

Article

Transition Metal (Mn, Fe, Ni) Doping of ZIF-67 for Enhanced Electrocatalytic Performance in Water Splitting

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Abstract

Electrocatalytic water splitting offers a viable route to sustainable hydrogen generation, yet the development of non-noble metal catalysts that combine high efficiency with long-term stability remains a significant hurdle. Zeolitic imidazolate framework-67 (ZIF-67) has emerged as a potential electrocatalyst, but its activity is often limited by insufficient active sites and poor conductivity. In this study, Mn, Fe, and Ni doped derivatives of ZIF-67 (ZIF-67/M, M = Mn, Fe, Ni) were synthesized via a post-synthetic modification method to improve the electrocatalytic performance. The effects of metal doping on structure, morphology, and water splitting activity were systematically investigated. XRD and FTIR confirmed the successful incorporation of heteroatoms without destroying the crystalline framework, while TGA revealed altered thermal stability. BET measurements showed a transformation from microporous to mesoporous structures upon doping, and SEM exhibited crystal distortion, aggregation, and increased surface roughness. Electrochemical tests demonstrated that doping significantly enhanced both oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) performances. At 10 mA cm⁻², ZIF-67/Fe exhibited the lowest overpotentials for OER (271 mV) and HER (338 mV), outperforming ZIF-67/Mn, ZIF-67/Ni, and pristine ZIF-67. Overall water splitting tests on ZIF-67/Fe showed negligible overpotential change after 24 h, confirming good ambient stability. In summary, metal doping effectively enhances the electrocatalytic water splitting performance of ZIF-67 by modulating its coordination environments and active site distribution, with ZIF-67/Fe exhibiting the best overall performance as a promising bifunctional electrocatalyst.

Keywords: ZIF-67; metal doping; electrocatalytic water splitting; oxygen evolution reaction; hydrogen evolution reaction



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1. Introduction

With the increasing global energy demand and growing environmental concerns, the development of clean and renewable energy resources has become an urgent priority [1,2]. Hydrogen energy, as an efficient and clean energy carrier, offers advantages such as high energy density, pollution-free combustion products, and diverse sources, positioning it as a key direction for future energy development [3,4]. Electrochemical water splitting is an efficient and environmentally friendly method for hydrogen production, where the basic principle involves the electrolysis of water into hydrogen and oxygen driven by

electrical energy; the main reactions include the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode [5]. The practical viability of electrochemical water splitting is primarily dictated by the intrinsic activity of the electrocatalyst; however, the overall process is substantially retarded by poor reaction kinetics and restricted interfacial charge transfer [6–8]. Therefore, the pursuit of robust electrocatalytic materials capable of lowering activation overpotentials and accelerating electron transport remains a central challenge and a key research priority.

Currently, commercial water-splitting catalysts are predominantly based on noble metals such as platinum and iridium. Despite the remarkable HER activity of Pt and the prominent OER performance of Ir/Ru-based oxides, the practical application of noble-metal electrocatalysts is severely restricted by their scarcity, cost, instability, and pH mismatch between the two half-reactions [9,10]. Given the non-viability of noble metals for large-scale commercialization, research efforts have increasingly focused on replacing them with highly abundant transition metals. Designing efficient electrocatalysts hinges on three key factors: optimizing interfacial properties, maximizing the surface-to-volume ratio, and creating abundant active sites to facilitate mass and charge transport. Transition metal catalysts, particularly those based on Fe, Co, and Ni, have attracted considerable interest due to their potential to achieve activity comparable to noble metals. Transition metal-based chalcogenides, nitrides, carbides, and MOFs have also emerged as highly attractive electrocatalytic materials, primarily owing to their low cost, earth abundance, and competitive catalytic performance that rivals conventional noble-metal-based catalysts.

MOFs also referred to as porous coordination polymers, represent a class of crystalline materials derived from the self-assembly of metal ions (or metal clusters) with organic linkers, thereby forming highly ordered porous architectures [11–13]. Their basic structural units include metal centers and organic ligands, which are connected through coordination bonds to form one-, two-, or three-dimensional porous networks [14,15]. Although this structure resembles that of traditional inorganic zeolites, MOFs exhibit much higher specific surface areas, tunable pore sizes and channels, and diverse chemical compositions, thus showing great promise in the field of electrocatalysis [16,17]. Among them, ZIF-67, a MOF material composed of Co^{2+} coordinated with 2-methylimidazole, possesses excellent chemical stability and open channel structures, making it an ideal platform for OER/HER catalysts [18–20]. Nevertheless, pristine ZIF-67 suffers from low intrinsic electrical conductivity and a suboptimal electronic structure of the Co active centers, which limit its catalytic performance and prevent it from meeting practical requirements [21].

In recent years, the introduction of heterometallic components to tune the electronic configuration of MOF materials has been validated as an effective strategy to enhance electrocatalytic activity [22,23]. A binder-free Co-MOF thin film was deposited on stainless steel via reaction-diffusion by Khandekar et al. [24], achieving an OER overpotential of 275 mV at 10 mA cm^{-2} and a low Tafel slope (76 mV dec^{-1}). Meanwhile, Konavarapu et al. [25] synthesized a CoNi-MOF that delivered 350 mV (OER) and 150 mV (HER) at the same current density. The bimetallic CoNi-MOF outperforms its monometallic counterpart in OER, a benefit attributed to the $\text{Co}^{2+}/\text{Ni}^{2+}$ synergy that enriches surface electroactivity, consequently boosting current density and diminishing overpotential. By combining chemical bath deposition with electrodeposition, Cao et al. [26] constructed a 3D self-supported NiCoP/ZIF-67/NF electrode. The resulting material shows remarkable OER activity, with an overpotential of only 175 mV at 10 mA cm^{-2} and durable operation exceeding 40 h at 20 mA cm^{-2} in alkaline medium (1.0 M KOH). Its excellent performance arises from three factors: a large accessible surface area, abundant active sites, and the synergistic effects both at the NiCoP/ZIF-67 interface and between Ni and Co ions in the NiCoP phase. Despite these advances, a systematic understanding of how different metal

