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Unveiling dynamic surface transformations: Modoped Fe-based MOFs as next-generation oxygen evolution catalysts[†]

Sheraz Muhammad,^a Bowen Yao,^a Aling Zhou,^a Zhiyang Huang,^a Sumayya Khan,^a Fengli Wei,^a Zuyang Luo,^a Tayirjan Taylor Isimjan*^b and Xiulin Yang ⁽¹⁾*^a

Unlocking the full potential of metal–organic frameworks (MOFs) for water-splitting applications requires innovative strategies to enhance their catalytic efficiency and stability. Here, we introduce a Mo-doped Fe-based MOF (MoFe-NH₂-BDC) with a unique 2D nanosheet and plate-like morphology to revolutionize the oxygen evolution reaction (OER). Mo incorporation optimizes electronic properties, accelerates charge transfer, and dynamically reconstructs the catalyst surface into highly active FeOOH species, ensuring long-term performance. This next-generation electrocatalyst achieves an ultra-low overpotential of 254 mV at 20 mA cm⁻², with a rapid Tafel slope of 66 mV dec⁻¹, surpassing conventional RuO₂ catalysts. *Operando* Raman and ATR-FTIR spectroscopy reveal that Mo facilitates an adsorbate evolution mechanism (AEM), stabilizing intermediates and boosting reaction kinetics. In a practical two-electrode system, MoFe-NH₂-BDC⁽⁺⁾||Pt/C⁽⁻⁾ demonstrates an exceptional cell voltage of 1.58 V at 100 mA cm⁻², maintaining stability for 85 h. These results underscore the transformative impact of Mo doping in MOFs, paving the way for highly efficient, durable, and scalable electrocatalysts for sustainable energy applications.

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1. A Mo-doped Fe-based MOF ($Mo_{0.2}Fe-NH_2-BDC$), synthesized using a solvothermal method, exhibits a unique 2D nanosheet and plate-like morphology, enhancing electron transfer and catalytic activity. This design reduces reliance on noble metals, offering a cost-effective, sustainable alternative for greener hydrogen production.

2. $Mo_{0.2}$ Fe-NH₂-BDC achieves an ultra-low overpotential of 254 mV at 20 mA cm⁻² with a 66 mV dec⁻¹ Tafel slope, outperforming RuO₂. It demonstrates 100 h stability at 20 mA cm⁻² and 80 h at 100 mA cm⁻², minimizing material degradation and energy consumption.

3. In a two-electrode water-splitting system, $Mo_{0.2}$ Fe-NH₂-BDC⁽⁺⁾||Pt/C⁽⁻⁾ achieves a cell voltage of 1.58 V at 100 mA cm⁻², with 85 h stability. Replacing noble metals with earth-abundant materials and optimizing energy-efficient synthesis will further enhance sustainability. Using renewable feedstocks and biobased ligands can further improve the green credentials of this technology.

1. Introduction

The electrochemical oxygen evolution reaction (OER) is a critical half-reaction in energy conversion systems such as metal–air batteries and water-splitting electrocatalysis, playing a key role in the producing sustainable, carbon-free energy resources.^{1,2} In

light of global efforts to achieve carbon neutrality in the coming decades, the urgent need to develop highly efficient and robust catalysts to enhance OER performance has gained significant attention.^{3,4} However, the inherently slow multi-electron transfer mechanism of OER significantly hampers the efficiency of these systems, posing a substantial challenge to hydrogen production through water electrolysis.⁵ Traditional catalysts, such as Pt/C, IrO₂, and RuO₂, exhibit excellent catalytic properties, yet their widespread application is strictly limited by several factors, including high cost, poor stability, and suboptimal performance in catalytic processes.^{6,7} In addition, the scarcity of these materials and the complexity of their extraction and processing limit their viability for long-term wide-scale application.^{8,9} Exploring non-noble metal electrocatalysts with efficient activity and high stability has emerged as a promising and essential

^aGuangxi Key Laboratory of Low Carbon Energy Materials, School of Chemistry and Pharmaceutical Sciences, Guangxi Normal University, Guilin 541004, China. E-mail: xlvang@exnu.edu.cn

^bSaudi Arabia Basic Industries Corporation (SABIC) at King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia. F-mail: isimiant@sabic.com

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Metal-organic frameworks (MOFs) are an exceptional class of materials formed by the coordination of central metal ions with organic ligands through strong and stable bonds. Their distinctive features, such as adjustable porosity, high specific surface area, and a diverse functional species at metal centers and organic linkers, have positioned MOFs as a promising candidate in energy-related applications, particularly in the OER.^{10,11} However, despite these promising features, pristine MOFs face certain limitations. These include poor electrical conductivity, moderate chemical stability, and saturation of active sites, which can restrict their catalytic efficiency and hinder their overall performance.¹² To overcome these limitations, a practical approach is to introduce other metals into the MOF structure. This strategy enhances the intrinsic activity of individual metal sites and improves the materials conductivity, stability, and ion transport properties.¹³ Adding additional metals can expose more active sites, facilitate better electron transfer, and reduce diffusion resistance, significantly boosting the catalytic efficiency.¹⁴ For example, Zheng et al., reported a series of bimetallic Fe/Ni-MOFs synthesized via a solvothermal method, exhibiting exceptional OER performance with low overpotentials and a remarkably low Tafel slope. The Fe-doped Ni-MOFs demonstrated enhanced catalytic kinetics and conductivity compared to monometallic Ni-MOF and maintaining stable performance.¹⁵ In another study, Wang et al. showed that the introduction of Fe into Co-HHTP not only increases the electronic conductivity of the material but also tailors the electronic structure of Co, leading to a downshift of the Co d-band center, which weakens the adsorption of oxygen intermediates on Co sites, ultimately enhancing the OER performance.¹⁶ Furthermore Gao et al., developed a facile synthesis of Si-Fe-MOF catalyst via flash nano-precipitation technique, which exhibited superior catalytic activity with low overpotentials attributed to the formation of active FeOOH during OER and optimized electronic structure through Si doping.¹⁷ Thus, incorporation of a second metal into MOFs is a promising strategy to enhance electrocatalytic performance for the OER. This work introduces Mo into iron-based MOFs to significantly improve their OER electrocatalytic activity. Incorporating Mo can improve the catalysts electronic conductivity, facilitating enhanced electron and ion transport, promoting faster charge transfer, and lowering the overpotential required for OER. Furthermore, Mo stabilizes the active sites within the Fe-MOF structure, preventing catalyst deactivation under harsh conditions. It also tunes the electronic properties of the framework, optimizing the adsorption of reaction intermediates. The synergy between Fe and Mo enhances catalytic activity and ensures a more durable and effective OER catalyst, making it a promising candidate for sustainable energy applications. While the incorporation of metals into MOFs has been widely studied, to the best of our knowledge, the integration of Mo into Fe-MOFs for OER has not been explored previously, presenting a novel approach with significant potential to improve catalytic activity.

