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Co-Ni alloy nanoparticles supported by carbon nanofibers for hydrogen evolution reaction



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ABSTRACT

Alloying, a general strategy to improve the electrocatalytic performance of non-precious metal catalysts. Herein, we adopt a simple method to in-situ grow a cobalt-nickel alloy on a three-dimensional network of N-doped carbon fibers that put spatial restriction to the alloy particles, making the size smaller and uniformly distributed. The electronic synergy between nickel and cobalt and the confinement effect of in-situ growth can make Co-Ni/NCNFs provide more feasible reaction sites for catalytic hydrogen evolution reaction. Simultaneously, the formation of cobalt-nickel alloys inhibits the generation of oxides during the synthesis process, so as to promote the quality of alloys with better activity. Co-Ni/NCNFs exhibits excellent electrocatalytic properties with only 61 mV overpotential and 152.3 dec⁻¹ at 10 mA cm⁻² current density and excellent long-term stability due to the in-situ growth approach. This research also provides a feasible method for designing self-supporting alloy catalysts by in-situ growth.

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1. Introduction

Benefit from the development of HER, OER and ORR, some advanced energy conversion technologies such as rechargeable metalair batteries, fuel cells and water electrolysis devices have been widely used worldwide [1–5]. Noble metals and their oxides exhibit the most excellent electrocatalytic performance, while scarcity and high cost limit their further application and development. Therefore, various transition metal-based catalytic materials (such as Fe, Co, Mo, Ni, V, Cu, etc.) have been studied and developed to prepare highly active electrocatalytic materials to replace noble metal catalysts [6–10].

Various effective strategies have been considered to improve the performance of non-precious metal catalysts, especially via using various physics, chemistry or electrochemistry designing and preparing nanostructured catalysts with bigger specific surface area, more active centers and better conductivity [11–13]. In these methods, alloying is a common method to improve and optimize the electrochemical performance of catalysts [14,15]. This strategy has gotten a miraculous effect on oxygen reduction, N₂ reduction, CO₂ emission and water splitting [16–19]. The main principle of alloying is to adjust the electrocatalyst, optimizing the adsorption/desorption

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strength of the adsorbate on the catalyst surface and improving the electrochemical performance [20-23]. The alloying between nonprecious metals sometimes produced a strong synergistic effect, which significantly changed the electronic structure of each component. Therefore, the bonding strength of the adsorbate on the alloy surface can be optimized, and greatly improving the electrochemical performance. For example, Zhang [24] et al. prepared an ultrathin Fe and N-co-doped carbon nanosheet encapsulated Fe-doped CoNi alloy nanoparticle (FeCoNi@FeNC) composite as a bifunctional catalyst for HER and OER, which can reach 10 mA cm⁻² at 102 mV. And Cheng [25] used three dimensional freestanding porous Cu foam in situ armored CoNi alloy nanosheet arrays with tunable compositions with the overpotentials of only 132 mV to reach a current density of 10 mA cm⁻² in 1.0 M KOH. Both nickel and cobalt are elements with very good electrocatalytic activity. In previous reports, their alloys also exhibit better performance than a single element. However, nickel and cobalt tend to accumulate during the process of preparing the alloy, which is not conducive to the performance of the catalyst.

Nano-carbon materials have the characteristics of tunable molecular structure, excellent electrical conductivity and environmental friendliness, which have been widely used in the field of energy conversion involving oxygen evolution and hydrogen evolution reactions [26]. However, compared with transition metal-based catalysts, carbon materials catalyst still has the problem of insufficient catalytic activity and requires a higher overpotential

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(>200 mV vs RHE) to reach the standard current density of 10 mA cm⁻². To further improve the catalytic activity, it's is necessary to rationally construct and design materials with active metal phase structures, such as carbon nanohybrid materials. Non-precious metal-based carbon composite materials (such as MoS₂/rGO [27], CoP/CNT [28], Mo₂C@NC [29], Co-NRCNTs [30], and WON@NC [31], etc.). In recent years, researchers have discovered that carbon fibers prepared by electrospinning nanofibers after carbonization have the advantages of good electrical conductivity, easily modified, and can also be used as self-supporting electrodes for electrolysis water catalyst applications. In the previous research of our team, a series of carbon fiber-based catalysts have been prepared through electrospinning and high-temperature carbonization and were applied in the hydrogen evolution reaction. Zhu [32] et al. prepared a series of Cobalt-Manganese compounds supported by PAN-derived carbon nanofibers. These materials showed excellent performance in the electrolysis water test. Zhang [33] et al. loaded single-atom Ru catalyst on the PVA(Polyvinyl alcohol)-derived carbon fiber. This material only needed 86 mV to reach 10 mA cm⁻² in the HER test.