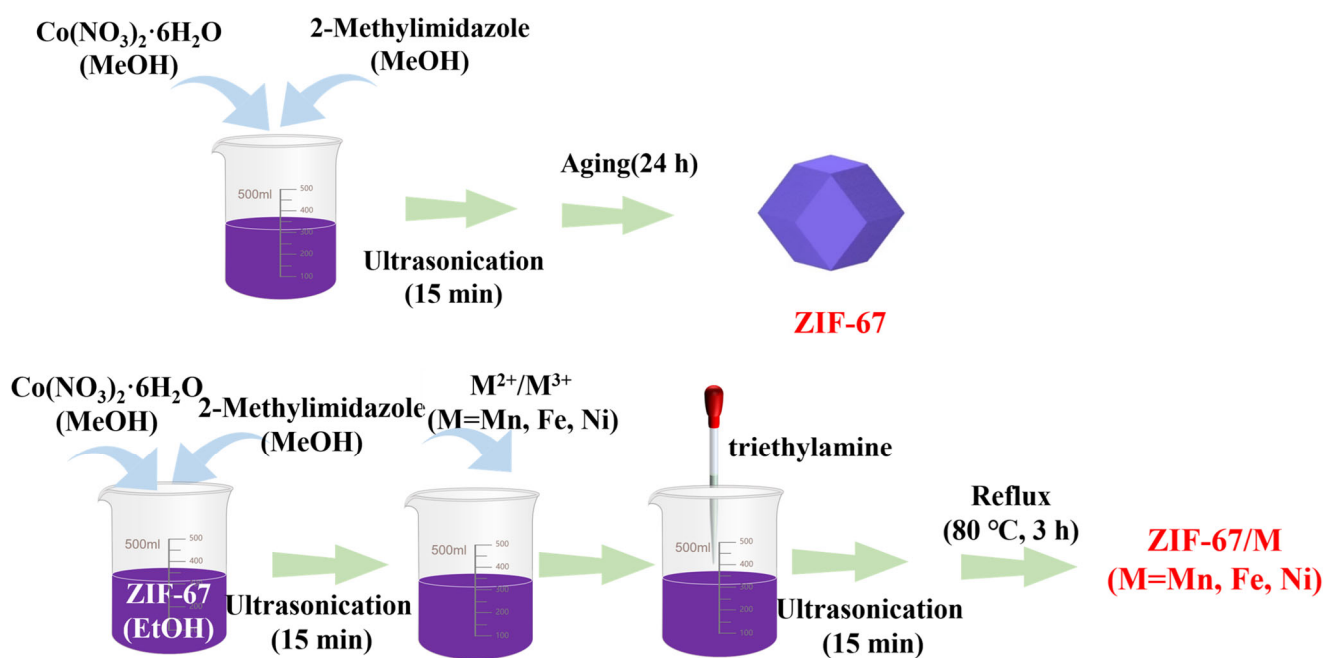
dopants regulate the coordination environments of MOF and their differential effects on both OER and HER performance is still lacking.

In this study, ZIF-67 was first synthesized via a simple coprecipitation method. Subsequently, three transition metals (Mn, Fe, and Ni) were individually introduced into the ZIF-67 framework through a post-synthetic incorporation strategy. The resulting doped materials were then systematically characterized to evaluate the influence of metal doping on their morphological features, crystalline structure, and surface chemical states. Notably, instead of carbonization, we directly employ these doped derivatives because metal doping already improves their intrinsic conductivity and modulates the coordination environment, while retaining the open framework and abundant active Co sites; the use of conductive additives in electrode preparation further compensates for any remaining conductivity limitation [27]. More importantly, the electrocatalytic performance of these modified ZIF-67 derivatives toward both OER and HER was comprehensively assessed under alkaline conditions. The distinct electronic configurations and ionic radii of Mn, Fe, and Ni lead to different coordination behaviors, which allow us to establish clear structure-activity correlations and to identify the optimal dopant. This investigation aims to provide a rational foundation for the future design of high-performance MOF-based electrocatalysts with tailored functionalities for sustainable energy conversion applications.

2. Results and Discussion

The ZIF-67 and ZIF-67/M were prepared by coprecipitation and post-synthetic modification methods, respectively, as illustrated in Scheme 1. The XRD profiles of ZIF-67 and its derivative ZIF-67/M are displayed in Figure 1a. All signals were assigned based on the ZIF-67 crystallographic data (CCDC 1429244), following the approach described in prior studies [28]. The distinct characteristic peaks of ZIF-67 appear at 7.32° , 10.38° , 12.72° , 14.7° , 16.4° , 17.98° , 22.1° , 24.5° , and 26.66° , which correspond to the (110), (200), (211), (220), (310), (222), (411), (332), and (510) planes of the simulated ZIF-67 phase, respectively. In the XRD patterns of ZIF-67/Mn, ZIF-67/Fe, and ZIF-67/Ni, no additional peaks distinct from those of ZIF-67 are observed, while the diffraction peaks such as (110), (200), (211), (310), (222) exhibit slight shifts in their positions (Figure S1). These results indicate that the incorporated Mn^{2+} , Fe^{3+} , and Ni^{2+} ions are atomically dispersed within the ZIF-67 framework without forming secondary crystalline phases, while the slight peak shifts are attributed to lattice distortion caused by partial substitution of Co^{2+} with heterometallic ions of different ionic radii [29].

The FTIR spectrum in Figure 1b exhibits characteristic bands at around 3130, 2920, 1580, and 1450 cm^{-1} , which are assignable to the C–H stretching of the aromatic ring, the $-\text{CH}_3$ stretching of methylimidazole, and the C=N and C=C stretching vibrations, respectively [30]. The absorption features located between 1300 and 1000 cm^{-1} are assignable to C–N stretching modes, which serve as a typical indicator of the imidazole ring and the resultant ZIF-67 coordination architecture. Meanwhile, the band observed at 760 cm^{-1} arises from Co–N stretching, providing evidence for the successful coordination between the organic linker and the Co cations. These results collectively confirm the formation of the ZIF-67 framework [31]. The additional peaks at 618 and 525 cm^{-1} observed for ZIF-67/Mn are likely related to Mn–N or Mn–O stretching, providing preliminary evidence for Mn incorporation. The small peak at 498 cm^{-1} in the ZIF-67/Fe spectrum may be associated with Fe-related vibrations, consistent with Fe doping. For ZIF-67/Ni, the bands at 560 and 580 cm^{-1} fall in the region typical of Ni–N stretching, implying the successful integration of Ni.



Scheme 1. Synthetic illustration of ZIF-67 and ZIF-67/M (M = Mn, Fe, Ni).

