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Ferrocene-MOFs: Optimizing OER Kinetics for Water Splitting

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ABSTRACT: Optimizing the adsorption and desorption kinetics of oxygen evolution reaction (OER) is crucial for efficient overall water splitting. Herein, we report a series of porous ferrocene-based metal-organic framework (MFc-MOF, M = Co, Ni, Fe, Mn) nanoflowers featuring a close $\pi-\pi$ stacking lattice structure as model catalysts, and explore the structure-activity relationship. Operando electrochemical impedance spectroscopy implies that the synthesized CoFc-MOF@NF facilitates intermediate adsorption and desorption. It exhibits an ultralow overpotential of 189 mV at 10 mA cm⁻² and maintains stability for 250 h. In an overall water splitting device, when CoFc-MOF@NF serves as the anode, it yields a significantly lower cell voltage than commercial RuO₂ and shows excellent stability at 100 mA cm⁻² for 100 h. In situ



Raman spectroscopy reveals that the CoFc-MOF@NF surface transforms into CoFeOOH, the OER-active species, while preserving the MOF framework. The inner MOF's ferrocene units act as efficient electron-transfer mediators. These findings highlight CoFc-MOF@NF's potential as a leading catalyst for sustainable water splitting hydrogen production, combining high catalytic activity, rapid kinetics, and robust stability. This work presents a new approach to balance activity and stability in MOF-based OER catalysts.

1. INTRODUCTION

Electrocatalytic water splitting has gained widespread acclaim as a sustainable and eco-friendly method for hydrogen production. It holds great promise in the pursuit of carbon neutrality and offers solutions to the challenges presented by global warming.^{1–3} However, the progress of electrocatalytic water splitting technology is currently hampered by the substantial energy consumption of the oxygen evolution reaction (OER). This reaction is marked by a high overpotential, which necessitates significant energy input.^{4–6} Therefore, the development of non-noble metal electrocatalysts that possess both high activity and durability becomes pivotal for enhancing OER efficiency. This advancement could potentially unlock the full potential of electrocatalytic water splitting, making it a more viable and scalable solution for clean energy production.

Various transition metal-based compounds, including transition metal oxides, hydroxides, sulfides, nitrides, phosphides, and metal–organic frameworks (MOFs) nanomaterials, have been explored as potential OER electrocatalysts.^{7–13} Among them, MOFs, periodically assembled from organic ligands and metal ions or clusters, have drawn substantial attention in the field of catalysis. This is attributed to their tunable nanoporous architectures, well-dispersed and accessible metal sites, and the ability to customize heteroatomic functional groups.^{14,15} However, the poor electrical conductivity of organic ligands and the restricted accessibility of

active metal centers in MOFs impede charge and mass transfer, resulting in sluggish reaction kinetics. Conventionally, MOFs are carbonized via high-temperature pyrolysis to boost charge transport for use as OER electrocatalysts. But this energy-consuming procedure can trigger shrinkage and aggregation, damaging the nanostructure, decreasing active sites, and ultimately weakening the OER catalytic performance.¹⁶ Moreover, MOFs usually face poor catalytic stability because of structural degradation during the electrochemical oxidation process.¹⁷ Consequently, devising highly efficient OER electrocatalysts that capitalize on the structural merits of MOF materials still poses a formidable challenge.

Ferrocene (Fc), an electron-rich transition-metal compound, is renowned for its high stability and aromaticity.¹⁸ It features two cyclopentadienyl rings, forming a sandwich structure with a π -electron cloud. This structure potentially facilitates through space charge transport pathways via $\pi - \pi$ interactions in subsequent organic crystals.¹⁹ Ferrocene and its derivatives possess excellent conductivity, high reversible redox properties, and chemical stability.^{20–22} For instance, the Budnikova group

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Figure 1. (a) Schematic illustration of the synthesis of MFc-MOF@NF (M = Co, Ni, Fe, Mn). (b) XRD patterns, (c) FTIR spectra, and (d) CoFc-MOF@NF simulated structure.

reported that a MOF synthesized from ferrocene diphosphonate and a 4,4'-bipyridine ligand shows excellent hydrogen evolution reaction (HER) performance.²³ Similarly, Liu and co-workers demonstrated that 2D MOF nanosheets, integrating electron-rich ferrocene-based organic linkers and nickel nodes, exhibit remarkable activity and durability for the oxygen evolution reaction (OER).²⁴ Hence, MOFs constructed from ferrocene-containing ligands are anticipated to exhibit high electrochemical performance.

