Electrocatalysis



Trimetallic Metal–Organic Framework Derived Carbon-Based Nanoflower Electrocatalysts for Efficient Overall Water Splitting

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Searching desirable cost-effective electrocatalysts for overall water splitting is of great importance for the hydrogen production industry. Here a facile synthesis of trimetallic carbon nanoflower electrocatalysts is reported which are derived from $Co^{2+}/Fe^{2+}/Ni^{2+}$ ratio adjustable metal–organic frameworks (MOFs). The unique nanosheet-assembled multiscale nanoflower morphology can enlarge the catalyst/electrolyte contact area, and the synergistic electronic effects between trimetallic components endow the trimetallic carbon nanoflower electrocatalysts with more oxygen vacancies and a higher degree of graphitization of carbon, thus showing excellent activity. The optimized Co0.2Fe0.8Ni-OCNF reaches a current density of 10 mA cm⁻² at low overpotential of 291 mV with a very small Tafel slope of 36.1 mV dec⁻¹ and 1.65 V@10 mA cm⁻² for a two-electrode water electrolysis in an alkaline solution, outperforming the commercial IrO₂ electrocatalysts. The results may pave the way to the development of more efficient multicomponent nanosheet-assembled multiscale nanomaterials for various catalytic applications.

1. Introduction

The rising consumption of fossil fuels and petroleum resources has led to serious energy and environmental issues. To liberate the energy supply from the dependency on conventional fuels, hydrogen derived from water splitting has attracted great attention as a kind of renewable, sustainable, and eco-friendly substitution.^[1] The electrocatalytic water splitting includes oxygen evolution reaction (OER) and hydrogen evolution reaction (HER).^[2] Relative to the latter, OER suffers from a slower fourelectron mechanism kinetic step, thus OER is a kernel process

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limiting the whole reaction. At present, the practical application of electrocatalytic water splitting is largely limited by the high cost of conventional electrocatalysts, such as noble metal RuO₂ and IrO₂ for OER and Pt for HER.^[3] In the past few decades, the inexpensive transition metal compounds have shown promising electrocatalytic activity.^[4] Moreover, realization of HER and OER simultaneously based on the same catalyst and electrolyte in one electrochemical cell is highly important for practical overall water splitting.^[5]

The formation of multimetallic structures is a common strategy to improve the performance of electrocatalysts, as the interactions among different compositions can, in principle, lead to synergistic effects and well-tunable electronical activities.^[6] For instance, Li et al. developed a strategy using bimetallic Prussian blue

analogues to obtain superior $\text{Co}_{1-x}\text{Fe}_x$ phosphide electrocatalysts.^[7] Zhang et al. constructed $\text{Fe}_x\text{Ni}_{1-x}$ phosphide nanosheet arrays to optimize OER performance under both alkaline and neutral conditions.^[8] Recently, there has been pioneering work revealing that the additional incorporation of a third metal into bimetallic component will lead to further enhancement in electrocatalytic activity and stability. For example, Li et al. reported that trimetallic metal–organic frameworks (MOFs) Fe/Ni/Co(Mn)-MIL-53 could lead to superior electrocatalytic performance.^[9] Huang and co-workers successfully fabricated the coralloid-like trimetallic $W_{0.5}\text{Co}_{0.5}\text{Fe}_x$ oxyhydroxide sponge on nickel foam or carbon nanotubes which shows highly active and stable electrocatalytic performance.^[10]

On the other hand, it is well known that the electrocatalyst with unique nanostructure is an important factor to improve their electrocatalytic properties. Intricate novel nanostructures such as hollow structures,^[11] nanocages,^[12] core@shell structures,^[13] 2D nanosheets,^[14] and nanoflowers^[15] have been proven to show ideal application value in the fields of catalysis, energy conversion, and storage. For instance, novel nickel-doped cobalt phosphide nanoflowers were successfully fabricated and exhibited remarkable electrocatalytic HER performance.^[16] And the 3D hierarchical porous CoP nanoflowers were also shown to be a promising HER catalyst.^[17]

MOFs have been widely developed as promising precursors, which provide a proper template for the synthesis of nanomaterials with high porosity, high surface area, and distinctive





nanostructures.^[18] MOF-derived materials are widely explored in electrocatalysis.^[19] After high temperature pyrolysis, MOFs will sacrifice and convert to nanocarbon materials while retaining their unique morphologies.^[20] In addition, it is convenience to synthesize trimetallic MOFs by controllable doping and trimetal-doped carbon materials can be obtained through pyrolysis.^[21] However, the research of trimetallic MOF-derived electrocatalysts is still at an early stage.