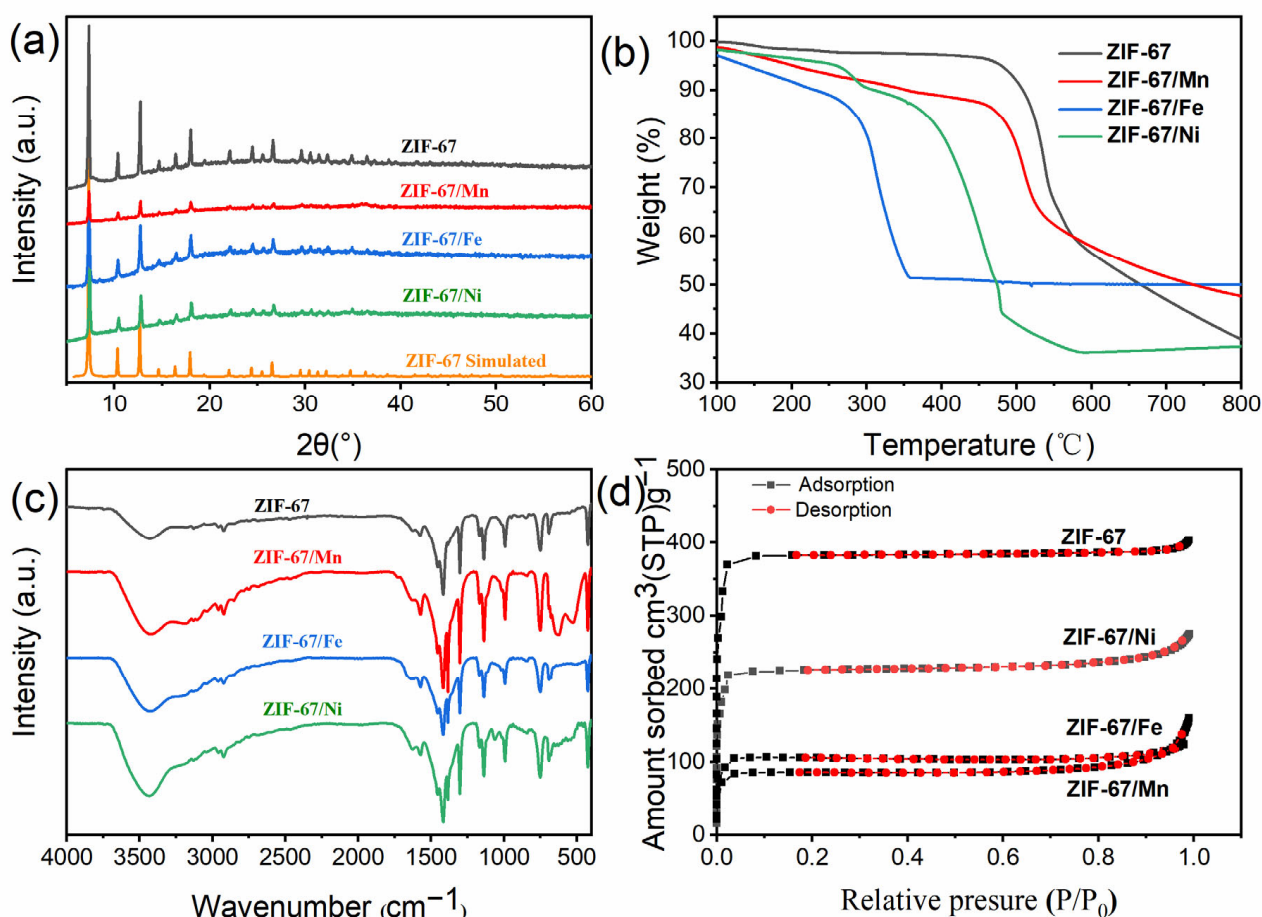


Figure 1. (a) PXRD patterns, (b) thermogravimetric curves, (c) FTIR spectra, and (d) N_2 adsorption/desorption isotherms of ZIF-67 and ZIF-67/M (M = Mn, Fe, Ni).

According to the TGA results (Figure 1c), the thermal degradation of pristine ZIF-67 proceeds in three stages. The first stage, from 40 to 460 °C, corresponds to a mild

weight loss attributed to the evaporation of physically adsorbed water and residual solvent (methanol), during which the framework remains intact. The second stage, from 460 to 550 °C, shows a sharp weight loss due to framework collapse and ligand decomposition [32]. The third stage, from 550 to 800 °C, involves a slow weight loss, leaving residual Co or Co/C amorphous carbon. In comparison, the metal-doped ZIF-67 (Mn, Fe, Ni) samples exhibit similar three-stage degradation behavior, but with notably shifted characteristic temperature ranges. Specifically, ZIF-67/Mn loses approximately 14% weight between 40 and 460 °C, followed by framework collapse between 460 and 540 °C. ZIF-67/Fe shows a 12% weight loss between 40 and 260 °C, with framework collapse occurring between 260 and 360 °C. ZIF-67/Ni exhibits a 6% weight loss between 40 and 270 °C, followed by framework collapse between 270 and 480 °C. Compared with pristine ZIF-67, the onset temperature of framework collapse is significantly reduced for all doped samples. Moreover, the final residue content is higher for all doped samples. The decreased thermal stability of the doped ZIF-67 arises from the weakened coordination environment, as well as lattice distortion and defect formation induced by heterometal incorporation and charge imbalance, which collectively promote earlier framework decomposition [33]. Given that aqueous electrocatalytic water splitting is operated at mild temperatures (room temperature to ~80 °C), the high-temperature thermal degradation is precluded, rendering the reduced thermal stability negligible for the catalytic performance.

Figure 1d illustrates the N₂ sorption profile of pristine ZIF-67, where the steep adsorption at $P/P_0 < 0.1$ signifies abundant micropores, and the hysteresis observed in the desorption branch at higher P/P_0 points to a relatively ordered mesoporous structure, yielding a BET surface area of 1128 m²·g^{−1}. For ZIF-67/Mn, the surface area significantly decreases to 719 m²·g^{−1}, accompanied by a slower adsorption rise at low P/P_0 (indicating reduced microporosity) and a more pronounced hysteresis loop, implying that Mn doping increases the mesopore proportion and broadens the pore size distribution. ZIF-67/Fe shows a BET surface area of only 263 m²·g^{−1}, with the adsorption isotherm continuously rising at higher P/P_0 , indicating a dominance of mesopores and near-disappearance of micropores. As for ZIF-67/Ni, the overall adsorption uptake is lower than that of pristine ZIF-67, giving a surface area of 334 m²·g^{−1} while still retaining some microporous features; the widened hysteresis loop suggests that Ni doping may introduce a small number of mesopores or partially disrupt the microporous structure. These results clearly indicate that the introduction of a second metal disrupts the ordered coordination between Co²⁺ and 2-methylimidazole, leading to poorer crystallinity and thus a marked reduction in surface area, with ZIF-67/Fe exhibiting the most pronounced effect. Such locally crystalline ZIF-67/M samples are rich in crystal defects, exposing more reactive sites. While pristine ZIF-67, with its high surface area, is suitable for gas adsorption or catalytic reactions requiring highly accessible active sites, the three doped samples—ZIF-67/Mn, ZIF-67/Fe, and ZIF-67/Ni—although having lower surface areas, show an increased mesopore fraction that may enhance mass transfer efficiency, making them more attractive for macromolecular catalysis or liquid-phase adsorption [34].

To elucidate the morphology, microstructure, and elemental homogeneity of ZIF-67 and ZIF-67/M (M = Mn, Fe, Ni), a combination of SEM, TEM, and EDS was utilized, and the corresponding micrographs are displayed in Figure 2. The SEM micrographs in Figure 2a reveal that pristine ZIF-67 adopts a well-defined rhombic dodecahedral shape, characterized by smooth surfaces, a narrow size distribution spanning roughly 500 nm to 1 μm, negligible particle aggregation, and clearly delineated grain boundaries. In contrast, the Mn, Ni, and Fe-doped ZIF-67 samples (Figure 2b–d) display significantly altered morphologies, characterized by crystal distortion, increased agglomeration, and enhanced surface roughness, which can be attributed to the introduction of transition metals disrupting

the crystal growth kinetics of ZIF-67. EDS elemental mapping (Figures 2d and S2) demonstrates the homogeneous distribution of C, N, O, Co, and the respective dopant metals (Mn, Fe, Ni) within each sample. TEM further reveals the nanostructure of ZIF-67/Fe (Figure 2e). Quantitative elemental analysis (Figures 2f and S3) confirms the successful incorporation of the second metal into the ZIF-67 framework, with the atomic ratio of Co to the dopant metal approaching 3:1 for all three doped materials.

