SCHOLARLY REVIEW

Research on the synthesis of transitional metal and post-transitional metal doping zeolitic imidazolate framework-based electrocatalysts and electrocatalytic hydrogen evolution reaction

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Author Biography

Zirui Fang is a senior at Experimental High School Attached to Beijing Normal University. He is passionate about Chemistry, history, and classical music and tries to understand the world from different perspectives. He is currently the president of his school's only chemistry club, "Enthalpy Change Club," and he is delving into some topics in the history of science. He hopes to learn across disciplines and address energy and environment-related problems in the future. He is also trying to be a classical guitar player who can always enjoy the beauty of music.

Abstract

Hydrogen, as a sustainable and green energy source, has gained significant attention in the context of the global energy crisis. The challenge underlying the hydrogen evolution reaction in electrochemical water splitting is to replace the noble metal-based electrocatalysts with effective low overpotential and kinetically favorable electrocatalysts. This research focused on the synthesis and modification of non-noble metal zeolitic imidazolate framework-based electrocatalysts. Using the heteroatom metal doping to improve electrocatalysts, Ni, Ce, Bi, and In are investigated as possible dopants. Herein, we successfully synthesized electrocatalysts combining CoM nanoalloy (M = Ni/Ce/In/Bi) with N-doped carbon nanostructure, denoted as CoM@NC. Among all synthesized electrocatalysts, CoNi@NC demonstrates to be the best HER electrocatalyst, with the lowest overpotential of 454.5mV at 10 mA cm^{-2} current density, Tafel slope of 86.3 mV dec^{-1}, and stability for more than 10 hours. The composition and structures of CoNi@NC optimize its electron structure, increase active sites, and improve its conductivity and stability, which makes it a possible effective nonnoble metal HER electrocatalyst. This electrocatalyst provides a possible method to design and synthesize hydrogen evolution electrocatalysts that can replace noble metal-based electrocatalysts.

Keywords: electrocatalyst, ZIF-67, hydrogen evolution, heteroatom metal doping, transitional and post-transitional metal, metal/metal nanoalloy, nickel doping, carbon nanostructure

Introduction

The limited reserve of non-renewable energy and the negative climate impact caused by the large-scale consumption of fossil fuels have intensified the global energy crisis. Therefore, it is vital to research and develop a sustainable, green, and affordable energy source.[1-2] Hydrogen energy has caught much attention among various clean energy sources due to its considerable energy density (142 $MJ \cdot kg^{-1}$), carbon-free quality, and practical storage and transportation nature.[3-4] However, after decades of research on hydrogen production, 96% of hydrogen is produced by the steam reforming process and partial oxidation of fossil fuels.[5] This technique requires high temperatures around 950-1100 °C and causes significant carbon emissions, which can hardly be a sustainable and clean energy source.[6] In light of this circumstance, producing hydrogen by water electrolysis has attracted increasing attention due to its zero-carbon emission, hydrogen purity, and relatively facile technique.[7]

However, unfavorable thermodynamics and sluggish kinetics are some characteristics of the hydrogen evolution reaction (HER). As a result, high overpotential is required to maintain a stable electrolysis of water, which prevents the commercialization of water splitting to produce hydrogen. In industrial production, the decomposition voltage of splitting water is much higher than the theoretical 1.23 V.[1, 8-9] The excess potential required is the overpotential of the reaction. The high overpotential and sluggish kinetics of HER can be overcome by applying proper electrocatalysts to the electrolysis to increase its efficiency.[10] Usually, noble metals are used as effective electrocatalysts in water splitting. For instance, Pt-based catalysts were recognized as the most effective HER electrocatalysts due to their nearly zero overpotential and small Tafel slope.[11-13] However, the problems of scarcity, high cost, and sometimes instability undermine noble metal catalysts' potential for commercialization.[14-15] This underscores the need to develop affordable, high-activity, and stable electrocatalysts to facilitate HER and produce hydrogen through water splitting.