Herein, we reported a synthetic strategy to prepare cobalt-nickel alloys supported on carbon nanofibers by in-situ growth. Cobalt and nickel element spontaneously formed cobalt-nickel alloy under high-temperature carbonization, due to the confinement effect of insitu growth, they grow in-situ on N-doped carbon nanofibers to obtain smaller and more uniform cobalt-nickel alloy nanoparticles. The synergistic effect of the strong electronic interaction of nickel and cobalt in the cobalt-nickel alloy made it have more excellent electrocatalytic performance. The three-dimensional network of N-doped carbon nanofibers also made Co-Ni/NCNFs have more usable active sites, which was beneficial to the hydrogen evolution reaction. The overpotential of the current density of Co-Ni/NCNFs was only 61 mV at 10 mA cm⁻² current density, and the in-situ growth also gave the catalytic material excellent stability.

2. Experimental

2.1. Reagents

The PAN (Polyacrylonitrile, Mw = 150,000) was purchased from Sinopec Shanghai Petrochemical Co., Ltd. Dimethylformamide (DMF, 99.5%) and Cobalt chloride hexahydrate (CoCl₂·6H₂O) were procured from Sigma-Aldrich. Nickel chloride hexahydrate (NiCl₂·6H₂O) and KOH were supplied by Shanghai Macklin Biochemical Co., Ltd. The KOH was dissolved in deionized water to prepare 1 M KOH solution.

2.2. Synthesis of Co-Ni/NCNFs

All samples were prepared as the typical synthesis process. First, 3 g PAN was dissolved in 22 g DMF, then a total metal salt of 4 mM with the different molar ratios of Co/Ni (4:0, 3:1, 2:2, 1:3, 0:4) was added to the above solution. After stirring for 12 h, pour the precursor solution into a disposable syringe for electrospinning. Spinning parameters: positive high voltage = 18 kV, negative high voltage = -0.5 kV, spinning speed of 0.5 ml/h, receiving distance of 15 cm, spinning environment temperature of 33 °C. Co-Ni/ nanofiber membrane was obtained after electrospinning for 12 h. Cut a certain size of fiber membrane and placed in an alumina ceramic boat in a tube furnace at a rate of 5 °C min⁻¹ to heat up to 230 °C and kept for 3 h to oxidize the nanofiber to form a stable structure. After that, the samples were heated at 1000 °C for 3 h under the Ar atmosphere to carbonize.

When Co:Ni = 2:2, the prepared sample was named Co-Ni/NCNFs. Co-Ni/NCNFs = 1:3 and Co-Ni/NCNFs = 3:1 was prepared by the spinning solutions in which the ratio of Co to Ni is 1:3 and 3:1. Co-CoO/NCNFs and Ni-NiO/NCNFs were synthesized by using only 4 mmol CoCl₂· $6H_2O$ or NiCl₂· $6H_2O$ to prepare the spinning solution. The other procedures were the same as above.

2.3. Apparatus

The apparent morphology of the prepared samples was characterized by a thermal field emission scanning electron microscope (ULTRA55, Zeiss) with 3 kV accelerating voltage. By a 200 kV transmission electron microscope (JEM-2100, JOEL), the characterization analysis of the internal structure of the sample was obtained. X-ray energy scattering spectroscopy (EDS) (with TEM) analyzes the composition of the prepared sample. High-angle dark-field image-scanning transmission electron microscope (STEM, Tecnai G2 F30S-Twin, Philips-FEI) and high-resolution element mapping (STEM-EDS) were used to analyze the elemental composition of the sample, using an accelerating voltage of 300 kV. ICP-MS was tested by PE optima 8000. The XRD pattern of the sample was measured by an X-ray diffractometer (XRD, Bruker D8 DIECOVER), used a Cu target K α (λ = 1.5406 Å) with a scanning range of 10–80° and a scanning rate of 5° min⁻¹. X-ray photoelectron spectrometer (XPS, Kratos Axis Ultra DLD) used Al target K α (1486.6 eV, 15 kV, 10 mA) is used to analyze the chemical structure and atomic valence of the sample surface.

2.4. Electrochemical characterizations

All electrochemical tests are performed in an electrolytic cell with an electrolyte of 1 M KOH by CHI660E workstation (Chenhua Instrument, China). Electrochemical measurements were performed in a three-electrode electrochemical cell using differently prepared samples as the working electrode (tailored into a 1×1 cm flake), a saturated calomel electrode as the reference electrode, and a graphite rod as the counter electrode. All electrochemical potentials are reported against the reversible hydrogen electrode (RHE) by using the equation: E (V versus RHE) =E (V versus SCE) + 0.059 *pH + 0.244.