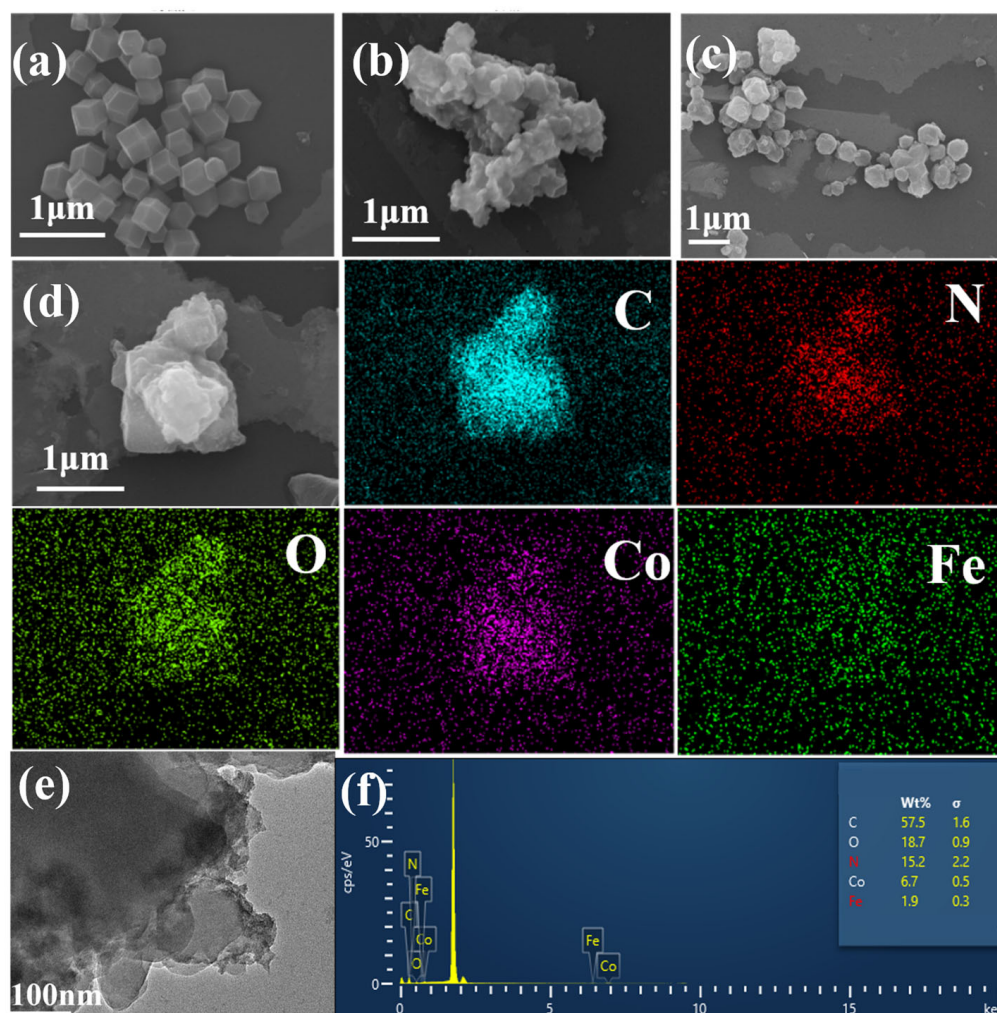


Figure 2. SEM images of ZIF-67 (a), ZIF-67/Mn (b), ZIF-67/Ni (c); and EDS mapping (d), TEM image (e) and EDS point analysis (f) of ZIF-67/Fe.

To gain deeper insight into the elemental composition and chemical states of the synthesized electrocatalysts, X-ray photoelectron spectroscopy (XPS) was performed on ZIF-67 and ZIF-67/M (M = Mn, Fe, Ni). The survey spectra in Figure 3a collectively confirm the coexistence of C, N, O, Co, and the corresponding heterometals (Mn, Fe, or Ni) in each catalyst, consistent with the EDS-mapping results. The high-resolution Co 2p spectrum (Figure 3b) reveals two major peaks at 795.2 eV (Co 2p_{1/2}) and 779.6 eV (Co 2p_{3/2}), both characteristic of Co²⁺ species. Additional satellite peaks at 801.1 eV and 784.1 eV are assigned to Co 2p electronic transitions [31]. Notably, relative to pristine ZIF-67, the Co 2p_{1/2} and Co 2p_{3/2} peaks of ZIF-67/M shift positively by 1.2–1.4 eV in binding energy. Such a shift implies a reduced electron cloud density around Co cations, which is plausibly due to the substitution of M ions that alters the local coordination geometry and elevates the effective oxidation state of cobalt, thus raising the core-level binding energies [26]. For the Mn 2p spectrum (Figure 3c), two well-resolved spin–orbit doublets appear at approximately

641.9 eV and 653.5 eV, corresponding to Mn 2p_{3/2} and Mn 2p_{1/2}, respectively. Mn 2p_{3/2} peak further resolves two components, assignable to Mn²⁺ and Mn³⁺ [35]. The Fe 2p XPS spectrum (Figure 3d) displays peaks at 713.7 eV (Fe 2p_{3/2}) and 725.4 eV (Fe 2p_{1/2}), which are deconvoluted into multiple contributions from Fe³⁺ and Fe²⁺ states; a satellite feature at 717.6 eV is also observed for the Fe 2p_{3/2} transition [36]. In the Ni 2p spectrum (Figure 3e), distinct peaks at 855.8 eV and 873.4 eV are attributable to Ni 2p_{3/2} and Ni 2p_{1/2} of divalent nickel, accompanied by satellite signals at 861.3 eV and 879.7 eV [31]. Peak deconvolution of the C 1s spectrum (Figure S4) yields three components at 284.8, 285.4, and 288.9 eV, corresponding to C–C/C=C, C=N, and C–N bonds, respectively [23]. The N 1s spectrum is resolved into pyridinic N (397.4 eV), C–N (397.9 eV), and N–O (405.8 eV) species, while the O 1s spectrum shows three peaks at 531.6, 532.9, and 533.8 eV, assigned to C–O, –OH, and C=O groups, respectively [25].

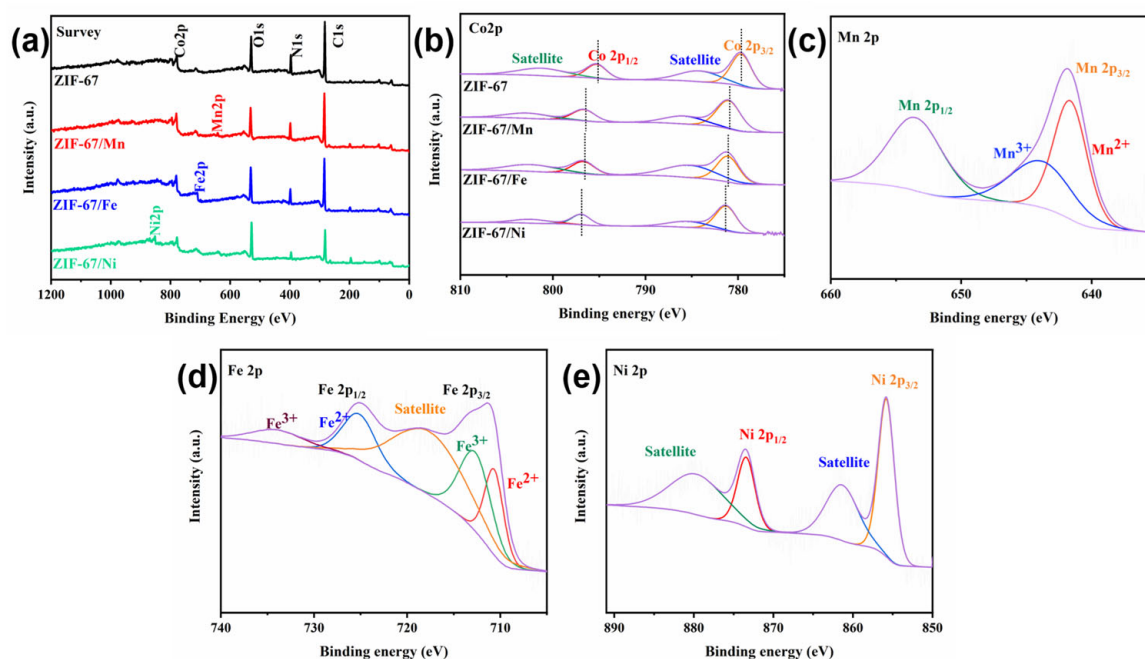


Figure 3. XPS spectra of ZIF-67 and ZIF-67/M (M = Mn, Fe, Ni): (a) survey spectra, and high-resolution spectra of (b) Co 2p, (c) Mn 2p, (d) Fe 2p, and (e) Ni 2p.

