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Bimetallic Metal-Organic Framework-Derived Nanosheet-Assembled Nanoflower Electrocatalysts for Efficient Oxygen Evolution Reaction

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Abstract: Non-noble metal-based metal-organic framework (MOF)-derived electrocatalysts have recently attracted great interest in the oxygen evolution reaction (OER). Here we report a facile synthesis of nickel-based bimetallic electrocatalysts derived from 2D nanosheet-assembled nanoflower-like MOFs. The optimized morphologies and large Brunauer-Emmett-Teller (BET) surface area endow FeNi@CNF with efficient OER performance, where the aligned nanosheets can expose abundant active sites and benefit electron transfer. The complex nanoflower morphologies together with the

Introduction

Great efforts have been made to alleviate the depletion of fossil energy and sever environmental pollution in the past few decades.^[1] Electrocatalytic water splitting is considered as a potential green hydrogen production technology, which includes oxygen evolution reaction (OER) and hydrogen evolution reaction (HER).^[2] OER is a kernel process limited by the sluggish kinetics due to its four-electron mechanism. Among all the potential and applied electrocatalysts, RuO₂ and IrO₂ are the most prominent electrocatalysts.^[3] Whereas, the scarcity, high cost and instability restrict their extensive application, which requires cost effective and abundant replacement for them.^[4]

It is well-known that complicated nanoporous structure can provide more opportunities to adjust physical and chemical properties of catalysts and also facilitate the exposure of active sites.^[5] For instance, core@shell structures,^[6] nanotubes,^[7] ultra-

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synergistic effects between two metals attributed to the OER activity of the Ni-based bimetallic catalysts. The optimized FeNi@CNF afforded an overpotential of 356 mV at a current density of 10 mA cm^{-2} with a Tafel slope of 62.6 mV dec^{-1} , and also exhibited superior durability with only slightly degradation after 24 hours of continuous operation. The results may inspire the use of complex nanosheetassembled nanostructures to explore highly active catalysts for various applications.

thin 2D nanosheets^[8] and graphene^[9] et.al. are widely applied in electrocatalytic field due to their high conductivity and mass transfer efficiency. Metal-organic frameworks (MOFs), as a branch of inorganic-organic hybrid materials, can be utilized as precursors and templates to prepare electrocatalysts with a wide variety of complex structures.^[10] MOFs with unique morphologies and well-tunable structures can be synthesized using suitable metal ions and ligands as feeding materials. More importantly, preparation of composite micro-/nano-structures using MOFs as precursors can manufacture catalysts with high porosity, uniform pore size and controllable morphologies.^[11] In addition, the MOFs derivatives obtained through appropriate pyrolysis conditions can approximately maintain the original morphology of MOFs, thereby regulating the morphologies of the electrocatalysts.^[11b, 12]

Reserve-rich first row (3d) transition metal-based nanomaterials have been excavated with good electrocatalytic activity, such as transition metal oxides, carbides, hydroxides and phosphides.^[13] Low-cost Ni-based electrocatalysts, benefiting from the active and massive nickel-containing chemical bonds, show comparable and even better inner activity for OER than noble metal compounds.^[14] Furthermore, recent researches have showed that multi-component electrocatalysts can provide additional synergic effects and tunable electronic structure, thus improving electrocatalytic properties.^[7a, 15] The coupling effect between bimetallic compounds and carbon matrix may induce further enhanced activity.

Herein, we report a facile synthesis of Ni-based bimetallic electrocatalysts (FeNi@CNF and CoNi@CNF) which are derived from nanosheet-assembled nanoflower-like MOFs (as shown in Scheme 1). MOFs sacrificed to be carbon nanoporous electro-catalysts while maintaining the original morphologies of MOF precursors. The optimized nanostructure is conducive to the

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Scheme 1. An illustration of the synthesis of bimetallic MOF-derived nano-flower electrocatalysts.

exposure of active sites. Moreover, the rough and porous morphology is essential for the entering of reactants and the release of O_2 bubbles. We also found that the morphologies may affect the activity of the catalysts. As a result, the optimized Fe-Ni@CNF exhibited a better OER performance with an overpotential of only 356 mV at 10 mA cm⁻² with a Tafel slope of 62.6 mV dec⁻¹. Moreover, FeNi@CNF showed excellent stability for continuous working at 10 mA cm⁻² for 24 hours.