3. Results and discussion

As shown in Scheme 1, after high-temperature carbonization, the nanofibers produced by electrospinning transformed to be N-doped carbon nanofibers (NCNFs). At the same time, during the high-temperature carbonization process, the metal ions on the surface of the nanofibers undergo a series of reactions that will form metal crystal particles. The growth of single cobalt and nickel element on the N-doped carbon nanofibers were similar, as shown in Fig. S1(a-b) and S2(a-b), the size of nanoparticles on the NCNFs was 20–200 nm and the distribution was not uniform. In Fig. S1(c), the lattice spacing of the crystal planes of Co and CoO, respectively; in Fig. S2(c), the lattice spacing of the nanoparticles was 2.03 Å and 2.08 Å, corresponding with the (111) and (012) crystal planes of Ni and NiO.

The nanoparticle size of the growth of a single element on carbon fiber was not uniform, and nanoparticles were heterostructure consisting of metal and its oxides. In contrast, the Fig. 1(a) and (b) showed that the nano-particles of both cobalt and nickel grown on carbon fibers were uniformly distributed and relatively smaller size. In Fig. 1(c), the TEM image of the Co-Ni/NCNFs indicated that the size of the nanoparticles was mainly between 10 and 50 nm on the carbon fibers. These uniformly distributed small-sized nanoparticles had a larger specific surface area compared with Co-CoO/NCNFs and Co-CoO/NCNFs, which could provide more usable active sites for electrocatalytic reactions and improved catalytic performance. In order to confirm the structure of the nanoparticles, in the HRTEM image of Fig. 1(d), the lattice spacing of the particles was measured



Scheme 1. The fabrication of Co-Ni/NCNFs.

to be 2.04 Å, which corresponds to the (111) crystal plane of the CoNi alloy, indicated the presence of cobalt-nickel alloy in the particles.

To further explore the distribution of cobalt and nickel elements on the carbon fibers, an EDS test was performed. Fig. 1(e) was the topography under dark field conditions, as seen in the mapping diagram in Fig. 1(f), cobalt and nickel element were distributed in the same position, and no separate cobalt or nickel distribution area, which indicated that nickel and cobalt element form alloys together. Besides, the EDS line scan on the carbon fiber in Fig. 1(h) represented that the changing trend of the signal intensity of cobalt and nickel element at different positions was the same. The atomic ratios of Co to Ni were also tested by ICP-MS, as shown in Table S1, were close to 1:1. The above EDS and ICP-MS analysis confirmed that cobalt and nickel elements form nanoparticles together, and did not form particles alone.

XRD was used to analyze the nano-particle crystal phase on the carbon fiber. In the XRD patterns of Fig. 2(a), for Co-CoO/NCNFs, except for the characteristic peaks of oxides (36.5° , 42.4° and 61.5°), 44.0° , 51.0° and 75.5° corresponding to Co. Similarly, Ni-NiO/NCNFs had Ni characteristic peaks at 44.8° , 52.1° and 76.6° , and the other characteristic peaks at 37.2° , 43.3° and 62.9° were corresponding to the crystal phase of NiO. While the distinct characteristic peaks of Co-Ni/NCNFs at 44.1° , 51.5° and 76.0° corresponding to the (111), (200) and (220) crystal planes of CoNi alloy respectively, which further confirms that the nanoparticle of Co-Ni/NCNFs was cobalt-nickel alloy. Besides, due to the larger unit cell parameters of Ni, during the



Fig. 1. SEM images of different multiplier (a and b), TEM images (c) and HRTEM images (d) of Co-Ni/NCNFs; HAADF-STEM plot (e), STEM-EDS mapping images (f) and EDS scan spectra (h) of Co-Ni/NCNFs.



Fig. 2. (a)XRD patterns of Co-Ni/NCNFs, Co-CoO/NCNFs and Ni-NiO/NCNFs; (b)XPS survey patterns of Co-Ni/NCNFs; Peaking fitting of Co 2p(c), Ni 2p(d), O 1 s(e) and N 1 s(f).

alloying process, some Ni atoms replaced the positions of Co atoms, increasing the unit cell parameters. Therefore, the diffraction peak of Co-Ni/NCNFs shifted to a higher angle than that of Co-CoO/NCNFs. Compared with Ni-NiO/NCNFs, the peaks appeared at low angles. The above structural analysis of Co-Ni/NCNFs confirms the successful preparation of CoNi alloy supported by carbon nanofibers.