Currently, many researchers are focusing on non-noble metal-based electrocatalysts using transitional and post-transitional metal. With their abundant composition reserve and high activity, non-noble metal catalysts demonstrated auspicious potential as effective and commercialized electrocatalysts in HER reaction.[16-17] Among many research studies, heteroatom metal doping has been proven to be an effective method of improving electrocatalysts' performances. Mainly, Ni, Fe, Ce, Mo, and other transitional metals have been widely investigated as dopants for fabricating electrocatalysts.[18-20] The electronic structures and metal/metal interfaces of electrocatalysts can be modified by combining different metals, resulting in enhanced interfacial stabilization and intrinsic activity.[21-23]

Moreover, encapsulating metal/metal nanoalloy (NA) by a few layers of thin graphic shell can prevent aggregation and protect them from harsh chemical environments, increasing the overall stability of catalysts. In addition, the carbon nanostructure outside nanoalloy particles can also promote electron transfer, which favors reaction kinetics. Dicyandiamide (DCD) was proven to form N-doped nanocarbon structures when carbonized at high temperatures.[18, 24-25] The formed carbon nanostructure can not only help disperse the formed nanoalloys but also generate graphitic carbon species coupled with metal/metal NA *in situ*. Single-atom catalysts (SAC) were also a primary focus of many researchers. With the help of forming carbon nanostructure, NA could be effectively dispersed on the surface of carbon nanostructure outside electrocatalysts, which could serve as effective active points for some reactions.[16, 23, 26]

Metal/metal NA encapsulated by carbon nanostructures could be acquired by controlled pyrolysis of the tunable metal-organic frameworks (MOF) and DCD mixture.[18, 22] One of the MOFs widely used as a precursor in the synthesis of electrocatalysts was the zeolitic imidazolate framework-67 (ZIF-67). ZIF-67 was composed of Co^{2+} cations and 2-methylimidazole ligands (2-MeIm). The Co-2-MeIm-Co angle is around 145°, similar to the Si-O-Si angle in the basic silicon-based zeolites. This structural property resulted in a stable and adjustable polyhedral shape of ZIF-67. As a result, ZIF-67 exhibited outstanding thermal and chemical stability. It possesses a large surface area, permanent porosity, and abundant active sites. Its composition can also be adjusted to the desired ratio to synthesize specified materials.[27-28] In addition, considering the transitional metal NA active sites are subjected to high surface energy, it is common for NA to agglomerate, which

can undermine the overall catalytic ability. ZIF-67 can disperse and anchor metals in carbon nanostructures to form metal active sites and protect metal NA from agglomeration after pyrolysis.[21, 25] All of those characteristics of ZIF-67 make it a suitable precursor for synthesizing electrocatalysts. The pyrolysis of the precursor, consisting of the mixture of ZIF-67 and DCD, allows for a one-step and facile conversion of precursors into effective electrocatalysts.[18, 22]

The electrocatalysts synthesized were aimed to perform in alkaline conditions. Electrolyzers working under alkaline conditions will produce less hazardous vapor under high temperatures and provide better stability to non-noble metals.[15] Those advantages compared to electrolyzers working under acidic conditions indicate advantageous industrialized potentials. As a result, investigating effective electrocatalysts suitable in alkaline conditions favors future expanded industrialization in hydrogen production. In addition, HER in alkaline conditions requires extra energy to break the water molecules.[9] Thus, it is harder to produce hydrogen. In light of this difficulty, research on effective electrocatalysts in alkaline conditions is valuable.

Based on prior studies, it has been observed that electrocatalysts that combine several kinds of transitional or post-transitional metals are effective HER electrocatalysts. In addition, encapsulating nanoalloys by N-doped carbon nanostructures can effectively protect nanoalloys from harsh chemical environments and promote electron transfer. Herein, utilizing heteroatom metal doping to adjust electrocatalysts' composition, we synthesized electrocatalysts composed of CoNi NA encapsulated by N-doped carbon nanostructure (denoted as CoNi@NC) by the pyrolysis of a mixture of modified ZIF-67 and DCD precursor and tested its catalytic ability in alkaline condition. We also adjusted the dopant to Ce, In, and Bi and synthesized CoCe@NC, CoIn@NC, and CoBi@NC. All four modified heteroatom metal doping electrocatalysts exhibited lower overpotential than the non-doping controlled group. CoNi@NC showed the lowest HER overpotential of 454.5 mV under a current density of 10 mV cm^{-2} among the four electrocatalysts.