Herein, we innovatively exploited a trimetallic Hofmann MOFs-derived 3D hierarchical nanoflower-like electrocatalysts, which are constructed by porous oriented 2D nanosheets (Scheme 1). The optimized electrocatalyst has many merits. First, the uniform distribution of trimetallic component at the molecular level of the MOFs ensured the abundant and strong synergetic electronic effects of trimetallic metal/metal oxidebased active sites in the N-doped carbon nanoflowers. Second, the multiscale structures formed by the aligned nanosheets have abundant exposed accessible active sites, which can promote the in-plane mass transfer.^[22] Third, the synergistic effect in the trimetallic electrocatalyst can induce more oxygen vacancies and higher degree graphitization, which is beneficial for electrocatalytic properties. As a result, the trimetallic carbon nanoflowers show excellent activity and high durability for OER and overall water splitting in alkaline solution, outperforming the commercial IrO₂ electrocatalysts.

2. Results and Discussion

2.1. Material Preparation and Characterization

The Hofmann MOFs were synthesized according to the method reported in the literature with some modifications.^[23] The 3D porous crystal structure of Hofmann MOFs is shown in Figures S1–S2 in the Supporting Information. The powder X-ray diffraction (PXRD) of the Hofmann MOFs exhibited clear and sharp diffraction peaks, which indicate its good crystallinity (Figure S3, Supporting Information). By adding surfactant PVP and tuning the doping ratio of Co²⁺ and Fe²⁺, the

morphologies of the Hofmann MOFs can be facilely tuned to microscale nanoflowers, which were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Figure 1a and Figures S4-S5 in the Supporting Information, the monodisperse nanoflowers show a typical diameter of \approx 1.2 µm. The nanoflowers are constructed from dozens of 2D nanosheets with smooth surfaces which are densely interpenetrated (Figure S5a-h, Supporting Information). The nanosheets are several hundreds of nanometers in width and \approx 20–60 nm in thickness. Interestingly, there are subtle morphology differences with different doping ratio of Co²⁺ and Fe²⁺ as shown in Figure S5a-h in the Supporting Information. The bimetallic Hofmann MOFs (CoNi-NF and FeNi-NF) exhibit only partly formed nanoflowers with the bottom of their nanostructures still aggregated, while the trimetallic Hofmann MOFs all exhibit regular nanoflowers with subtle differences with the thickness of the nanosheets. Among the trimetallic Hofmann MOFs, the Co0.2Fe0.8Ni-NF shows thinnest nanosheets with the thickness of ≈ 30 nm.

After pyrolysis and oxidization, the obtained carbon samples inherited the MOF precursors' nanoflowers morphologies while the surface of the nanosheets become rough, as shown in Figure 1b-d and Figure S5i-p in the Supporting Information. Each nanosheet in the nanoflower structure exhibits porous feature, which is composed of loosely packed fine carbon nanotubes, and numerous small nanoparticles are imbedded in the nanosheets with diameters of about 20 nm. These metal nanoparticles were encapsulated in the carbon shells as shown in Figure 1e,f, which may be prevented from being corroded by the electrolyte, thus enhancing the long-term stability of electrocatalysts.^[24] In addition, there is no significant change in the morphology of the catalysts after oxidation. The unique carbon nanoflower structure is highly important for constructing highperformance catalysts by providing a large number of active sites and high surface area. The energy dispersive X-ray spectroscopy (EDS) elemental mapping exhibited a homogeneous distribution of Ni, Fe, and Co metals at the bottom of carbon nanotubes as shown in Figure 1g-j. The uniform distribution of trimetallic component at the molecular level of the MOFs



Scheme 1. A flowchart for the preparation of Hofmann MOF-derived electrocatalysts.