The XPS test was used to characterize the chemical valence state of the elements on the surface of the material. All the XPS data were

corrected with the C 1 s (284.8 eV) standard peak. Fig. 2(b) is the total spectrum. For the Co element in Co-Ni/NCNFs, a characteristic peak at 778.9 eV belonged to the $2p_{3/2}$ orbital of Co (Fig. 2(c)), which was related to the valence state of Co in CoNi alloy. The characteristic peaks at 780.3 eV, 794.8 eV and 796.5 eV were related to the oxidation state of cobalt, which was duo to the pre-oxidation process of PAN-based carbon fibers, Co atoms were inevitably oxidized on the surface. Other characteristic peaks at 786.0 eV and 803 eV were

the satellite peaks of Co $2p_{3/2}$ and $2p_{1/2}$. Moreover, compared with the two characteristic peaks of Co $2p_{1/2}$ in Co-CoO/NCNFs, the two characteristic peaks of Co $2p_{1/2}$ in Co-Ni/NCNFs shifted by 0.75 eV to the right, which was also due to the formation of the CoNi alloys made the Co element bond energy shift. And that also proved the electronic interaction between Co and Ni in CoNi alloy was strong.

Similarly, in Fig. 2(d), in the XPS spectrum of Ni 2p, the Ni $2p_{3/2}$ of Co-Ni/NCNFs at 835.1 eV corresponds to the alloy state of Ni, and the other the characteristic peaks of Ni $2p_{3/2}$ and Ni $2p_{1/2}$ all correspond to the oxidation state of Ni. The characteristic peaks of Ni 2p orbitals in Ni-NiO/NCNFs all correspond to the oxidation state of Ni. This further confirmed that the formation of the CoNi alloy makes the Ni atoms that were originally in the oxidized state transformed into the alloyed nickel atoms after forming a cobalt-nickel alloy with Co. Similarly, due to the formation of the total of nickel and cobalt, the characteristic peak of Ni-O or Co-O in O 1 s is also shifted by 0.25 eV in the negative direction. The main peaks in Fig. 2(f) are attributed to pyrrole and pyridine nitrogen [34], and their presence can promote the progress of HER. The other peaks at 397.7 eV and 403.3 eV correspond to N-Co/Ni [35] and N-O, which indicated the existence of coupling interaction between Co and N, while N-O is attributed to the oxidation of the matrix [36].

The prepared various hybrid materials were made into working electrodes, and electrochemical performance tests were carried out in 1 M KOH. Before the HER test, each working electrode must complete 200 cycles of CV cycles within the voltage range of -0.2-0.6 V to activate and stabilize the electrode material. The curves in Fig. 3(a) are the hydrogen evolution polarization curves (LSV) of pure carbon fibers (NCNFs), Co-CoO/NCNFs, Ni-NiO/NCNFs, and Co-Ni/NCNFs. It can be observed that pure carbon fiber has almost no catalytic activity. The hybrid materials with cobalt or nickel supported carbon fibers have better catalytic activity. At a current density of 10 mA cm⁻², the overpotential were 138 and 117 mV, respectively. In contrast, Co-Ni/NCNFs show very excellent performance, with an overpotential of only 61 mV, which was a little higher than the Pt/C electrode (52 mV).

The Tafel slope was calculated from the polarization curve and reflected the speed of the reaction kinetics. The Tafel slope of the material was calculated by the LSV polarization curve (as shown in Fig. 3(b)). Co-CoO/NCNFs and Ni-NiO/NCNFs are 174 mV dec^{-1} and 212 mV dec⁻¹, respectively. Compared with this, the hydrogen evolution reaction kinetics of Co-Ni/NCNFs was faster with a lower Tafel slope of 152.3 mV dec⁻¹. When the Tafel slope value is more than 120 mV dec⁻¹, the main rate-determining step is water adsorption [37], which was also the most important factor limiting the performance of the Co-Ni/NCNFs in HER. The electric double-layer capacitance (C_{dl}) of the material reacts to the electrochemically active area, and they show a proportional relationship. By testing the CV curve under different sweep speed conditions from -0.265-0.265 V (Fig. S3), the C_{dl} value of different materials was calculated (as shown in Fig. 3(c)). The C_{dl} values of Co-CoO/NCNFs and Ni-NiO/NCNFs are 168 mF cm⁻² and 234 mF cm⁻², respectively. The Co-Ni/NCNFs were 349 mF cm⁻², better than Co-CoO/NCNFs and Ni-NiO/NCNFs. Therefore, compared with Co-CoO/NCNFs and Ni-NiO/NCNFs, Co-Ni/NCNFs had a larger electrochemically active area which was corresponding with SEM results that Co-Ni/NCNFs had evenly distributed catalytic particles.

Combined with the characterization of the morphology and structure of various hybrid materials, the excellent electrocatalytic performance of Co-Ni/NCNFs came from two aspects. On the one hand, the catalytic activity of cobalt-nickel alloys was better; cobaltnickel alloys grow in situ on the carbon fiber to form uniform nanoparticles with a larger specific surface area and provided more usable active sites for catalytic reactions.