Experimental Section

Chemicals and Reagents

Cobalt nitrate hexahydrate (99%, $Co(NO_3)_2 \cdot 6H_2O$), 2-Methylimidazole (98%), dicyandiamide (99%), bismuth nitrate pentahydrate (99.0%, $Bi(NO_3)_3 \cdot 5H_2O$), indium nitrate hydrate (99.99%, $In(NO_3)_3 \cdot xH_2O$), and methanol (99.5% anhydrous) were brought from Aladdin. Cerium nitrate hexahydrate (99.5%, $Ce(NO_3)_3 \cdot 6H_2O$) was brought from Macklin. Nickle nitrate hexahydrate (98.5%, $Ni(NO_3)_2 \cdot 6H_2O$) was brought from Sinopharm. Nafion solution (5 wt % in lower aliphatic alcohols and water) was acquired from Macklin. The above materials were not subjected to any pre-treatment prior to their utilization. Carbon cloth (CC) was obtained from CeTech (W1S1011 type) and was refluxed in concentrated HNO_3 at 200 °C for 2 h, then cleaned with ethanol and water and dried under Ar to make it hydrophilic. All solutions used were prepared in Milli-Q water.

Synthesis

Synthesis of CoNi@NC

ZIF-67 was synthesized using coprecipitation. 0.33 mmol $Co(NO_3)_2 \cdot 6H_2O$, 1.8 mmol DCD, and a fixed amount of $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved into 30 mL of anhydrous methanol. After stirring for 30 min, when all materials were completely dissolved, imidazole solution (6mmol in 45 mL anhydrous methanol) was slowly poured into the metal precursor solution with continuous stirring for 4 hours at room temperature. The solution immediately turned purple after the addition of the imidazole solution. The final product was obtained by centrifugation, washed with methanol, and dried under a vacuum at 60 °C. The product was then carbonized in a tube furnace at 750 °C in a static Ar atmosphere. The tube furnace was heated from room temperature to 750 °C in 2 hours, maintained at 750 °C for 3 hours, and naturally cooled down to ambient temperature in the Ar atmosphere.

Synthesis of Co@NC

The composite was prepared according to the same method of CoNi@NC except for the addition of $Ni(NO_3)_2 \cdot 6H_2O$ and DCD.

Synthesis of CoCe@NC

The composite was prepared using the same method of CoNi@NC expect for the addition of $Ni(NO_3)_2 \cdot 6H_2O$. $Ce(NO_3)_3 \cdot 6H_2O$ was added after the metal precursor solution was stirred for 4 hours and the formation of ZIF-67. After the addition of $Ce(NO_3)_3 \cdot 6H_2O$, the solution was then continuously stirred for 2 hours. The product was treated as the same method in the preparation of CoNi@NC.

Synthesis of CoIn@NC

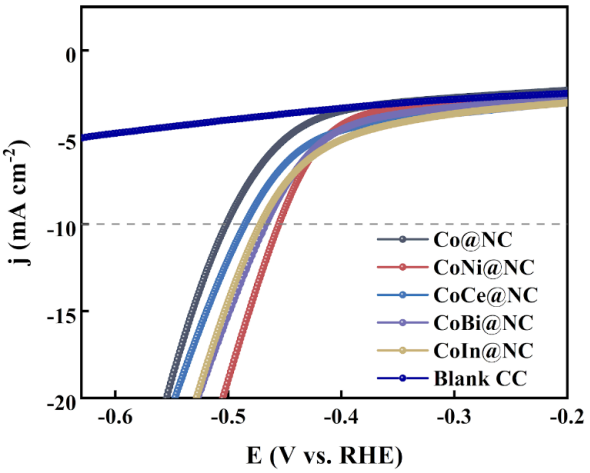
The composite was prepared using the same method as CoCe@NC. $In(NO_3)_3 \cdot xH_2O$ was added after the formation of ZIF-67.