Interestingly, during the OER process, numerous MOFs experience in situ structural changes. A strong electric field often drives this transformation, ultimately causing the MOF matrix to break down. Under alkaline conditions, the resulting metal (oxy)hydroxides are identified as the true active species.^{25,26} In this scenario, the MOF scaffold not only acts as a precursor but also plays a crucial role in regulating the evolved nanostructured catalyst layer.²⁷ Despite recent efforts to elucidate the catalytic species, a deeper understanding of the intrinsic role of MOF matrices in structural transformation and OER properties remains essential yet challenging.

In this work, we fabricate a series of ferrocene-based MOF nanoflowers (referred to as MFc-MOF@NF, where M = Co, Ni, Fe, Mn) on conductive Ni foam (NF) via a straightforward hydrothermal method for efficient OER. Among them, CoFc-MOF@NF stands out with a low overpotential of 189 mV at 10 mA cm⁻², outperforming the benchmark RuO₂ (244 mV) and several recently reported MOF catalysts. Moreover, CoFc-MOF@NF demonstrates exceptional stability without significant decay over 250 h. Importantly, the assembled electrolyzer using CoFc-MOF@NF and commercial Pt/C achieves ultralow cell voltages of 1.45 and 1.67 V to drive current densities of 10 and 100 mA cm⁻² for overall water splitting under alkaline conditions, surpassing the performance of $RuO_2^{(+)}||Pt/$ C⁽⁻⁾. Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and in situ Raman spectroscopy characterizations reveal that the MOF surfaces undergo structural transformation to form metal oxyhydroxides in situ during the OER process. The surface-formed CoFeOOH serves as the actual active material, while the retained ferrocene units within the MOF function as efficient electron transfer

mediators, contributing to the observed OER performance. The study positions CoFc-MOF@NF as a promising candidate for advancing renewable energy technologies.

2. EXPERIMENTAL SECTION

2.1. Synthesis of MFc-MOF@NF (M = Co, Ni, Fe, Mn). Initially, a piece of nickel foam $(2.2 \text{ cm} \times 3.0 \text{ cm})$ was sequentially cleaned with 0.5 M diluted H₂SO₄, deionized water, and ethanol by ultrasonication for 15 min to remove impurities, respectively. A series of MFc-MOF@NF (M = Co, Ni, Fe, Mn) were fabricated via a facile hydrothermal approach. For instance, to prepare CoFc-MOF@ NF, 0.4 mmol of Co(NO₃)₂·6H₂O and 0.4 mmol of 1,1'-ferrocene dicarboxylic acid (FcDA) were added to 15 mL of DMF and stirred vigorously for 30 min. Subsequently, 1 mL of ethanol was incorporated to continue blending for 15 min, followed by the rapid addition of 1 mL of deionized water. The resulting solution was then transferred into a 20 mL Teflon-lined stainless-steel autoclave, and the pretreated NF was vertically immersed, and maintained at 140 °C for 12 h. After cooling to room temperature, the sample was washed with deionized water and ethanol, and then dried in a vacuum oven at 60 °C. The other MFc-MOF@NF (M = Ni/Fe/Mn) were synthesized in a similar process, except that the metal salts employed in the hydrothermal treatment were substituted with the corresponding Ni, Fe, or Mn salts.

2.2. Synthesis of RuO₂ and Pt/C on NF. 2 mg of RuO₂ or 20 wt % Pt/C was separately dispersed into a mixture consisting of 200 μ L of deionized (DI) water, 200 μ L of ethanol, and 5 μ L of 5 wt % Nafion. The resulting mixtures were then ultrasonicated for 30 min to ensure the formation of a homogeneous ink. Finally, the entire volume of each ink was carefully pipetted onto the surface of a 1 cm × 1 cm nickel foam (NF) substrate and left to air-dry naturally.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Structural Analysis. The MFc-MOF@NF was synthesized via a straightforward hydrothermal method. In this process, metal ions $(Co^{2+}, Ni^{2+}, Fe^{3+}, Mn^{2+})$ were coordinated with 1,1'-ferrocene dicarboxylic acid as the organic linker, as illustrated in Figure 1a. Powder X-ray diffraction (XRD) was initially employed to analyze the crystal structure and atomic arrangement of the synthesized MOFs. Figure 1b shows that the diffraction patterns of all synthesized MFc-MOF@NF samples match those reported in the



Figure 2. (a) SEM (inset: the lower magnification SEM image), (b) TEM image, (c) HR-TEM image, (d) SAED pattern, (e) elemental mapping images of CoFc-MOF@NF, and (f) N_2 adsorption-desorption isotherms and pore-size distribution curves of CoFc-MOF@NF.