Figure 1. SEM images of a) Co0.2Fe0.8Ni-NF, b) Co0.2Fe0.8Ni-CNF, c) Co0.2Fe0.8Ni-OCNF, d) high magnification Co0.2Fe0.8Ni-OCNF. TEM images of e) Co0.2Fe0.8Ni-CNF, f) Co0.2Fe0.8Ni-OCNF. g-j) The EDS mapping of Ni, Fe, and Co.

can ensure the strong synergetic effects of metal/metal oxide active sites in multiscale carbon nanoflowers. Moreover, the uniform and large distribution of C, N, and O can be clearly observed in Figure S6 in the Supporting Information.

The X-ray diffraction (XRD) pattern of carbon nanoflower samples is shown in the **Figure 2a** and it confirms the presence of crystalline carbon and different metal/metal oxide/ alloy nanoparticles. For the sample Co0.8Fe0.2Ni-OCNF, the peak located at 26.6° was indexed to the (002) plane of graphitic carbon, the diffraction peaks at 37.3° was indexed to the (111) plane of NiO (PDF no.73-1519), and the peaks at 44.5° and 51.8°can be assigned to (111) and (200) planes of metallic Ni (PDF no.04-0850). While for the sample Co0.2Fe0.8Ni-OCNF, the main diffraction peaks are at 26.6°, 44.5°, 47.4°, and 51.8°, which are indexed to the (002) plane of graphitic carbon, (111) and (200) planes of metallic Ni (PDF no.04-0850), and (101) plane of Co (PDF no.89-4308).

The element compositions of Co0.2Fe0.8Ni-OCNF were further analyzed by X-ray photoelectron spectroscopy (XPS). As shown in Figure 2b, the fitted peaks of Ni²⁺ (located at 854.5 and 872.3 eV) were attributed to NiO species, and the peaks at 855.9 and 874.0 eV were ascribed to Ni³⁺,^[25] together with two satellite peaks at 861.5 and 880.0 eV, which is consistent with the XRD pattern. The Co 2p spectrum exhibits Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks respectively. The Co $2p_{1/2}$ can be deconvoluted to Co^{2+} and Co^{3+} oxidation state at 797.8 and 795.6 eV, and the peaks at 782.1 and 780.1 eV account for the $Co^{2+} 2p_{3/2}$ and Co³⁺ 2p_{3/2} respectively as shown in Figure 2c.^[10] The Fe 2p spectrum reveals the coexistence of Fe^{2+} and Fe^{3+} . The peaks at 710 and 724.0 eV are characteristic peaks of Fe²⁺ and the peaks centered at 712.3 and 725.4 eV can be assigned to Fe^{3+} , which may be attributed to the formation of Fe_2O_3 .^[26] As shown in Figure 2e and Figure S7 in the Supporting Information, the deconvolution of O 1s spectrum revealed the existence of three bonds including metal-oxygen bond (O1, 529.8 eV), oxygen vacancy (O2, 531.5 eV), and carbon-oxygen bond (O3, 533.0 eV),^[24] in which the oxygen vacancy and metal-oxygen bond are dominant. Oxygen vacancy is known to lead to the improvement of the conductivity.^[27] The content of the oxygen vacancy was further calculated in XPS analysis, the oxygen vacancy content for bimetallic FeNi-OCNF, CoNi-OCNF and trimetallic Co0.2Fe0.8Ni-OCNF is 47.0%, 43.6%, and 51.0%, respectively. The result indicated that the strong synergistic effect in trimetallic electrocatalyst may induce more oxygen vacancies, thus boosting the catalytic properties. As shown in Figure S8 in the Supporting Information, the C 1s spectrum of Co0.2Fe0.8Ni-OCNF can be divided into two peaks located at 284.7 and 285.2 eV, suggesting the C-C and C-N structure in the sample,^[28] and the N spectrum can be deconvoluted to four peaks centered at 398.2, 400.0, and 401.0 eV, corresponding to







Figure 2. a) XRD patterns of carbon nanoflower catalysts with various Co/Fe ratio. b) Ni 2p, c) Co 2p, d) Fe 2p, e) O 1s XPS spectrum of Co0.2Fe0.8Ni-OCNF.

pyridinic N, pyrrolic N, and graphitic N respectively.^[29] The formation trimetallic metal/metal oxide in the nanoflower electrocatalysts can provide numerous active sites and synergy effect between different metallic component, thus promoting efficient electron transfer and improve the OER and HER processes.