The OER electrocatalytic performance of ZIF-67 and its M-doped counterparts (M = Mn, Fe, Ni) was systematically investigated in 1.0 M KOH using a standard three-electrode system. The corresponding LSV curves, Tafel slopes, EIS spectra, and C_{dl} values are presented in Figure 4, providing a comprehensive comparison of their catalytic activity. The LSV curves in Figure 4a demonstrate that the OER performance of all ZIF-67/M catalysts (M = Mn, Fe, Ni) is markedly superior to that of pristine ZIF-67. At a current density of 10 mA·cm^{−2}, ZIF-67/Fe affords an overpotential of only 271 mV, which is much lower than those of ZIF-67/Mn (350 mV), ZIF-67/Ni (325 mV), and pristine ZIF-67 (402 mV), indicating that although metal doping reduces the OER overpotential, Fe doping proves most effective. Compared with commercial RuO₂ (Figure S5a) and other metal-doped counterparts, ZIF-67/Fe exhibits the lowest overpotential, demonstrating its optimal OER catalytic performance. Figure 4b presents the corresponding Tafel plots. Among the tested samples, ZIF-67/Fe delivers the lowest Tafel slope at 104 mV·dec^{−1}, followed by ZIF-67/Ni (189 mV·dec^{−1}) and ZIF-67/Mn (205 mV·dec^{−1}), whereas pristine ZIF-67 exhibits a substantially higher value of 232 mV·dec^{−1}. A smaller Tafel slope implies a faster increase in current density with overpotential, reflecting superior reaction kinetics [35,36]. These results further confirm that ZIF-67/Fe possesses the optimal OER kinetics.

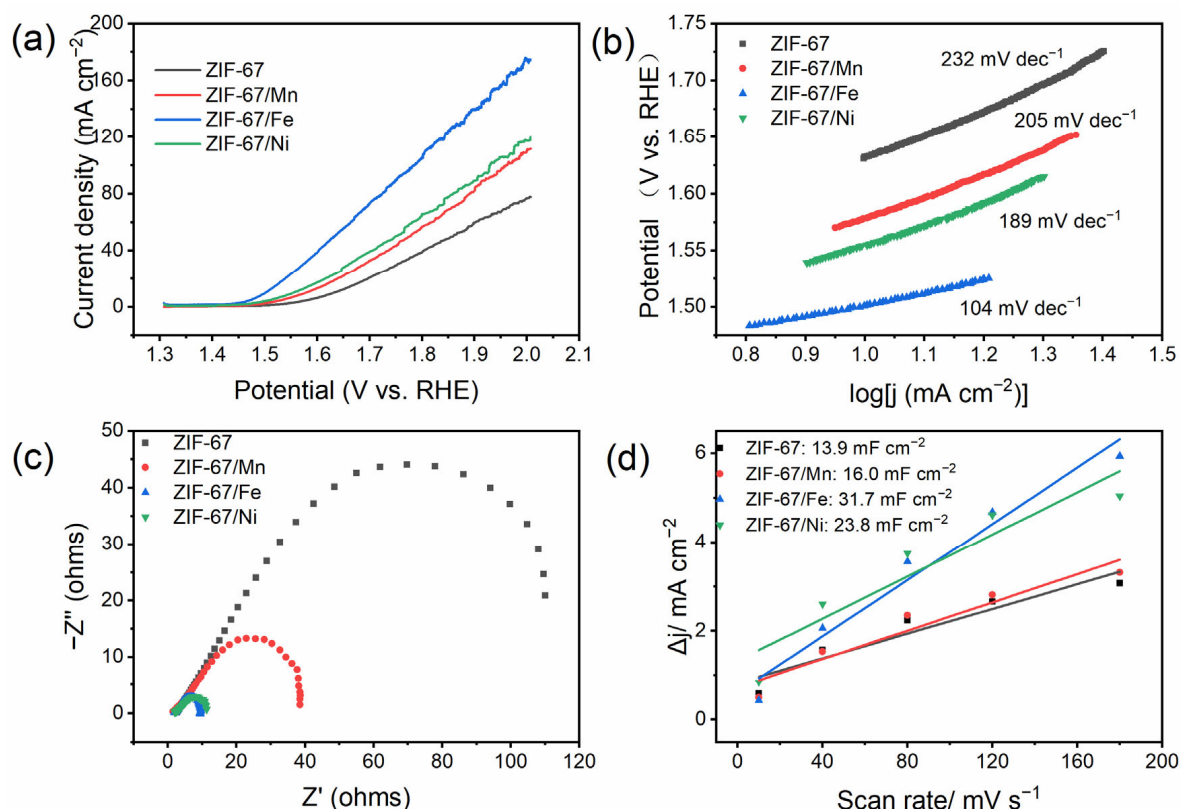


Figure 4. OER performances of the electrocatalysts in 1.0 M KOH. (a) LSV curves, (b) Tafel plots, (c) Nyquist plots, and (d) double-layer capacitance.

Subsequently, EIS analysis was employed to reveal the reaction kinetics of the electrocatalytic processes and the charge-transfer kinetics at the electrode-electrolyte interface. In the Nyquist plots (Figure 4c), ZIF-67/Fe exhibits the smallest semicircle diameter, corresponding to the lowest charge-transfer resistance (R_{ct}) of 7.5 Ω , which is substantially lower than those of ZIF-67 (107.6 Ω), ZIF-67/Mn (37.1 Ω), and ZIF-67/Ni (9.06 Ω). The significantly reduced R_{ct} value of ZIF-67/Fe implies a faster electron transfer rate at the electrode-electrolyte interface and superior conductivity, which collectively contribute to the enhanced electrocatalytic performance [37]. The C_{dl} values of the catalysts were determined from CV curves at different scan rates in the non-Faradaic region (Figure 5). As C_{dl} is proportional to the ECSA, a higher C_{dl} reflects a larger ECSA. As shown in Figure 4d, ZIF-67/Fe exhibits the highest C_{dl} of 31.7 mF cm^{-2} , significantly higher than those of ZIF-67/Ni (23.8 mF cm^{-2}), ZIF-67/Mn (16.0 mF cm^{-2}), and pristine ZIF-67 (13.9 mF cm^{-2}). This indicates that ZIF-67/Fe possesses the greatest number of accessible active sites, which directly contributes to its superior OER activity [38]. Interestingly, although the BET surface area of the doped samples decreased compared with pristine ZIF-67, the ECSA (C_{dl}) increased significantly after Fe doping. This counterintuitive observation indicates that the physical surface area measured by nitrogen physisorption does not fully reflect the actual electrochemically accessible active sites under operating electrolyte conditions. In our case, the increased ECSA after doping, despite the reduced BET surface area, can be attributed to the creation of structural defects, improved pore accessibility, and the exposure of additional active sites that are electrochemically accessible but not fully captured by nitrogen physisorption measurements [39].