Synthesis of CoBi@NC

The composite was prepared using the same method as CoCe@NC. $Bi(NO_3)_3 \cdot 5H_2O$ was added after the formation of ZIF-67.

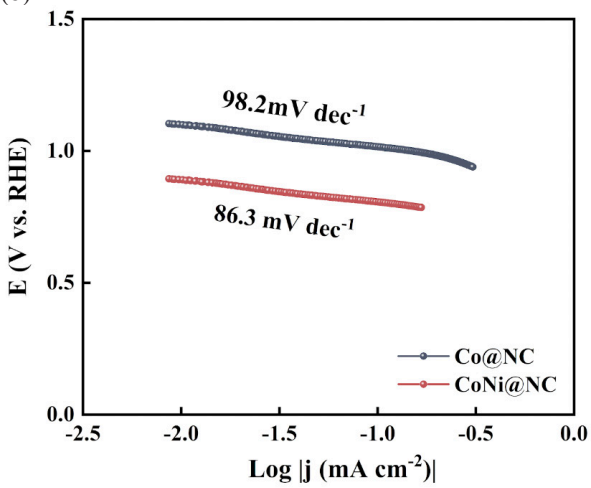
Electrochemical measurements

HER electrochemical measurements were performed with a standard three-electrode system using a CHI 760e electrochemical workstation (CHI Instrument, Inc.) at room temperature. The prepared electrocatalyst/CC film was used as the working electrode. Mercuric oxide electrode was used as the reference electrode. A graphite rod was used as the counter electrode. The catalyst ink was prepared by dispersing 1mg of catalyst in 500 uL deionized water, 480 ul isopropanol, and 20 uL Nafion solution. A Single-cell electrolyzer was used, and the electrolyte was 1 M KOH (pH=14). Linear sweep voltammetry was conducted at a scan rate of 10 mV s^{-1}. All potentials were calibrated to the reversible hydrogen electrode (RHE). $E_{(RHE)} = E_{(Hg/HgO)} + 0.9265V$.



	Co@NC	CoNi@NC	CoCe@NC	CoBi@NC	CoIn@NC
E (mV vs. RHE)	501.5	454.5	485.5	466.5	471.5

(b)



(c)

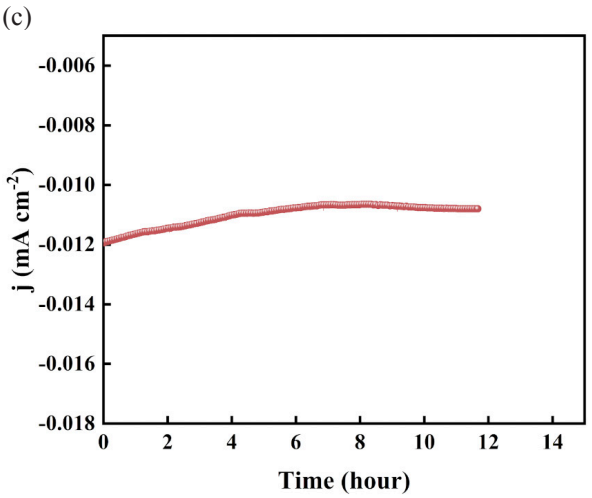


Figure 1. HER electrochemistry measurements a) LSV curves of Co@NC, CoNi@NC, CoCe@NC, CoIn@NC, and CoBi@NC at the scan rate of 10 mV s^{-1} in 1 M KOH electrolyte for HER (B) Tafel plots corresponding to Co@NC and CoNi@NC, indicating Tafel slopes of 98.2 mV dec^{-1} and 86.3 mV dec^{-1} respectively. (C) I-T graph showing the long-term stability of CoNi@NC at the potential corresponding to a current density of 10 mA cm^{-2}