Figure S9 in the Supporting Information shows the XPS survey scan of CoxFe1-xNi-OCNF and the quantitative analyses of metal content were characterized by XPS (Table S1, Supporting Information). The lattice fringes with a distance of 0.20 and 0.21 nm can be clearly observed in the TEM images of Co0.2Fe0.8Ni-OCNF, corresponding to (111) plane of Ni and (200) plane of NiO (Figure S10 in the Supporting Information, which further confirms the metal/metal oxide composition. The porosity of electrocatalysts was studied by N2 adsorption isotherm analysis in Figure S11 in the Supporting Information; they are all type IV adsorption isotherm, and adsorption hysteresis can be observed. This phenomenon is related to pore size, which reveals the structure of both micropore and mesopore. The specific surface area of Co0.2Fe0.8Ni-OCNF, Co0.67Fe0.33Ni-OCNF, CoNi-OCNF, and FeNi-OCNF was 214.8, 236.6, 353.6, and 283.1 $m^2\ g^{-1}$ respectively, the cumulative pore volume is 0.894, 0.845, 1.344, and 1.069 $\text{cm}^3 \text{g}^{-1}$ respectively, and the diameter of the pore size is 16.6, 14.3, 15.2, and 15.1 nm, respectively. High porosity can offer affluent active sites and also promote the diffusion of ions in the electrolyte to accelerate the electrocatalytic process.

The Raman spectrum was conducted to investigate to carbon content of the electrocatalysts. As shown in Figure S12 in the Supporting Information, the Raman spectrum of Co0.2Fe0.8Ni-OCNF, CoNi-OCNF and FeNi-OCNF displayed two distinct peaks at around 1350 and 1580 cm⁻¹, corresponding to the D band and G band of carbon. The integrated I_D/I_G ratio of Co0.2Fe0.8Ni-OCNF, CoNi-OCNF, and FeNi-OCNF is 1.27, 1.35, and 1.31. The low I_D/I_G ratio of trimetallic Co0.2Fe0.8Ni-OCNF implied the higher degree of graphitization than bimetallic CoNi-OCNF and FeNi-OCNF.

2.2. Electrocatalytic Performance

The OER activity of CoxFe1-xNi-OCNF was measured in 1 м KOH solution using a three-electrode system. Linear sweep voltammetry (LSV) was conducted to attain polarization curves of catalysts at a scan rate of 5 mV s⁻¹ with 90% iR compensation (where i refers to the current and R refers to electrolyte resistance). The oxidation process improves the capability of charge transfer. The electrochemical performance of CoxFe1xNi-OCNF is compared to CoxFe1-xNi-CNF, and it can be clearly observed that the overpotential at 10 mA cm⁻² declined sharply after oxidation (Figure S13a, Supporting Information). As indicated in **Figure 3**a, the overpotential at 10 mA cm⁻² was shown as follows: CoNi-OCNF (341 mV), Co0.8Fe0.2Ni-CNF (329 mV), Co0.67Fe0.33Ni-OCNF (308 mV), Co0.5Fe0.5Ni-OCNF (304 mV), Co0.2Fe0.8Ni-OCNF (291 mV), Co0.1Fe0.9Ni-OCNF (303 mV), FeNi-OCNF (305 mV), and commercial IrO2 (309 mV). Especially when the source ratio of Co/Fe/Ni was 1:4:5, the overpotential reached below 300 mV, highlighting the optimized performance by trimetallic component adjustment. The performance was compared with the best OER electrocatalysts reported recently (Table S2, Supporting Information); numerous electrocatalysts exhibit the overpotential above 300 mV at a current density of 10 mA cm^{-2.[30]} It can be calculated that when the content of Fe²⁺ was higher than Co²⁺, the improvement of overpotential after oxidation is more obvious, which may due to the fact that the iron element was converted to Fe₂O₃ during oxidation, and the existence of Fe₂O₃ improved the OER activity remarkably.^[31] The overpotential of Co0.2Fe0.8Ni-OCNF is lower than that of commercial IrO₂, and Co0.2Fe0.8Ni-OCNF can reach a much higher current density than IrO₂. Tafel plot was used to get a further understanding of catalytic kinetics and activity of OER, which was based on polarization curves. The Tafel slope of CoxFe1-xNi-CNF was all around 70 mV dec⁻¹ (Figure S13b, Supporting Information), while the Tafel curves showed a smaller Tafel value after oxidation. As shown in Figure 3b, the Tafel slopes were all around