Results and Discussion

The synthesis procedures of FeNi@CNF and CoNi@CNF are shown in Scheme 1. Metal ions coordinate with -CN and pyrazine to form MOFs, and PVP was utilized as a surfactant to control morphology and structures. The X-ray diffraction (XRD) patterns of the obtained MOFs were exhibited in Figure S1, the distinct peaks implied the successful synthesis of MOF precursors. Subsequently, the templates were treated with high temperature under N₂ gas atmosphere, followed with soaking acid $(0.5 \text{ M H}_2\text{SO}_4)$ to remove metal species on the surface. The morphologies of FeNi@CNF and CoNi@CNF was investigated by scanning electron microscope (SEM) and transmission electron microscope (TEM). As shown in Figure 1a, d, the nanoflower showed a diameter of approximately 600 nm, and the microscale flower is composed of dozens radially aligned 2D nanosheets with a thickness ranging from 20-60 nm. Interestingly, subtle differences can be observed between two bimetallic MOFs. MOF-FeNi showed a more complete nanoflower morphology while MOF-CoNi only showed partially formed nanoflower shape. After pyrolysis at a high temperature, the basic multi-layered morphology has been maintained while the sur-



Figure 1. SEM image of (a) MOF-FeNi, (b) FeNi@CNF, (d) MOF-CoNi, (e) CoNi@CNF, TEM images of (c) FeNi@CNF, (f) CoNi@CNF.

face of the carbon nanostructure turned rugged and uneven. Such a structure can expose additional active sites and the capillary force of the unique structure can pump the electrolyte to the surface of the electrocatalysts.^[16] Figure 1 c and 1f display the TEM images of FeNi@CNF and CoNi@CNF and tiny hollow carbon nanotube (≈ 20 nm) structure can be observed. Some metal particles were wrapped in the end of the carbon nanotubes and the carbon coats can prevent the metal active sites from being eroded in the electrolyte. Moreover, the encapsulated metal nanoparticles can form a host-guest effect, which may promote the catalytic properties of the carbon layer surround.^[17] The intricate multi-structure may play a key role in OER catalytic performance.

The X-ray diffraction (XRD) patterns of two Ni-based electro-catalysts are shown in Figure 2. The peaks centered at 26.6°



Figure 2. The XRD patterns of FeNi@CNF and CoNi@CNF.

can be indexed as (002) plane of graphitic C. As for CoNi@CNF, two obvious diffraction peaks located at 44.5° and 51.8° are attributed to the (111) and (200) planes of cubic Ni (PDF no.70-1849), and the peak at 44.2° can be assigned to the (111) planes of cubic Co (PDF no. 15-0806). While for FeNi@CNF, a slight shift can be observed, which indicate the change of lattice. Some iron atoms inserted into the original Ni crystal, forming FeNi alloy. The diffraction peaks at 43.6° and 50.8° can be indexed as (111) and (200) planes of Fe_{0.64}Ni_{0.36} (PDF no. 47-1405).

The X-ray photoelectron spectroscopy (XPS) was further conducted to investigate the chemical properties of the catalyst surface. As illustrated in Figure 3a, the XPS survey revealed the presence of Fe, Ni, C and N in FeNi@CNF. The high-resolution Fe 2p spectra showed two peaks which were assigned to Fe $2p_{1/2}$ and Fe $2p_{3/2}$. The peaks located at 711.8 eV and 726.0 eV are characteristic peaks of Fe³⁺ and the peaks located at 710.4 eV and 724.0 eV are ascribed to Fe²⁺ as shown in Figure 3a.^[18] The Ni 2p spectra displayed two main peaks and two satellite peaks. The Ni $2p_{1/2}$ can be fitted as Ni²⁺ (871.1 eV) and Ni³⁺ (874.5 eV) while the Ni $2P_{3/2}$ spectra exhibited two peaks at 853.8 eV and 855.8 eV, which were assigned to Ni²⁺ and Ni³⁺ (Figure 3b).^[19] The observed binding energy at 284.6 eV and 285.2 eV corresponding to C–C and C–N respectively (Figure 3c).^[20] The N 1s spectra revealed the presence of three

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Figure 3. (a) Fe 2p, (b) Ni 2p, (c) C 1 s, (d) N 1 s spectra of FeNi@CNF.

kinds of Nitrogen species: pyridinic N (398.5 eV), pyrrolic N (399.8 eV) and graphitic N (401.2 eV) as shown in Figure 3 d.^[21] It has been reported in the previous literature that most of *N*-bonding compound can be attributed to the electrocatalytic activity.^[22]

The number of exposed active sites is a key factor affecting performance. The Brunauer-Emmett-Teller (BET) method was conducted to measure the specific surface area and pore structure (as shown in Figure 4). A typical type-IV adsorption isotherm with a hysteresis loop can be observed, which indicated the existence of micro/mesopore.^[17] The specific surface area of FeNi@CNF is found to be 290.1 m²g⁻¹, which can be attributed to the mature pore structure of the MOFs precursors. The large specific surface is beneficial to the exposure of active sites and improve electrocatalytic properties.