In addition, the effect of the ratio of Co and Ni on the catalytic performance of the catalyst was also explored, and hybrid materials with the ratios of Co:Ni = 1:3 and 3:1 were prepared. In Fig. 3(d) and (e), the HER tests result of materials with different cobalt and nickel ratios showed that: Co-Ni/NCNFs-1:3 had an overpotential of 100 mV at a current density of 10 mA cm⁻². Co-Ni/NCNFs-3:1 was 104 mV, and the Tafel slopes were 172.2 mV dec⁻¹ and 177.4 mV dec⁻¹, respectively. The Co-Ni/NCNFs-2:2 was only 61 mV and 152.3 mV dec⁻¹. And the C_{dl}



Fig. 3. Polarization curves of hydrogen evolution reactions (a), Tafel (b) and electric double layer capacitance diagram (c) of different materials; Hydrogen evolution reaction polarization curve (d), Tafel (e) and electric double layer capacitance diagram (f) of hybrid materials with molar ratios of Co and Ni of 1:3, 2:2 and 3:1.



Fig. 4. (a) Comparison of polarization curves of Co-Ni/NCNFs; (b) Chronoamperometric test of Co-Ni/NCNFs at a constant voltage of - 1.16 V.

Table 1

| Comparison of the electrocatalytic activities of | Co-Ni/NCNFs with s | some recently reported | Co-Ni alloy electrocatalysts for HER. |
|--|--------------------|------------------------|---------------------------------------|
|--|--------------------|------------------------|---------------------------------------|

| Catalysts | $\eta_{10} \left(m V \right)$ | Tafel slope (mV dec ⁻¹) | Stability (h) | Substrate | Counter Electrode | Electrolyte | Reference |
|---|--------------------------------|-------------------------------------|---------------|---------------------------|-------------------|--------------------------------------|-----------|
| This work | 61 | 152.3 | 25 | N-doped Nano Carbon Fiber | Graphite rod | 1.0 M KOH | 1 |
| FeCoNi@FeNC | 102 | 67 | 10 | Glassy carbon electrode | Pt wire | 1.0 M KOH | [24] |
| Co ₈₁ Ni ₁₉ @CF | 132 | 84.39 | 10 | Cu foam | Graphite rod | 1.0 M KOH | [25] |
| Co _{0.75} Ni _{0.25} /CC | 108 | 100 | 24 | Carbon cloth | Graphite rod | 1.0 M KOH | [38] |
| CoNi@NCNTs-700 | 130 | 82.1 | 5 | Glassy carbon electrode | Carbon rod | 0.5 M H ₂ SO ₄ | [39] |
| CoNi@N-C/rGO-3 | 512 | 133.7 | 22 | Glassy carbon electrode | Pt foil | 0.5 M H ₂ SO ₄ | [40] |
| CoNi(1: 1)-TB-800N ₂ | 114 | 59 | 1 | Glassy carbon electrode | Carbon rod | 1.0 M KOH | [41] |
| CoNi@NC-NCNTs | 85 | 110 | 24 | Carbon cloth | Graphite rod | 1.0 M KOH | [42] |
| CoNi@NC | 142 | 105 | 1 | Glassy carbon electrode | Graphite rod | $0.1 \text{ M H}_2\text{SO}_4$ | [43] |

of Co-Ni/NCNFs-2:2 (349 mF cm⁻²) was also higher than Co-Ni/NCNFs-1:3 (231 mF cm⁻²) and Co-Ni/NCNFs-3:1 (293 mF cm⁻²) (as shown in Fig. 3(f) and Fig. S4). Therefore, 2:2 was the best ratio of Co and Ni elements. Under this ratio, Co-Ni/NCNFs had the most excellent electrocatalytic performance.

Stability is another important indicator of catalytic performance. The hydrogen evolution polarization curves before and after the 1000 CV cycles were compared as shown in Fig. 4(a). Almost no change in the measured LSV curves before and after the CV cycle, indicated that Co-Ni/NCNFs had good stability. Another stability test was measured to observe the changes of the working curve of the material under constant voltage. By using Co-Ni/NCNFs as a working electrode to work at a constant voltage of -1.16 V for at least 25 h, as the reaction time increases, the current density was very stable and the loss was little, which also confirmed that Co-Ni/NCNFs had great stability. Especially, when compared with the catalytic performance of other recently reported nickel-cobalt alloy catalysts (Table 1), Co-Ni/NCNFs also exhibited very excellent electrocatalytic performance, lower overpotential and better stability. Combined with the analysis of the morphology and phase characterization of the Co-Ni/NCNFs hybrid material, in-situ growth gave Co-Ni/NCNFs the exceedingly stability.