Figure 3. (a) XPS survey spectra of MFc-MOF@NF. High-resolution XPS of (b) Co 2p, (c) Ni 2p, (d) Fe 2p, and (e) Mn 2p in the corresponding MFc-MOF@NF samples. (f) High-resolution Fe 2p XPS spectra of MFc-MOF@NF.

literature.²⁸ Crystal structure analysis indicates that these MFc-MOFs possess a monoclinic topology within the C2/m space group. Figure 1d depicts the ligands and MOF structure of CoFc-MOF@NF, emphasizing the interlayer spacing. In CoFc-MOF@NF, cobalt atoms are densely arranged in an octahedral pattern along the (200) plane. There are two distinct octahedral Co sites: Co-1 has a distorted octahedral geometry, coordinated by four oxygen atoms from water molecules at the equatorial position and two carboxyl oxygen atoms at the apical position. Conversely, the Co-2 atom is octahedrally coordinated by two apical oxygen atoms from water molecules and four equatorial carboxyl oxygen atoms (Figure S2). These pseudo-octahedra are interconnected through numerous edgeand corner-centered connections along the crystallographic plane, forming three-dimensional metal layers separated by ferrocene ligands. The cyclopentadiene (Cp) rings between the layers are closely stacked, exhibiting strong $\pi - \pi$ stacking interactions (Figure S3). The abundant edge/corner structure

increases the number of effective catalytic sites. Meanwhile, the electron-rich ferrocene ligands, through $\pi - \pi$ interactions, establish through-space charge-transport pathways.^{29,30} This synergy enhances mass transport, thereby improving the electrocatalytic performance.

The successful coordination of metal ions with the carboxylic groups of the ferrocene units was verified by Fourier transform infrared (FT-IR) spectroscopy (Figure 1c). When compared to ferrocene dicarboxylic acid (FcDA), the stretching vibrations of the C=O group at 1685 cm⁻¹ and the C-O group at 1299 cm⁻¹ completely vanish in these metal-organic frameworks (MOFs). Instead, a new $-COO^-$ vibrational band emerges at 1583 cm⁻¹ after MOF formation. This indicates that FcDA has successfully coordinated to the metal-oxygen clusters through the deprotonation of the carboxyl group.²⁴ Notably, the characteristic bands at 495 and 1030 cm⁻¹, corresponding to the cyclopentadiene (Cp) ring of the ferrocene unit, remain well-preserved. This suggests

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Figure 4. OER activities of prepared catalysts in 1.0 M KOH solution. (a) LSV polarization curves. (b) Corresponding Tafel slopes. (c) Comparison with the overpotentials and Tafel slopes of recently reported catalysts for OER activity at 10 mA cm⁻². Bode plots of (d) CoFc-MOF@NF, (e) NiFc-MOF@NF, (f) FeFc-MOF@NF and (g) MnFc-MOF@NF at different potentials (vs RHE). (h) Double-layer capacitance (C_{dl}) plots. (i) Chronopotentiometry of CoFc-MOF@NF at 10 mA cm⁻².

that the ferrocene structure remains intact within the MOFs. Furthermore, electron paramagnetic resonance (EPR) tests confirmed the presence of metal cation defects in MFc-MOF@ NF (M = Co, Ni, Fe, Mn).³¹⁻³⁴ These defects modulate the electronic structure, enhance electrical conductivity, and thus facilitate rapid charge transport, ultimately improving the catalytic performance (Figure S4).³⁵