Figure 3. a) Polarization curves of CoxFe1-xNi-OCNF and commercial IrO₂ in 1 KOH solution for OER. Scan rate: 5 mV s⁻¹. b) Tafel plots of CoxFe1-xNi-OCNF and IrO₂ in 1 KOH solution. c) EIS Nyquist plots of CoxFe1-xNi-OCNF at a potential of 0.6 V. d) Chronopotentiometric measurements (*I*-*T* curve) of Co0.2Fe0.8Ni-OCNF at the constant voltage of 1.50 V versus RHE for 12 h.

40 mV dec⁻¹ except for CoNi-OCNF, suggesting the satisfactory OER kinetics, which can be ascribed to the combined effect of synergistic properties of trimetallic components and the unique nanoflower morphology. The Tafel slope of Co0.2Fe0.8Ni-OCNF is 36.1 mV dec⁻¹, which is smaller than commercial IrO2 and most reported OER electrocatalysts, indicating an advantageous kinetics for electrocatalytic OER. Furthermore, electrochemical impedance spectroscopy (EIS) was conducted to investigate the kinetics of CoxFe1-xNi-OCNF. As shown in Figure 3c, the catalysts exhibited a lower charge transfer resistance, which means a much faster charge transfer with the iron doped, the existence of iron provides more edge sites. The CoxFe1-xNi-OCNF showed charge resistance of $10-30\Omega$, except for CoNi-OCNF. The long-term stability of the catalyst plays an important role in practical applications; as shown in Figure 3d, when working at a constant voltage, the current density even shows a small increment. This phenomenon may be caused by a small amount of activation process during this the *I*-*T* test.^[32] It is speculated that the stability of the catalyst is derived from its unique microscopic flower-like morphology, and the carbon shells encapsulated around the metal/metal oxide nanoparticles can slower the corrosion rate of the active sites in the electrolyte. Furthermore, we characterize the structural stability after I-T test, the morphology of Co0.2Fe0.8Ni-OCNF remained

the same after 12 hours' operation as shown in Figure S14 in the Supporting Information, which further illustrates that the morphology of CoxFe1-xNi-OCNF contributes to its stability. When the LSV curve after 1000 potential sweeps was recorded to measure the cycling durability (Figure S15, Supporting Information), it only showed slight change from the initial one, demonstrating high durability of Co0.2Fe0.8Ni-OCNF in alkaline electrolyte. Furthermore, double layer capacitance (C_{dl}) is often used to indicate the electrochemical active surface area (ECSA); the enhancement of ECSA represents an increase in electrocatalytic properties.^[33] Therefore, the cyclic voltammogram is conducted to calculate the C_{dl} of the electrocatalysts. Figure S16 in the Supporting Information shows the CV curves of Co0.2Fe0.8Ni-OCNF, FeNi-OCNF, and CoNi-OCNF at different scan rates, and the $C_{\rm dl}$ of Co0.2Fe0.8Ni-OCNF, FeNi-OCNF, CoNi-OCNF is 9.01, 6.43, 2.19 mF cm⁻² respectively. It is clear that Co0.2Fe0.8Ni-OCNF, as a trimetallic MOFderived electrocatalyst, has much higher electroactive sites than bimetallic electrocatalysts, which leads to its superior catalytic performance.