4. Conclusion

In this research work, we designed the cobalt-nickel nano-alloy particles to be supported on N-doped carbon fibers. The alloying process of cobalt and nickel elements on the carbon fibers reduces the production of oxides and forms an alloy catalyst with more excellent performance. And it reduces the size of the particles grown on the carbon fiber, giving the catalyst more active sites. It exhibits excellent electrocatalytic performance under alkaline conditions (η_{10} = 61 mV, 152.3 mV dec⁻¹). And benefit from the in-situ growth method, and the cobalt-nickel alloy catalyst was embedded on the carbon fiber, making it in the process of electrolytic hydrogen evolution, not easy to fall off, so it can maintain very excellent catalytic activity and stability. This work not only revealed exceedingly

electrocatalytic performance of Co-Ni/NCNFs, but also provided a feasible method for designing self-supporting alloy catalysts by insitu growth.

CRediT authorship contribution statement

Jibiao Guan: Conceptualization, Methodology, Formal analysis, Validation, Investigation, Data curation, Writing - original draft, Writing - review & editing. **Yuanjian Liu:** Validation, Investigation. **Yini Fang:** Writing - original draft. **Xiangheng Du:** Writing - review & editing. **Yaqin Fu:** Resources. **Lina Wang:** Resources. **Ming Zhang:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2021.159172.

References

- M.-Q. Wang, C. Ye, H. Liu, M. Xu, S.-J. Bao, Nanosized metal phosphides embedded in nitrogen-doped porous carbon nanofibers for enhanced hydrogen evolution at all pH values, Angew. Chem. Int. Ed. 130 (2018) 1981–1985.
- [2] J. Duan, S. Chen, M. Jaroniec, S.Z. Qiao, Heteroatom-doped graphene-based materials for energy-relevant electrocatalytic processes, ACS Catal. 5 (2015) 5207–5234.