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were utilized to explore the morphology and microstructure of the catalysts. As depicted in Figures 2a and S5, CoFc-MOF@NF, NiFc-MOF@NF, FeFc-MOF@NF, and MnFc-MOF@NF all display a unique 3D nanoflower morphology constructed from interconnected nanosheets. The TEM image in Figure 2b further validates the nanosheet structure of CoFc-MOF@NF. This architecture offers a large number of electroactive sites and helps dislodge large gas bubbles during the OER process, thus enhancing the electrocatalytic performance. The high-resolution TEM (HR-TEM) images in Figure 2c reveal distinct lattice fringes. The interplanar spacings of 0.27 and 0.31 nm correspond to the (402) and $(\overline{2}02)$ planes of CoFc-MOF@NF, respectively. The selected area electron diffraction (SAED) pattern in Figure 2d identifies the same lattice planes, further verifying the successful synthesis of CoFc-MOF@NF. Energy Dispersive X-ray spectroscopy (EDS) detected the presence of Co, Fe, C, and O elements. The molar ratio of Co to Fe was calculated to be approximately 1:1 (Figure S6). Additionally, the corresponding elemental mapping results in Figure 2e confirm the uniform distribution of Co, Fe, C, and O throughout the structure. Furthermore, the specific surface area and pore-size

distribution of MFc-MOF@NF were evaluated using the Brunauer–Emmett–Teller (BET) method (Figures 2f and S7). CoFc-MOF@NF exhibited the lowest BET surface area of 88.83 m² g⁻¹, which implies a high utilization rate of active sites.³⁶ The relatively large pore size of CoFc-MOF@NF promotes more efficient diffusion of electrolyte ions, thereby facilitating mass and charge transport and accelerating reaction kinetics.³⁷

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X-ray photoelectron spectroscopy (XPS) was employed to analyze the surface chemical composition and elemental valence states of the synthesized MFc-MOF@NF. As depicted in Figure 3a, the full-range spectra of MFc-MOF@NF clearly show the presence of Fe, C, O, and the respective transition metals (Co, Ni, Fe, or Mn). In the high-resolution Co 2p spectrum of CoFc-MOF@NF (Figure 3b), the peaks at 780.69 and 796.59 eV correspond to the $2p_{3/2}$ and $2p_{1/2}$ states of Co²⁺, respectively. The satellite peaks at 785.59 and 802.24 eV indicate the existence of antibonding orbitals between Co and O atoms, further validating the formation of $Co-O_6$ sites.³⁴ Similarly, in the Ni 2p spectrum of NiFc-MOF@NF (Figure 3c), the peaks at 854.90 and 872.25 eV are ascribed to the Ni $2p_{3/2}$ and Ni $2p_{1/2}$ states of Ni²⁺ in the Ni-O bond, respectively. The accompanying satellite peaks further confirm the antibonding interactions between Ni and O atoms, verifying the formation of the Ni-O₆ site.³⁸ In the Fe 2pregion of FeFc-MOF@NF (Figure 3d), the two prominent peaks at 708.47 and 721.10 eV correspond to Fe²⁺ within the ferrocene unit,^{24,26} while the peaks at 711.51 and 723.42 eV are attributed to Fe³⁺.³⁹ Notably, compared to those in pristine FcDA (Figure 3f), the binding energies of the Fe species in



Figure 5. (a) High-resolution Co 2*p* spectra and (b) high-resolution Fe 2*p* spectra of CoFc-MOF@NF post-OER test. In situ Raman spectra (c) 3D projection image and (d) 2D Raman intensity image of CoFc-MOF@NF. (e) OER mechanistic illustration of CoFc-MOF/CoFeOOH.

FeFc-MOF@NF show a slight increase, suggesting that the Fc group might play a role in electronic regulation.⁴⁰ Moreover, in the MnFc-MOF@NF (Figure 3e), the peaks at 640.78 eV $(2p_{3/2})$ and 652.45 eV $(2p_{1/2})$ are associated with Mn²⁺ coordinated with the oxygen atoms of the carboxylic groups within the ferrocene units.⁴¹