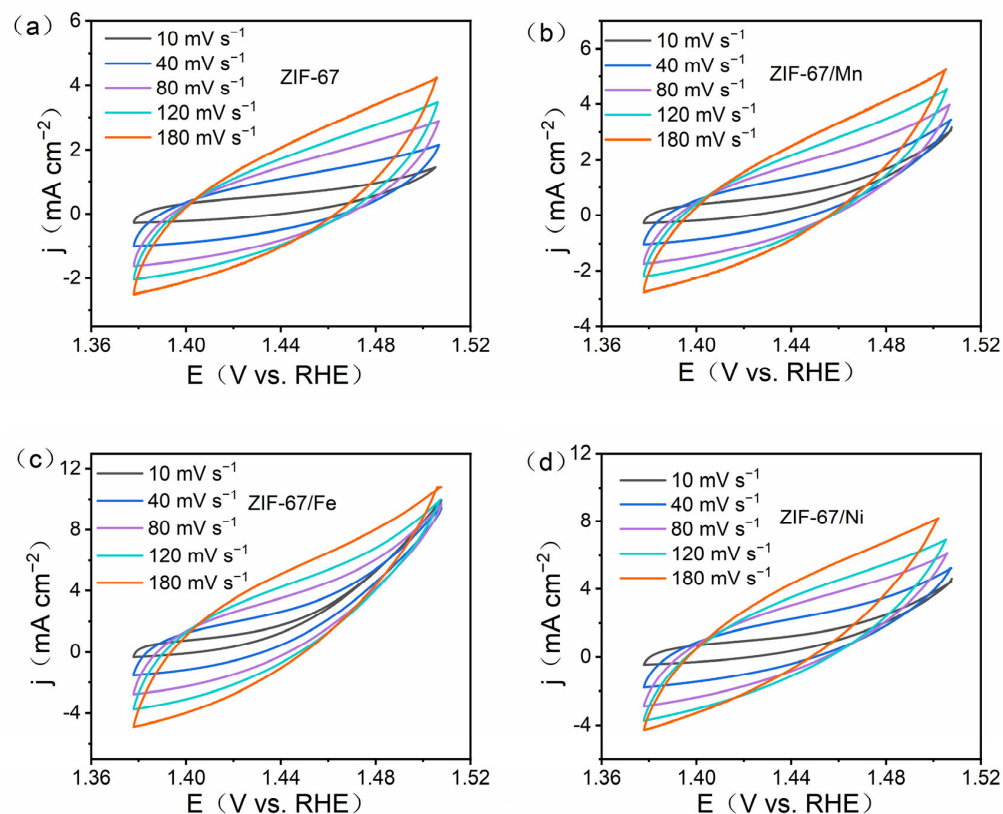


Figure 5. CV curves of (a) ZIF-67, (b) ZIF-67/Mn, (c) ZIF-67/Fe, and (d) ZIF-67/Ni in OER.

Collectively, the above results demonstrate that doping ZIF-67 with transition metal ions, particularly Fe, synergistically enhances the OER activity through three complementary effects: a reduced overpotential, a decreased charge-transfer resistance, and an increased electrochemically active surface area. To contextualize the performance of our catalysts, Table 1 compares the obtained overpotential (η) and Tafel slope values with those reported for other ZIF-67-based and transition-metal electrocatalysts in the literature. Notably, the ZIF-67/Fe composite exhibits OER performance that are comparable to, and in some cases surpass, those of previously reported catalysts with analogous compositions. The exceptional OER performance of ZIF-67/Fe is mainly attributed to the inherent activity of the metal centers, the heteroatom doping effect, and synergistic structural effects [21].

Table 1. Comparative OER performance of the electrocatalysts developed in this study and those documented in prior reports.

Catalyst	η @10 mA cm ⁻² (mV vs. RHE)	Tafel Slope (mV dec ⁻¹)	Solution	Ref.
Fe-ZIF-67/NF	278	77	1 M KOH	[21]
Ni-BDC-3R	332	132	1 M KOH	[40]
Ni-MOFs	415	93	1 M KOH	[41]
Co-MOF-C	342	119	1 M KOH	[42]
2D CoZIF-9(III) sheets	380	55	1 M KOH	[43]
Co/Cu-MOF(3)	395	94	1 M KOH	[44]
CoFe-MOF	355	49.05	1 M KOH	[45]
NiCoTe ₂ -10 wt%/MG	270	106	1 M KOH	[46]
ZIF-67	402	232	1 M KOH	This work
ZIF-67/Fe	271	104	1 M KOH	This work
ZIF-67/Ni	325	189	1 M KOH	This work
ZIF-67/Mn	350	205	1 M KOH	This work

The HER electrocatalytic activities of ZIF-67 and ZIF-67/M ($M = \text{Mn, Fe, Ni}$) were systematically evaluated using LSV, Tafel slope analysis, EIS, and C_{dl} measurements, as presented in Figure 6. The LSV (Figure 6a) indicates that ZIF-67/Fe exhibits the lowest overpotential of 338 mV, followed by ZIF-67/Ni (385 mV) and ZIF-67/Mn (440 mV), all of which are significantly lower than that of pristine ZIF-67 (446 mV). Thus, the incorporation of Mn, Fe, or Ni effectively reduces the HER overpotential, with Fe doping yielding the most pronounced decrease. However, its overpotential (338 mV) remains considerably higher than that of commercial Pt/C (25 mV) (Figure S5b), indicating substantial room for further improvement. The reaction kinetics of the catalysts were analyzed using Tafel plots (Figure 6b). ZIF-67/Fe presents the smallest Tafel slope of 200 mV dec^{-1} , while those of ZIF-67/Ni and ZIF-67/Mn are 213 mV dec^{-1} and 373 mV dec^{-1} , respectively. In contrast, pristine ZIF-67 shows a much higher Tafel slope of 822 mV dec^{-1} . These results demonstrate that metal doping significantly enhances the HER kinetics, and the charge transfer rate is most substantially improved by Fe incorporation. Table 2 presents a comparative overview of the HER performance between our synthesized catalysts and those from prior studies. The data indicate that our catalysts exhibit moderate HER activity, falling between the lower and higher performing benchmarks in the literature.

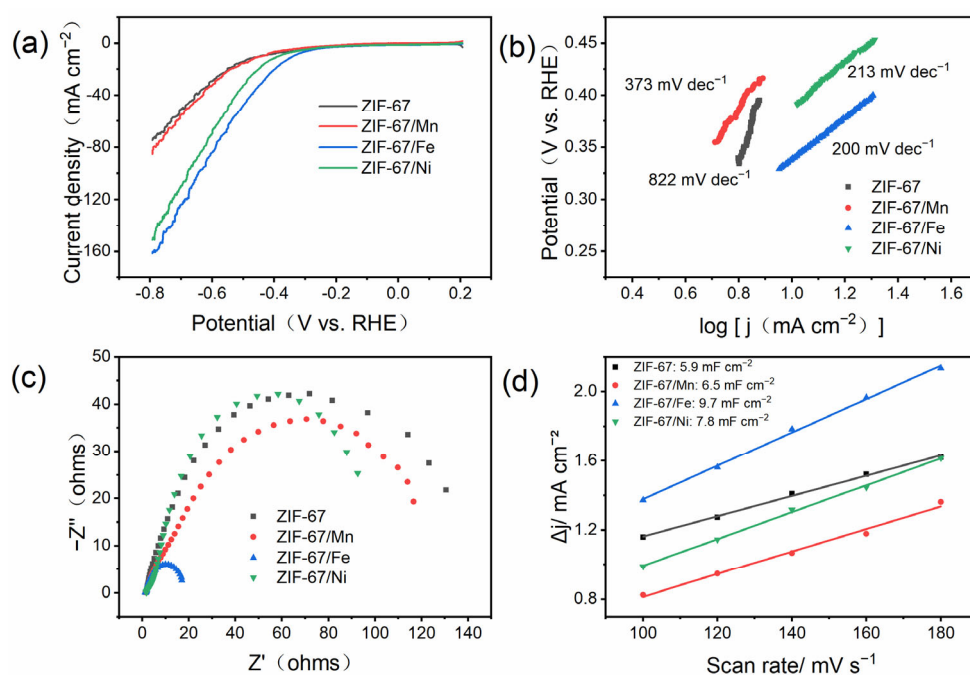


Figure 6. HER performances of the electrocatalysts in 1.0 M KOH. (a) LSV curves, (b) Tafel plots, (c) Nyquist plots, and (d) double-layer capacitance.