- [3] Y. Ito, W. Cong, T. Fujita, Z. Tang, M. Chen, High catalytic activity of nitrogen and sulfur co-doped nanoporous graphene in the hydrogen evolution reaction, Angew. Chem. Int Ed. 54 (2015) 2131–2136.
- [4] T. Palaniselvam, V. Kashyap, S.N. Bhange, J.-B. Baek, S. Kurungot, Nanoporous graphene enriched with Fe/Co-N active sites as a promising oxygen reduction electrocatalyst for anion exchange membrane fuel cells, Adv. Funct. Mater. 26 (2016) 2150–2162.
- [5] X. Cui, S. Yang, X. Yan, J. Leng, S. Shuang, P.M. Ajayan, Z. Zhang, Pyridinic-nitrogen-dominated graphene aerogels with Fe-N-C coordination for highly efficient oxygen reduction reaction, Adv. Funct. Mater. 26 (2016) 5708–5717.
- [6] L. Han, S. Dong, E. Wang, Transition-Metal (Co, Ni, and Fe)-based electrocatalysts for the water oxidation reaction, Adv. Mater. 28 (2016) 9266–9291.
- [7] S. Dou, X. Wang, S. Wang, Rational design of transition metal-based materials for highly efficient electrocatalysis, Small Methods 3 (2019) 1800211.
- [8] J. Wang, W. Cui, Q. Liu, Z. Xing, A.M. Asiri, X. Sun, Recent progress in cobalt-based heterogeneous catalysts for electrochemical water splitting, Adv. Mater. 28 (2016) 215–230.
- [9] K. Zeng, D. Zhang, Recent progress in alkaline water electrolysis for hydrogen production and applications, Prog. Energy Combust. Sci. 36 (2010) 307–326.
- [10] M. Gong, D.-Y. Wang, C.-C. Chen, B.-J. Hwang, H. Dai, A mini review on nickelbased electrocatalysts for alkaline hydrogen evolution reaction, Nano Res. 9 (2015) 28–46.
- [11] J. Staszak-Jirkovsky, C.D. Malliakas, P.P. Lopes, N. Danilovic, S.S. Kota, K.C. Chang, B. Genorio, D. Strmcnik, V.R. Stamenkovic, M.G. Kanatzidis, N.M. Markovic, Design of active and stable Co-Mo-Sx chalcogels as pH-universal catalysts for the hydrogen evolution reaction, Nat. Mater. 15 (2016) 197–203.
- [12] S. Zhao, D.W. Wang, R. Amal, L. Dai, Carbon-based metal-free catalysts for key reactions involved in energy conversion and storage, Adv. Mater. 31 (2019) 1801526.
- [13] W.F. Chen, J.T. Muckerman, E. Fujita, Recent developments in transition metal carbides and nitrides as hydrogen evolution electrocatalysts, Chem. Commun. 49 (2013) 8896–8909.
- [14] Q. Wu, M. Luo, J. Han, W. Peng, Y. Zhao, D. Chen, M. Peng, J. Liu, F.M.F. de Groot, Y. Tan, Identifying electrocatalytic sites of the nanoporous copper-ruthenium alloy for hydrogen evolution reaction in alkaline electrolyte, ACS Energy Lett. 5 (2019) 192–199.
- [15] J. Chen, Y. Yang, J. Su, P. Jiang, G. Xia, Q. Chen, Enhanced activity for hydrogen evolution reaction over cofe catalysts by alloying with small amount of Pt, ACS Appl. Mater. Interfaces 9 (2017) 3596–3601.
- [16] K. Jiang, P. Wang, S. Guo, X. Zhang, X. Shen, G. Lu, D. Su, X. Huang, Ordered PdCubased nanoparticles as bifunctional oxygen-reduction and ethanol-oxidation electrocatalysts, Angew. Chem. Int. Ed. 55 (2016) 9030–9035.
- [17] R. Zhao, H. Xie, L. Chang, X. Zhang, X. Zhu, X. Tong, T. Wang, Y. Luo, P. Wei, Z. Wang, X. Sun, Recent progress in the electrochemical ammonia synthesis under ambient conditions, EnergyChem 1 (2019) 100011.
- [18] W. Luc, C. Collins, S. Wang, H. Xin, K. He, Y. Kang, F. Jiao, Ag-Sn bimetallic catalyst with a core-shell structure for CO₂ reduction, J. Am. Chem. Soc. 139 (2017) 1885–1893.
- [19] Y. Pi, Q. Shao, P. Wang, J. Guo, X. Huang, General formation of monodisperse IrM (M = Ni, Co, Fe) bimetallic nanoclusters as bifunctional electrocatalysts for acidic overall water splitting, Adv. Funct. Mater. 27 (2017) 1700886.
- [20] W. Tong, B. Huang, P. Wang, L. Li, Q. Shao, X. Huang, Crystal-phase-engineered PdCu electrocatalyst for enhanced ammonia synthesis, Angew. Chem. Int Ed. 59 (2020) 2649–2653.
- [21] L. Bu, S. Guo, X. Zhang, X. Shen, D. Su, G. Lu, X. Zhu, J. Yao, J. Guo, X. Huang, Surface engineering of hierarchical platinum-cobalt nanowires for efficient electrocatalysis, Nat. Commun. 7 (2016) 11850.
- [22] J. Ding, L. Bu, S. Guo, Z. Zhao, E. Zhu, Y. Huang, X. Huang, Morphology and phase controlled construction of Pt-Ni nanostructures for efficient electrocatalysis, Nano Lett. 16 (2016) 2762–2767.
- [23] K. Jiang, P. Wang, S. Guo, X. Zhang, X. Shen, G. Lu, D. Su, X. Huang, Ordered PdCubased nanoparticles as bifunctional oxygen-reduction and ethanol-oxidation electrocatalysts, Angew. Chem. Int Ed. 55 (2016) 9030–9035.
- [24] Q. Zhang, R.F. Webster, S. Cheong, R.D. Tilley, X. Lu, R. Amal, Ultrathin Fe-N-C nanosheets coordinated Fe-Doped CoNi alloy nanoparticles for electrochemical water splitting, Part. Part. Syst. Charact. 36 (2019) 1800252.