3.2. OER Performance in Alkaline Medium. The electrocatalytic activities of different MFc-MOF@NF samples for OER were initially assessed via linear sweep voltammetry (LSV) in a standard three-electrode system, with a 1.0 M KOH aqueous electrolyte. As shown in Figure 4a, CoFc-MOF@NF exhibited the lowest overpotential, merely 189 mV at a current density of 10 mA $\rm cm^{-2}$. Notably, the catalytic activities of NiFc-MOF@NF (203 mV), FeFc-MOF@NF (212 mV), and MnFc-MOF@NF (227 mV) were also substantially lower than that of the advanced RuO₂ catalyst (244 mV). Even at a high current density of 100 mA cm⁻², the CoFc-MOF@NF, NiFc-MOF@NF, FeFc-MOF@NF, and MnFc-MOF@NF catalysts retained remarkable electrocatalytic activity, with overpotentials of 239, 249, 263, and 275 mV, respectively. These findings highlight the outstanding OER activity of MFc-MOF@NF. Figure 4b shows that the Tafel slopes of the synthesized MFc-MOF@NF series are significantly lower than that of RuO2 (80.6 mV dec⁻¹), indicating that MOFs featuring ferrocene ligands facilitate rapid OER kinetics.^{42,43} Specifically, CoFc-MOF@NF has a Tafel slope of 40.38 mV dec⁻¹, lower than those of NiFc-MOF@NF (40.75 mV dec⁻¹), FeFc-MOF@NF $(43.55 \text{ mV dec}^{-1})$, and MnFc-MOF@NF $(43.68 \text{ mV dec}^{-1})$, highlighting its superior kinetic performance during the OER process.44 Moreover, MFc-MOF@NF constructed from ferrocene ligands significantly outperforms the majority of the currently reported advanced OER electrocatalysts (Figure 4c and Table S1).

Operational electrochemical impedance spectroscopy (EIS) serves as an effective means to elucidate the kinetics of reactant adsorption and desorption on electrode surfaces during electrochemical reactions.⁴⁵ The Nyquist plots of MFc-MOF@NF, measured in 1.0 M KOH over a potential range from 1.10 to 1.60 V, are illustrated in Figure S8. At a potential of 1.40 V (vs RHE), all MFc-MOF@NF catalysts display a distinct semicircle, signaling the initiation of electrocatalytic

OER. The corresponding equivalent circuit models are provided in Figure S9. Within the applied potential range, the charge transfer resistance (R_{ct}) of CoFc-MOF@NF is significantly lower than that of other MFc-MOF@NF catalysts (M = Ni, Fe, Mn). This indicates that oxygen-containing reactive species adsorb more rapidly during the OER process on CoFc-MOF@NF. Moreover, as the potential increases, the semicircle of CoFc-MOF@NF diminishes most rapidly, suggesting that CoFc-MOF@NF is more prone to polarization.⁸ Similar trends are observable in the phase peak values within the Bode diagram (Figures 4d–g and S10). Notably, as the potential rises, the phase peak frequency values for NiFc-MOF@NF and FeFc-MOF@NF shift more rapidly toward higher frequencies compared to CoFc-MOF@NF. This leads to overly strong adsorption behavior, impeding the desorption of intermediates.⁴⁶ Conversely, the phase peak frequency of MnFc-MOF@NF shifts the slowest toward higher frequencies, indicating weaker adsorption of intermediates. The phase peak frequency of the CoFc-MOF@NF catalyst shifts toward higher frequencies at a moderate pace. This implies favorable adsorption and desorption behavior of intermediates, thus enhancing the OER performance.

Moreover, CoFc-MOF@NF exhibits a superior electrocatalytically active surface area (ECSA), which is determined by the double-layer capacitances ($C_{\rm dl}$) obtained from CV measurements in the nonfaradaic region (Figures 4h and S11). The activated CoFc-MOF@NF has the highest $C_{\rm dl}$ value of 10.46 mF cm⁻², surpassing those of NiFc-MOF@NF (7.68 mF cm⁻²), FeFc-MOF@NF (3.43 mF cm⁻²), and MnFc-MOF@ NF (1.59 mF cm⁻²). This indicates that CoFc-MOF@NF exposes more catalytic active sites, thereby accelerating electron and mass transfer during the OER process.⁴⁷ Longterm stability is a crucial parameter for assessing electrocatalytic performance in practical applications. As illustrated in Figure 4i, CoFc-MOF@NF sustains a constant potential for over 250 h with minimal decay at 10 mA cm⁻², demonstrating exceptional catalytic stability for water oxidation.