ZIF-derived transitional metal and post-transitional metal doped electrocatalysts were prepared using the above-described method. ZIF-67 was first synthesized by mixing Co^{2+} and 2-MeIm in methanol at room temperature. DCD and Ni^{2+} were introduced during the formation of ZIF-67. During the formation process of ZIF-67, coordinated nickel ions were introduced, which had a competitive coordination effect with 2-MeIm. This process introduces Ni^{2+} as a dopant into ZIF-67. It is crucial to control the ratio of the amount of Ni^{2+} and Co^{2+} introduced into the precursor, as an excessive Ni^{2+} will interfere with the formation of ZIF-67, which means a fragile structured ZIF-67 will be formed and cannot precipitate from the solution after centrifugation. After the centrifugation, the powder produced consisted of Ni-doped ZIF-67 and DCD. CoNi@NC will be formed after the pyrolysis of ZIF-67 doped with Ni. CoNi NA will be encapsulated by carbon nanostructure. After pyrolysis, DCD will form additional N-doped carbon nanostructure outside the encapsulated CoNi NA. Considering the relatively sizeable atomic radius of Ce, In, and Bi, introducing those atoms into ZIF-67 during the formation process may interfere with the successful synthesis of ZIF-67. Therefore, Ce, In, and Bi doping were introduced into the precursor after forming ZIF-67. Co and doped metal formed nanoalloys after the pyrolysis and were encapsulated by carbon nanostructures. For comparison, pure cobalt-based ZIF-67 was synthesized and carbonized without any metal doping and DCD, giving the reference material Co@NC. It is evident that during the doping process, the amount of metal doping and the procedure to introduce them can largely affect the formation of electrocatalysis.

The electrochemical measurements were conducted in a single-cell electrolyzer filled with 1M KOH. All electrocatalysts loaded on carbon cloth were activated by 20 cycles of cyclic volumetry scan before LSV measurements. The area of carbon cloth loaded with electrocatalysts injected into the electrolyte was controlled near 1 cm^{-2}. The working electrode served as a cathode and went through a reduction reaction $2H_2O + 2e^- = H_2 + 2OH^-$. LSV was scanned from 0.2 V to -2.0 V under a scanning rate of 10 mV s^{-1}. The potential data were calibrated to $E_{(RHE)}$ and plotted against current density. In 1 M KOH condition, Co@NC, CoNi@NC, CoCe@NC, CoIn@NC, and CoBi@NC exhibit overpotential of 501.5 mV, 454.5 mV, 485.5 mV, 471.5 mV, and 466.5 mV (at j = 10 mA cm^{-2}), respectively. All of the doping electrocatalysts exhibit lower overpotential than the reference material Co@NC. CoNi@NC exhibits the lowest overpotential of 454.5 mV. The Tafel slope of Co@NC and CoNi@NC was calculated, and the values are 98.2 mV dec^{-1} and 86.3 mV dec^{-1} respectively. A smaller Tafel slope for CoNi@NC shows a smaller overpotential increment required to raise the current density by tenfold, which is energy efficient. This also indicates that the HER kinetics is favorable to a Volmer-Heyrovsky mechanism when using the synthesized electrocatalysts.[15] The stability of CoNi@NC was tested under continued electrolysis under the potential corresponding to the current density of 10 mA cm^{-2} and exhibited stability of more than 10 hours. This proves that N-doped carbon nanostructure formed outside metal NA protected metal NA active sites from harsh chemical environments and maintained electrocatalysts' stability during electrolysis.