The OER performance of Ni-based bimetallic electrocatalysts is tested in 1 M KOH using glass carbon electrode (GCE) as



Figure 4. The nitrogen sorption isotherm of FeNi@CNF.

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working electrode. The linear sweep voltammetry (LSV) was conducted to gain to polarization curves of FeNi@CNF, CoNi@CNF and commercial RuO2. As shown in Figure 5a, the overpotential of FeNi@CNF, CoNi@CNF and commercial RuO2 at 10 mA cm⁻² is 356 mV, 388 mV, 270 mV respectively. When the current density is larger than 38 mA cm⁻², FeNi@CNF need a smaller potential than RuO₂, which may result from the oxidation of RuO₂ at high potential. To avoid the sample deposited on GCE might be been rinsed out by the released gas bubbles, we further conducted the LVS curves on the Ni foam electrode (in Figure S2) and the trend of OER activities remained unchanged. To further investigate the synergetic effect between two different metals, the monometallic Ni@CNF were synthesized with similar method and the OER activities were studied (in Figure S3). It can be observed that the overpotential of Ni@CNF (401 mV@10 mA cm⁻²) is 49 mV and 13 mV higher than that of FeNi@CNF and CoNi@CNF respectively, indicating the synergistic effects between two metals were proved. The electrocatalytic kinetics of the Ni-based electrocatalysts was further evaluated by Tafel slopes, which was calculated through the polarization curves. The Tafel slope of FeNi@CNF $(62.6 \text{ mV dec}^{-1})$ is comparable to the commercial $RuO_2(60.0 \text{ mV dec}^{-1})$ and is much smaller than that of the CoNi@CNF (84.7 mV dec⁻¹), indicating the superior OER activity of FeNi@CNF. Electrochemical impedance spectroscopy (EIS) was conducted from 0.1 Hz to 100 kHz and the Nyquist plots of Fe-Ni@CNF and CoNi@CNF were depicted in Figure 5 c. The semicircle of FeNi@CNF is much smaller than that of CoNi@CNF, illustrating the small charge transfer resistance (R_{ct}) of the bimetallic FeNi@CNF. The superior performance of FeNi@CNF may benefit from its more complete and denser nanoflower morphology. Moreover, the long-time durability is considered as a crucial indicator for practical application. As it is demon-



Figure 5. (a) The Linear sweep voltammetry (LSV) curves of FeNi@CNF, CoNi@CNF and RuO_2 at a scan rate of 5 mV s⁻¹. (b) The Tafel slope plots of FeNi@CNF, CoNi@CNF and RuO_2 . (c) The Nyquist plots of FeNi@CNF, CoNi@CNF at the overpotential of 0.6 mV. (d) Chronopotentiometric measurements (V-t curve) of FeNi@CNF for 24 h.

strated in Figure 5d, the chronopotentiometry measurement of FeNi@CNF was measured at a constant current density (10 mA cm^{-2}) . The voltage only showed a negligible increase after 24 hours of continuous working, which implied the excellent stability of FeNi@CNF. The carbon shell formed during pyrolysis may protect the active sites from electrolyte corrosion. The SEM image of FeNi@CNF after continuous operation was shown in Figure S4 and it can be observed that the morphology of FeNi@CNF maintained very well. Moreover, the electrochemically active surface area (ECSA) was measured by double-layer capacitance (C_{dl}) as shown in Figure S5. The C_{dl} for FeNi@CNF and CoNi@CNF is 8.11 mF cm⁻² and 4.22 mF cm⁻² respectively. Therefore, FeNi@CNF owned much enhanced ECSA compared to CoNi@CNF. What's more, the C_{dl} of the bimetallic electrocatalysts is much higher than that of Ni@CNF (1.44 mF cm⁻²), indicating the superiority of bimetallic electrocatalysts.

Conclusions

To conclude, we described a facile synthesis of nanosheetassign MOFs at room temperature and the obtained bimetallic MOFs were utilized as precursors to prepare porous carbon electrocatalysts. The as-made FeNi@CNF displayed efficient OER performance with an overpotential of 356 mV and longterm stability in alkaline media. The uniform hierarchical nanosheet-assembled structure and large BET surface area is beneficial for the exposure of active sites and mass transfer. After pyrolysis, the electrocatalysts inherited the original structure of multi-layer MOFs and the surface of the FeNi@CNF became rough and porous, which may promote the access of reactants and the release of O_2 . We expect the present study to inspire the design and synthesis of intricate structure of MOFs/MOF-derived nanomaterials for various catalysis.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: electrochemistry • metal–organic frameworks • nanosheets • overpotential • oxygen evolution reaction

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