3.3. Analysis of the Active Phase and Dynamic Surface Reconstruction. To elucidate the phase changes of MOFs during the OER process and identify the intrinsic active species, SEM, TEM, and XPS characterizations were

performed on the post-OER CoFc-MOF@NF. As depicted in Figure S12a-c, although the nanosheets show some degradation with a noticeably rougher and bumpier surface, the overall 3D nanoflower morphology is preserved after electrocatalysis. This is likely due to the surface reconstruction of CoFc-MOF@NF during the OER process.^{26,48} The HR-TEM image of CoFc-MOF@NF after the OER test (Figure S12d) reveals the coexistence of the MOF and oxyhydroxide layers. The appearance of additional distinct lattice fringes corresponds to CoFeOOH (JCPDS: 08-0098), indicating that the MOF has been partially transformed into CoFeOOH. This transformation is further corroborated by the SAED results of the post-OER sample (Figure S12e). EDS analysis of CoFc-MOF@NF after OER (Figure S12f) confirms the presence of carbon, suggesting the retention of the organic framework, possibly due to incomplete structural evolution, consistent with previous findings.^{26,49} The preservation of the MOF structure leverages the inherent advantages of MOF materials, with the ferrocene unit serving as an efficient electron transfer medium. Additionally, the MOF structure facilitates the formation of metal hydroxides, preventing the aggregation of active species and thus exposing more catalytically active

sites.^{24,2} The XPS spectra of MFc-MOF@NF after the OER test revealed changes in surface chemical states (Figures 5a,b and S13–S14). As shown in Figure 5a, the Co 2p XPS spectrum of CoFc-MOF@NF post-OER displayed higher binding energies compared to the fresh CoFc-MOF@NF, and new Co³⁺ peaks appeared at 779.54 and 794.52 eV, indicating the formation of CoOOH during the OER process.^{41,50} Similarly, the Ni 2p and Mn 2p peaks also exhibited positive shifts after OER, with new signals corresponding to trivalent cations (Figure S13a,d), suggesting that the MOF materials were partially transformed into the respective metal (oxy)hydroxides, consistent with previous reports.⁵⁰ The Fe 2p XPS spectra of post-OER FeFc-MOF@NF (Figure S13c) demonstrated a significant increase in the proportion of trivalent Fe cations with the formation of oxyhydroxides. Additionally, the high-resolution Fe 2p XPS spectra of post-OER MOFs (Figures 5b and S13b,c,e) revealed new peaks at around 711.9 eV, which could be attributed to Fe³⁺ in FeOOH.²⁶ The O 1s spectra of the post-OER samples (Figure S14) showed notable changes, with a sharp decrease in the intensity of the C-O peak on the surface of MFc-MOF@ NF, while the intensity of the M-O peak increased significantly. These results confirm that the MOF surfaces undergo self-reconstruction to form the corresponding metal oxyhydroxides during the OER test, which are likely the active species responsible for OER catalysis.^{41,51}

To further identify the active phase and dynamic surface reconstruction of MFc-MOF@NF catalysts during the OER process, a series of in situ Raman tests were carried out at various potentials. When the applied potential was below 1.40 V (vs RHE), no significant peak changes were detected, suggesting that surface remodeling did not occur under these conditions (Figure 5c,d). However, at 1.42 V (vs RHE), new vibrational peaks emerged at 460 and 539 cm⁻¹, corresponding to the E_g bending vibration and A_{1g} stretching vibration of Co/Fe–O in CoFeOOH, respectively.^{52,53} As the potential increased, these peaks grew more prominent, indicating that CoFeOOH is the active species in the OER process for CoFc-MOF@NF. Interestingly, as the potential rose, the MOF structure's characteristics remained mostly intact, with minimal peak intensity loss, evidence of the stability of ferrocene-based

MOFs. The surface-evolved metal (oxy)hydroxide layer likely provides a shielding effect, safeguarding the inner MOF and enhancing the catalyst's durability.^{48,54} The ferrocene units retained within the inner MOF function as efficient electron transfer mediators through π - π interactions. They establish through-space charge transport pathways, facilitating electron transport.^{24,29} A similar tendency was observed in other MFc-MOF@NF (M = Ni, Fe, Mn) catalysts (Figure S15).^{55–58} Notably, the potential required for surface reconstruction of CoFc-MOF@NF is significantly lower than that of other MFc-MOF@NF (M = Ni, Fe, Mn), further demonstrating the superior catalytic activity of CoFc-MOF@NF.