The improved electrocatalytic effect of CoNi@NC is attributed to the synergistic effect of CoNi NA and N-doped carbon nanostructure. According to the research done by Bao et al., CoNi NA encapsulated by N-doped nanocarbon layers tuned the electronic structure of the electrocatalysts, resulting in an adjusted free energy of hydrogen absorption, making it neither too strong nor too weak compared to pure CoNi NA or N-doped carbon layer. It is shown that the electron density is increased on the carbon structure near the CoNi NA cluster. This increment in the electron density facilitated a stronger attraction between hydrogen and the electrocatalyst, promoting HER activity.[20] It is concluded that CoNi NA and N-doped carbon nanostructure synergistically promoted hydrogen absorption. In addition, the N-doped carbon nanostructure also provided good conductivity for electron transfer in HER, promoting faster reaction kinetics.[22] It was also reported that Ni is more beneficial in OH^- desorption in alkaline conditions.[29] An increase in active sites due to the dispersed CoNi NA in many carbon nanostructures is also related to the lower overpotential of HER.

In addition, it was reported that introducing Ni in precursor could form SAC on N-doped carbon nanostructure.[22-23, 26] These dispersed Ni SAC carbon nanostructures might also contribute to HER performances. It was reported by Jie Yin et al. that a hybrid Ni-C-N nanosheet was an effective HER catalyst, proven by the SCN^- poison effect on electrocatalysts and the XPS analysis, showing Ni-site is prone to attack by an electrophile.[23] It was also shown by quantum mechanical calculations in a research that Ni-N bonds in Ni dispersed on N-doped porous carbon can promote the electronic activity of N atoms. This increase in electronic activity could facilitate hydrogen absorption.[26] It can be concluded that the composition and structures of CoNi@NC, modified by Ni dopants, optimized its electron structure and active sites and improved its conductivity and stability. Introducing Ce into electrocatalysts is also an effective way of tailoring the electronic structure of electrocatalysts. When Ce is added to the precursor, it will be oxidized in the atmospheric environment during the formation of doped ZIF-67. CeO_x will be formed due to the change of valence between Ce^{3+} and Ce^{4+}. The doping of Ce will facilitate electron transfer by the formation of "d-f ladders" between the interaction of electron orbitals of Ce^{3+}/Ce^{4+}, Co^{2+}, and O^{2-}. It was suggested that the 4f orbital of Ce^{3+}/Ce^{4+} has strong π-donation with O^{2-}, then electrons could easily transfer from O^{2-} to Co^{2+}, promoting reaction kinetics.[19, 30] In addition, the combination of Co and CeO_x creates oxygen vacancies in CeO_x, which can serve as active sites for HER. The hydrogen binding energy is larger in CeO_2 than in other transitional metals, which might not benefit hydrogen evolution. However, oxygen vacancies decrease the hydrogen binding energy according to the DFT calculations.[31] Compared to Ni and Ce, In is rarely investigated as an HER electrocatalyst dopant. Combining Co^{2+} and In^{3+} to form CoIn NA might promote electron transfer, which contributes to the additional electron given by In^{3+}.[32] Incorporating In can also provide more active sites for HER.[33] For Bi dopant, it was proven that introducing Bi to form electrocatalysts with Co optimized the free energy of hydrogen binding in alkaline media and promoted hydrogen evolution.[34]

It is easy to conclude that the theories behind improved HER are related to the modification of the electronic and characteristic structure of electrocatalysts after the introduction of dopants. Adjusting hydrogen binding energy according to Sabatier's principle and promoting electron conductivity of electrocatalysts are two main roles of introducing dopants.[15]

Conclusions

This research focuses on synthesizing ZIF-based electrocatalysts for HER using heteroatom metal doping. Ni, Ce, In, and Bi were investigated as dopants that modified electrocatalysts' electronic configuration, structural properties, and stability. CoNi@NC showcases the optimal HER performance, with the lowest overpotential attributed to the synergistic effect of CoNi NA, carbon nanostructure, and Ni SAC. Introducing Ce, In, and Bi as dopants optimized the free energy of hydrogen binding by adjusting electronic structure and provided better electron conductivity. This work provides possible ways of designing nonnoble-metal electrocatalysts by heteroatom metal doping for HER.

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