HER tests were performed to evaluate the bifunctional electrocatalytic activity. As shown in Figure S17 in the Supporting Information, Co0.2Fe0.8Ni-OCNF possesses optimum performance—it demands an overpotential of -259 mV to







Figure 4. a) The polarization curves of Co0.2Fe0.8Ni-OCNF loading on Ni foam and bare Ni foam simultaneously as cathode and anode for overall water splitting. b) Chronopotentiometric curve of Co0.2Fe0.8Ni-OCNF at 10 mA cm⁻². c) An illustration of water splitting device driven by an AA battery with a nominal voltage of 1.5 V. d) An optical photograph of H₂ and O₂ bubbles generated on Ni foam substrate.

reach the current density at 10 mA cm⁻², and the Tafel slope is 94.2 mV dec⁻¹. While the overpotential of FeNi-OCNF, CoNi-OCNF, and Co0.8Fe0.2Ni-OCNF is -293.6, -273.6, and -272.0 mV at 10 mA cm⁻² respectively, which illustrates that when the ratio of cobalt to iron source is 1:4, the fabricated electrocatalyst produces the strongest synergistic effects and shows the best properties both in OER and HER. The EIS was conducted to further observe their HER kinetics; Co0.2Fe0.8Ni-OCNF exhibits the smallest semicircle radius, corresponding to the smallest charge resistance, so Co0.2Fe0.8Ni-OCNF has the best electron transfer efficiency during both OER and HER process. Due to the excellent bifunctional properties of Co0.2Fe0.8Ni-OCNF, the overall water splitting was further explored in 1 M KOH on Ni foam substrate. A two-electrode system was used where hydrogen and oxygen are generated at the cathode and anode respectively. As shown in Figure 4a, the cell voltage reaching a current density at 10 mA cm⁻² is 1.65 V, which is much smaller than that of bare Ni foam (1.88 V) in water splitting. The small cell voltage is comparable to the best water splitting electrocatalysts reported recently in Table S2 in the Supporting Information. The long-term durability was displayed through chronopotentiometric method at 10 mA cm⁻²;

the curve in Figure 4b showed no obvious degradation after 24 hours, which exhibited excellent durability of Co0.2Fe0.8Ni-OCNF for overall water splitting. Moreover, the water splitting cell can be powered by a 1.5 V AA battery. A prototype water electrolysis device was assembled as illustrated in Figure 4c, several gas bubbles can be observed on the electrodes, which further proves the efficiency of the electrocatalyst Co0.2Fe0.8Ni-OCNF. After 24 hours of continuous testing, a large amount of bubbles can still be released from the catalyst surface as demonstrated in Figure 4d. It can be observed that the catalyst has no loss with the production of a large amount of hydrogen and oxygen. This result implies the structural stability and the application value of Co0.2Fe0.8Ni-OCNF, which may be due to the unique porous nanoflower structure, high specific surface area, and the uniformly distributed trimetallic active sites.

3. Conclusions

To sum up, we innovatively synthesized porous nanosheetassembled nanoflower-like MOF-derived electrocatalysts for overall water splitting through a controllable pyrolysis–oxidation ADVANCED SCIENCE NEWS _____

strategy. The electrocatalysts successfully inherited a compact, multilayered and hierarchical structure of the precursors. In particular, Co0.2Fe0.8Ni-OCNF can reach 10 mA cm⁻² at a cell voltage of 1.65 V with excellent durability and it can be driven by an AA battery. The excellent catalytic property can be attributed to the unique nanostructure and the trimetallic composition modulating strategy. The carbon matrix can act as a buffer to reduce changes in the nanostructure during electrocatalysis while the trimetallic metal/metal oxide synergistically endows Co0.2Fe0.8Ni-OCNF with remarkable bifunctional properties. These results demonstrate the promising combined strategy of trimetallic component tuning and morphologically controllable MOF nanoflowers as effective templates and precursors to produce trimetallic metal/metal oxide@carbon nanoflower electrocatalysts, which will lead to more efficient electrocatalytic performance.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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