To elucidate the catalytic mechanism, a model of CoFe-MOF/CoFeOOH was simulated based on experimental results (Figure S16). In alkaline media, the OER process follows the traditional adsorbate evolution mechanism, involving four concerted proton-electron transfer steps with oxygen intermediates (*OH, *O, and *OOH) at the metal sites.⁵ Typically, the Fe site does not stably adsorb OER intermediates, whereas the Co sites, which are likely the active sites with superior catalytic activity, play a dominant role during the reaction.^{26,54} Therefore, we propose that the Co atoms on the CoFeOOH surface act as the active sites and suggest a potential OER catalytic mechanism for CoFe-MOF/ CoFeOOH from a theoretical perspective, as illustrated in Figure 5e. Initially, OH⁻ from the electrolyte is adsorbed onto the Co sites (Co), forming Co–OH species (Co–*OH) (Step 1). Subsequently, deprotonation of Co-*OH occurs, generating Co-O species (Co-*O) and releasing water from the surface (Step 2). As the reaction progresses, Co-*O binds with OH⁻ to form superoxide species, leading to the formation of intermediates (Co-*OOH). Finally, Co-*OOH further reacts with OH⁻ and undergoes deprotonation, where electron removal from the Co-*OOH surface facilitates proton elimination and oxygen release, accompanied by structural reconstruction.^{60,61}

3.4. Electrocatalytic Performance for Overall Water Splitting. Encouraged by the high activity and favorable stability of CoFc-MOF@NF, we further evaluated its overall water-splitting performance. As shown in Figure 6a, a twoelectrode system, namely CoFc-MOF@NF⁽⁺⁾||Pt/C⁽⁻⁾, was assembled, with CoFc-MOF@NF as the anode and commercial Pt/C supported on an NF substrate serving as the cathode. The CoFc-MOF@NF⁽⁺⁾ $||Pt/C^{(-)}$ system demonstrated low cell voltages of 1.45 and 1.67 V at current densities of 10 and 100 mA cm^{-2} , respectively, in a 1.0 M KOH solution (Figure 6b). This performance significantly surpasses that of commercial $RuO_2^{(+)}||Pt/C^{(-)}$ electrolyzers, which require 1.54 and 1.74 V at the same current densities. Moreover, the performance of CoFc-MOF@NF exceeds that of other electrocatalysts reported in the literature (Figure 6c and Table S2). Importantly, the two-electrode system showed no substantial fluctuations over 100 h at constant current densities of 10 and 100 mA cm^{-2} , respectively (Figure 6d). These findings underscore the considerable potential of CoFc-MOF@NF for achieving efficient and practical overall water splitting.

4. CONCLUSIONS

In summary, we have successfully prepared a series of MFc-MOF@NF (M = Co, Ni, Fe, Mn) nanoflowers with close $\pi - \pi$ stacking lattice structure as efficient OER catalysts by a facile hydrothermal strategy. The nanoflower, consisting of inter-



Figure 6. (a) Schematic diagram of overall water splitting in a twoelectrode system. (b) LSV curves of overall water splitting for CoFc-MOF@NF⁽⁺⁾||Pt/C⁽⁻⁾ and RuO₂⁽⁺⁾||Pt/C⁽⁻⁾ in 1.0 M KOH. (c) Comparison of the cell voltage of CoFc-MOF@NF at 10 mA cm⁻² with recently reported catalysts. (d) Chronopotentiometry test at 10 and 100 mA cm⁻².

connected nanosheets, provides numerous catalytically active sites and buffers substantial volume changes during electrochemical processes. Significantly, CoFc-MOF@NF delivers a low overpotential of 189 mV at 10 mA cm⁻², a decent Tafel slope of 40.38 mV dec⁻¹, and robust catalytic stability, outperforming most recently reported MOF catalysts. In a two-electrode system, CoFc-MOF@NF achieves low cell voltages of 1.45 and 1.67 V at 10 and 100 mA cm^{-2} , respectively, surpassing commercial electrolyzers. Its structural integrity and catalytic activity remain stable over 100 h of continuous operation, supported by the formation of a protective metal (oxy)hydroxide layer. Moreover, structural evolution analysis during the OER process shows that the CoFeOOH formed on the surface of the MOF is regarded as the actual active phase, while the π -conjugated ferrocene units of the internal MOF act as the electron transfer mediator. This work not only highlights the importance of designing appropriate MOF structures as precatalysts to enhance OER activity but also advances our understanding of the correlation between structural evolution and OER catalytic performance.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.5c00334.

Details on the experimental materials, characterization, electrochemical measurements, EIS study, comparison of the OER activities of recently reported electrocatalysts, and summary of various catalytic electrodes for overall water splitting (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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