From the Nyquist plots (Figure 6c), the R_{ct} follows the order ZIF-67/Fe (15.56 Ω) < ZIF-67/Ni (90.96 Ω) < ZIF-67/Mn (115.21 Ω) < pristine ZIF-67 (129.06 Ω), with the Fe-doped sample showing the smallest semicircular arc. This finding confirms that metal doping facilitates a reduction in the charge transfer resistance at the electrode/electrolyte interface, with Fe doping being most effective in improving the interfacial reaction kinetics. The ECSA was evaluated by determining the C_{dl} (Figure 6d) from CV curves (Figure S6) recorded at various scan rates. The calculated C_{dl} values are 9.7 mF cm^{-2} for ZIF-67/Fe, 7.8 mF cm^{-2} for ZIF-67/Ni, and 6.5 mF cm^{-2} for ZIF-67/Mn, all higher than that of pristine ZIF-67 (5.9 mF cm^{-2}). This indicates that metal doping effectively increases the number of active sites and thus the electrochemically active area, with the highest increase achieved by Fe doping. As discussed in the OER section, the increased ECSA despite reduced BET surface

area can be rationalized by the creation of structural defects and improved pore accessibility, which also contribute to the enhanced HER performance of the Fe-doped catalyst.

Table 2. Comparative HER performance of the electrocatalysts developed in this study and those documented in prior reports.

Catalyst	η @10 mA cm ⁻² (mV vs. RHE)	Tafel Slope (mV dec ⁻¹)	Solution	Ref.
Co-BDC	529	111	1 M KOH	[47]
Co-BTC/CC	437	115.1	1 M KOH	[48]
Mo-MOF	257	138	1 M KOH	[49]
Mn-MOF	201	116	1 M KOH	[50]
1-CFP	350	160	1 M KOH	[51]
Co-Ba-TPA	414.5	145.23	1 M KOH	[52]
Ru(CO)(PPh ₃) ₂ L	439	222	1 M KOH	[53]
ZIF-67	446	822	1 M KOH	This work
ZIF-67/Fe	338	200	1 M KOH	This work
ZIF-67/Ni	385	213	1 M KOH	This work
ZIF-67/Mn	440	373	1 M KOH	This work

To further evaluate the stability of ZIF-67/Fe under overall water splitting conditions, we employed ZIF-67/Fe as both the anode and cathode in a dual-electrode system for overall water splitting, LSV curves before and after the stability test were compared, and the chronoamperometric response during continuous operation for 24 h was recorded (Figure 7). As illustrated in Figure 7a, the ZIF-67/Fe coupling achieved a current density of 10 mA cm⁻² at a cell voltage of only 1.513 V before the stability test, which increases only slightly to 1.515 V after the 24 h test, indicating negligible degradation. Meanwhile, the chronoamperometric curve (Figure 7b) reveals that, although minor fluctuations occur, the current density remains stable around 9.3 mA cm⁻² throughout the 24 h continuous electrolysis. These results demonstrate that ZIF-67/Fe possesses excellent electrochemical stability under overall water splitting conditions. When benchmarked against recently reported bimetallic MOF electrocatalysts, our ZIF-67/Fe delivers a competitive voltage of 1.51 V, lower than that of NiCd-MOF (1.52 V) [54] and slightly higher than that of Ni/Co-MOF/NF (1.41 V) [55].

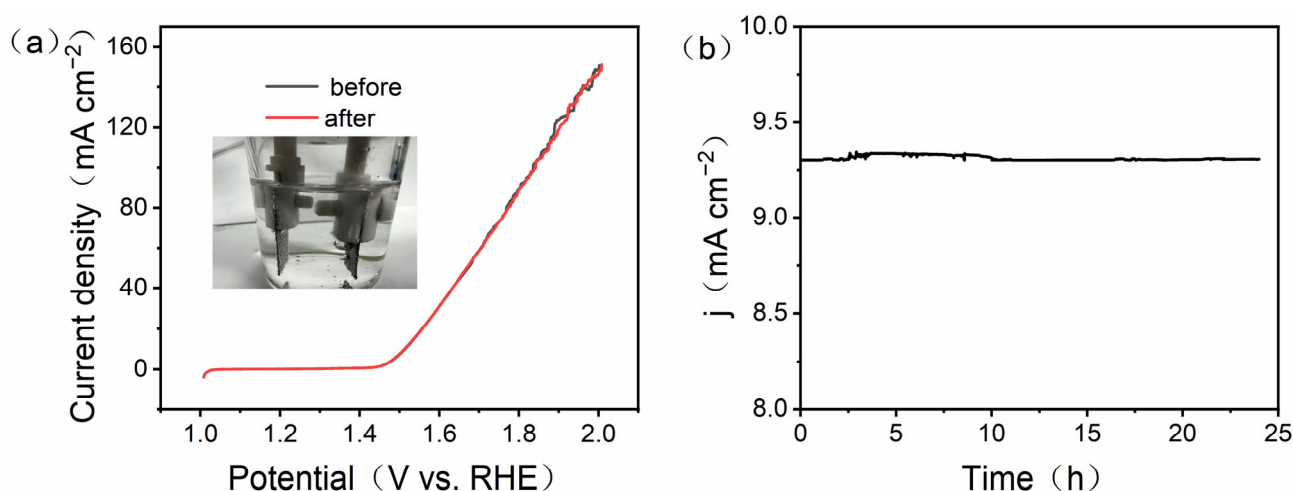


Figure 7. Electrochemical performance of the ZIF-67/Fe||ZIF-67/Fe couple for overall water splitting: (a) LSV curves before and after stability testing, and (b) chronoamperometric curve.

3. Experimental Section

3.1. Chemicals

C₂H₅OH, 99.7%, Macklin (Shanghai, China), DMF, 99.5%, Tianjin De'en Chemical (Tianjin, China), 2-methylimidazole, 98%, Macklin (Shanghai, China), Co(NO₃)₂·6H₂O, 99%, Macklin, Mn(CH₃COO)₂·4H₂O, 99%, Macklin, Fe(NO₃)₃·9H₂O, 99%, Macklin, NiCl₂·6H₂O, 99%, Macklin, Nafion 5 wt%, DuPont (Wilmington, DE, USA), CH₃OH, 99.5%, Macklin, Triethylamine, 99%, Macklin, KOH, 95%, Macklin.

All solutions were prepared using ultrapure water with a resistivity of 18.2 MΩ·cm.

3.2. Material Synthesis

Synthesis of ZIF-67: Co(NO₃)₂·6H₂O (9.8 mmol, 2.86 g) and 2-methylimidazole (79 mmol, 6.488 g) were each dissolved in 200 mL of methanol. Under ultrasonication, the imidazole solution was slowly poured into the cobalt nitrate solution. After 15 min of ultrasonication, the mixed solution was left to age at room temperature for 24 h. The resulting purple precipitate was collected by centrifugation, washed twice with methanol, and dried at room temperature for subsequent use.