- [25] C. Cheng, F. Zheng, C. Zhang, C. Du, Z. Fang, Z. Zhang, W. Chen, High-efficiency bifunctional electrocatalyst based on 3D freestanding Cu foam in situ armored CoNi alloy nanosheet arrays for overall water splitting, J. Power Sources 427 (2019) 184–193.
- [26] M.A. Rosen, S. Koohi-Fayegh, The prospects for hydrogen as an energy carrier: an overview of hydrogen energy and hydrogen energy systems, Energy Ecol. Environ. 1 (2016) 10–29.
- [27] Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong, H. Dai, MoS2 nanoparticles grown on graphene: an advanced catalyst for the hydrogen evolution reaction, J. Am. Chem. Soc. 133 (2011) 7296–7299.
- [28] Q. Liu, J. Tian, W. Cui, P. Jiang, N. Cheng, A.M. Asiri, X. Sun, Carbon nanotubes decorated with CoP nanocrystals: a highly active non-noble-metal nanohybrid electrocatalyst for hydrogen evolution, Angew. Chem. Int Ed. 53 (2014) 6710–6714.
- [29] Y. Liu, G. Yu, G.D. Li, Y. Sun, T. Asefa, W. Chen, X. Zou, Coupling Mo2C with nitrogen-rich nanocarbon leads to efficient hydrogen-evolution electrocatalytic sites, Angew. Chem. Int Ed. 54 (2015) 10752–10757.
- [30] X. Zou, X. Huang, A. Goswami, R. Silva, B.R. Sathe, E. Mikmekova, T. Asefa, Cobaltembedded nitrogen-rich carbon nanotubes efficiently catalyze hydrogen evolution reaction at all pH values, Angew. Chem. Int Ed. 53 (2014) 4372–4376.
- [31] Q. Li, W. Cui, J. Tian, Z. Xing, Q. Liu, W. Xing, A.M. Asiri, X. Sun, N-doped carboncoated tungsten oxynitride nanowire arrays for highly efficient electrochemical hydrogen evolution, ChemSusChem 8 (2015) 2487–2491.
- [32] H. Zhu, L. Gu, D. Yu, Y. Sun, M. Wan, M. Zhang, L. Wang, L. Wang, W. Wu, J. Yao, M. Du, S. Guo, The marriage and integration of nanostructures with different dimensions for synergistic electrocatalysis, Energy Environ. Sci. 10 (2017) 321–330.
- [33] Z. Zhang, J. Cai, H. Zhu, Z. Zhuang, F. Xu, J. Hao, S. Lu, H. Li, F. Duan, M. Du, Simple construction of ruthenium single atoms on electrospun nanofibers for superior alkaline hydrogen evolution: A dynamic transformation from clusters to single atoms, Chem. Eng. J. 392 (2020) 123655.
- [34] Y. Pan, K. Sun, S. Liu, X. Cao, K. Wu, W.C. Cheong, Z. Chen, Y. Wang, Y. Li, Y. Liu, D. Wang, Q. Peng, C. Chen, Y. Li, Core-shell ZIF-8@ZIF-67-derived CoP nano-particle-embedded n-doped carbon nanotube hollow polyhedron for efficient overall water splitting, J. Am. Chem. Soc. 140 (2018) 2610–2618.
- [35] X. Feng, H. Wang, X. Bo, L. Guo, Bimetal-organic framework-derived porous rodlike cobalt/nickel nitride for All-pH value electrochemical hydrogen evolution, ACS Appl. Mater. Interfaces 11 (2019) 8018–8024.
- [36] Y. Fang, T. Zhang, Y. Wu, Y. Liu, J. Guan, X. Du, L. Wang, M. Zhang, Stacked Co6W6C nanocrystals anchored on N-doping carbon nanofibers with excellent electrocatalytic performance for HER in wide-range pH, Int. J. Hydrog. Energy 45 (2020) 1901–1910.
- [37] J. Wang, F. Xu, H. Jin, Y. Chen, Y. Wang, Non-noble metal-based carbon composites in hydrogen evolution reaction: fundamentals to applications, Adv. Mater. 29 (2017) 1605838.
- [38] Q. Zhang, X.L. Li, B.X. Tao, X.H. Wang, H.Q. Luo, CoNi based alloy/oxides@Ndoped carbon core-shell dendrites as complementary water splitting electrocatalysts with significantly enhanced catalytic efficiency, Appl. Catal. B Environ. 254 (2019) 634–646.
- [39] Y. Xie, C. Feng, Y. Guo, S. Li, C. Guo, Y. Zhang, J. Wang, MOFs derived carbon nanotubes coated CoNi alloy nanocomposites with N-doped rich-defect and abundant cavity structure as efficient trifunctional electrocatalyst, Appl. Surf. Sci. 536 (2021) 147786.
- [40] L. Chen, S. Yang, K. Qian, W. Wei, C. Sun, J. Xie, In situ growth of N-doped carbon coated CoNi alloy with graphene decoration for enhanced HER performance, J. Energy Chem. 29 (2019) 129–135.
- [41] X. He, F. Yin, G. Li, B. Chen, S. Wang, M. Gu, CoNi alloys with slight oxidation@N,O Co-doped carbon: enhanced collective contributions of cores and shells to multifunctional electrocatalytic activity and Zn-air batteries, J. Mater. Chem. A 8 (2020) 25805–25823.
- [42] R. Li, X. Li, C. Liu, M. Ye, Q. Yang, Z. Liu, L. Xie, G. Yang, Enhanced electron transport through a nanoforest-like structure of CoNi nanoalloy@nitrogendoped carbon nanotubes for highly efficient catalysis of overall water splitting, Appl. Surf. Sci. 517 (2020) 145841.
- [43] J. Deng, P. Ren, D. Deng, X. Bao, Enhanced electron penetration through an ultrathin graphene layer for highly efficient catalysis of the hydrogen evolution reaction, Angew. Chem. Int Ed. 54 (2015) 2100–2104.