Synthesis of ZIF-67/M (M = Mn, Fe or Ni): A suspension of ZIF-67 (120 mg) in ethanol (37.5 mL) was first prepared under ultrasonication, designated as Solution 1. Separately, Co(NO₃)₂·6H₂O (0.49 mmol, 0.143 g) was dissolved in methanol (10 mL) and then introduced into Solution 1 with continuous sonication. In another vessel, 2-methylimidazole (3.95 mmol, 0.3244 g) was dissolved in methanol (10 mL) and slowly added to the above mixture under ultrasonication. After ultrasonication for 15 min, 0.49 mmol (0.1201 g) of Mn(CH₃COO)₂·4H₂O was added. Once the manganese salt had completely dissolved, 1.6 mL of triethylamine was rapidly added dropwise. The mixture was ultrasonicated for another 15 min at room temperature, followed by a post-treatment consisting of heating under reflux at 80 °C for 3 h. Upon cooling to room temperature, the product was isolated by centrifugation, repeatedly washed with ethanol, and dried under vacuum at room temperature.

The same procedure as for ZIF-67/Mn was followed, except that the manganese salt was replaced with the same molar amount (0.49 mmol) of Fe(NO₃)₃·9H₂O for ZIF-67/Fe or NiCl₂·6H₂O for ZIF-67/Ni. The products were dried at room temperature for subsequent use.

3.3. Material Characterization

The crystalline structure was characterized by XRD on a Rigaku MiniFlex600 diffractometer (Rigaku Corporation, Tokyo, Japan) (2θ = 3–60°, step = 0.02°, scan rate = 5° min^{−1}). Chemical bonding information was obtained from FTIR spectroscopy (Nicolet iS50, Thermo Fisher Scientific, Waltham, MA, USA, KBr pellets) in the range of 400–4000 cm^{−1}. Thermal stability was evaluated by TGA using a thermal analyzer, with heating from room temperature to 800 °C at 10 °C min^{−1} under a synthetic air flow of 50 mL min^{−1}. Nitrogen physisorption was used to determine the BET specific surface area. The surface morphology and elemental composition were examined via FE-SEM (JSM-7900F, JEOL, Tokyo, Japan) equipped with EDS, while the fine nanostructure was further visualized by TEM (JEM-2100PLUS, JEOL, Tokyo, Japan). XPS measurements were conducted on a Thermo Fisher K-alpha spectrometer (Thermo Fisher Scientific), and the binding energies were normalized to the C 1s level at 284.8 eV.

3.4. Electrochemical Measurements

The as-prepared ZIF-67, ZIF-67/Mn, ZIF-67/Fe, and ZIF-67/Ni were each ground for at least 1 h. 3 mg of each sample was mixed with 40 µL of 5 wt% Nafion and 960 µL

of N,N-dimethylformamide, then ultrasonicated for 30 min. Subsequently, the resulting suspension was drop-cast onto carbon cloth pieces ($1 \times 1 \text{ cm}^2$) via a micropipette to reach a catalyst loading of 1 mg cm^{-2} . The resulting electrode was dried at room temperature prior to electrochemical measurements.

For HER and OER measurements, a three-electrode system was used in 1.0 mol L^{-1} KOH solution at 25°C using an electrochemical workstation (CHI 760E). The prepared electrode loaded with the sample served as the working electrode, while a Hg/HgO electrode and a platinum plate were used as the reference and counter electrodes, respectively. The measured potentials were converted versus RHE, $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 + 0.0592 \times \text{pH}$. The overpotential (η) for the OER was calculated using the equation: $\eta = E_{\text{RHE}} - 1.23 \text{ V}$. All linear sweep voltammetry (LSV) tests were performed at a scan rate of 5 mV s^{-1} with 90% IR compensation. Tafel slopes were obtained by fitting the corresponding Tafel plots. Electrochemical impedance spectroscopy (EIS) for OER was carried out at 0.5 V (vs. Ref) with an amplitude of 5.0 mV over a frequency range of $0.01\text{--}10^6 \text{ Hz}$. EIS for HER was carried out at -0.1 V (vs. Ref) with an amplitude of 5.0 mV over a frequency range of $0.01\text{--}10^6 \text{ Hz}$. The double layer capacitance was evaluated to determine the electrochemically active surface area (ECSA) through CV scans conducted within a nonFaradaic potential range using scan rates ranging from 10 to 180 mV s^{-1} . The double-layer capacitance (C_{dl}) was determined as the slope of the linear fit of the current density difference at the midpoint of the potential window versus the scan rate.

For overall water splitting, measurements were performed in a standard two-electrode electrochemical cell, using the as-prepared catalyst as both the anode and cathode. The catalyst was loaded onto nickel foam with a mass loading of 1 mg cm^{-2} , and the electrolyte was 1.0 mol L^{-1} KOH solution at 25°C . LSV was conducted at a scan rate of 5 mV s^{-1} with 90% IR compensation, and chronoamperometry stability tests were performed at a constant potential of 1.5 V vs. RHE for 24 h.

4. Conclusions

In this study, ZIF-67 was successfully prepared via a coprecipitation method, followed by the synthesis of Mn, Fe, and Ni-doped ZIF-67-based materials. The effects of metal doping on the structure, morphology, and electrocatalytic water splitting performance of the materials were systematically investigated. Metal doping preserves the ZIF-67 framework while inducing lattice variations, confirmed by XRD and FTIR. It significantly affects thermal stability, alters surface area and pore structure with increased mesoporosity, and causes crystal distortion, aggregation, and rougher morphology. Electrochemical tests confirmed that doping significantly enhanced the OER and HER performances. At a current density of 10 mA cm^{-2} , ZIF-67/Fe exhibited the lowest overpotentials for both OER (271 mV) and HER (338 mV), outperforming ZIF-67/Mn, ZIF-67/Ni, and pristine ZIF-67 (402 mV for OER and 446 mV for HER). The ZIF-67/Fe||ZIF-67/Fe electrode pair exhibited a low operating voltage of 1.513 V at 10 mA cm^{-2} for overall water splitting, along with long-term stability without noticeable activity decay over 24 h, demonstrating its good stability under ambient conditions. Metal doping, especially with Fe, effectively enhances the electrocatalytic water splitting performance of ZIF-67, likely through modifications to the coordination environments and active site distribution, rendering ZIF-67/Fe a highly promising candidate for efficient energy conversion applications.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16080739/s1>, Figure S1: Enlarged superimposed PXRD patterns of pristine ZIF-67 and doped ZIF-67/M (M = Mn, Fe, Ni); Figure S2: The EDS -mapping of (a) ZIF, (b) ZIF/Mn, and (c) ZIF/Ni; Figure S3: EDS point analysis of (a) ZIF, (b) ZIF/Mn, and (c) ZIF/Ni; Figure S4: High-resolution XPS spectra of C 1s, O 1s, and N 1s for (a–c) ZIF-67, (d–f) ZIF-67/Mn, (g–i) ZIF-67/Fe, and (j–l) ZIF-67/Ni; Figure S5: LSV polarization curves of commercial RuO₂ for OER (a) and Pt/C for HER (b) in 1.0 M KOH at 5 mV s^{−1}; Figure S6: CV curves of (a) ZIF-67, (b) ZIF-67/Mn, (c) ZIF-67/Fe, and (d) ZIF-67/Ni in HER.

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