Herein, we synthesized MoFe-NH2-BDC using a solvothermal method. The resulting MoFe-NH2-BDC exhibits a 2D nanosheet and plate-like morphology, providing increased accessibility to active sites and a larger contact area with the electrolyte. The surface of the MoFe-NH₂-BDC rapidly reconstructs into FeOOH, which serves as the actual active site during the OER process. The prepared material demonstrates an overpotential of 254 and 301 mV to deliver 20 and 100 mA cm⁻² with exceptional durability over 100 and 80 h. Furthermore, the MoFe-NH₂-BDC⁽⁺⁾||Pt/C⁽⁻⁾ system achieves ultra-low cell voltages of 1.49 V and 1.58 V at 20 and 100 mA cm^{-2} , respectively, while exhibiting robust stability for 85 h in 1.0 M KOH. The 2D nanosheet and plate-like morphology of MoFe-NH₂-BDC optimizes the energy barriers in the OER process, facilitating more efficient electron and ion transport. This structural feature accelerates reaction kinetics, enhancing catalytic efficiency and overall performance in an alkaline environment.

2. Experimental section

2.1. Materials

Iron(II) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, \geq 99%), ethanol (C₂H₅OH, 99.7%), N,N-dimethylformamide (DMF, \geq 99%), sulfuric acid (H_2SO_4 , 37%), 2-aminoterephthalic acid (\geq 98%), and ammonium heptamolybdate tetrahvdrate $((NH_4)_6MO_7O_{24}\cdot 4H_2O, \geq 99\%)$, all of which were purchased from Xilong Science Co., Ltd. Additionally, RuCl₃·xH₂O (35-42%) was sourced from Shanghai Aladdin Chemical Reagent Co., Ltd. In contrast, potassium hydroxide (KOH, 90%) was obtained from Shanghai Macklin Chemical Reagent Co., Ltd. Commercial platinum on carbon (Pt/C, 20 wt%) and Nafion solution (5 wt%) were purchased from Suzhou Sinero Technology Co., Ltd. RuO₂ powder was synthesized by calcining RuCl₃ in air at 400 °C. Nickel foam (NF), used as the substrate in the experiments, was acquired from Guang Sheng Jia New Materials Co., Ltd. The NF with a thickness of 1.6 mm and was cut into pieces of size 1.5 cm × 3 cm. All reagents were of analytical grade and used without further purification.

2.2. Synthesis of Mo_xFe-NH₂-BDC

The synthesis of MoFe-NH₂-BDC and Fe-NH₂-BDC was carried out using a solvothermal method. For MoFe-NH₂-BDC, 4 mmol of 2-aminoterephthalic acid and 1 mmol of Fe (NO₃)₃·9H₂O were dissolved in 25 mL of DMF, 5 mL of water, and 5 mL of ethanol, and sonicated for 20 min to form solution A. In a separate beaker, dissolving varying amounts (x =0.1, 0.2 and 0.3 mmol) of ammonium heptamolybdate tetrahydrate (NH₄)₆Mo₇O₂₄·4H₂O in 15 mL of water to make solution B. Solution B was then added to solution A, and the resulting precursor solution was thoroughly mixed. A piece of NF, prewashed with 0.5 M H₂SO₄, ethanol, and deionized water for 10 min, respectively, was submerged into the precursor solution, and the mixture was transferred into a Teflon-lined stainless-steel autoclave. The autoclave was sealed and heated at

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125 °C for 12 h. After the autoclave cooled naturally, the sample was washed several times with ethanol and dried at 60 °C overnight to obtain MoFe-NH₂-BDC.

For Fe-NH₂-BDC, the identical procedure was employed, albeit without the incorporating of ammonium heptamolybdate tetrahydrate. Solution A was utilized, but the molybdenum component was omitting.

2.3. Synthesis of RuO_2/NF and Pt/C/NF electrodes

To prepare RuO₂ and Pt/C catalysts for comparison, the coating solution was prepared by dispersing 2.5 mg of RuO₂ and 20 wt% Pt/C into a mixture containing of 220 μ L of deionized water, 220 μ L of ethanol, and 5 μ L of a 5 wt% Nafion solution. The resulting mixture was sonicated for 30 min to achieve a homogeneous suspension. Subsequently, the solution was meticulously drop-coated onto a pristine NF substrate measuring 1 cm \times 1 cm and allowed to dry in air under ambient condition.

3. Results and discussion

3.1. Fabrication method and structural analysis

The synthesis of Mo-doped Fe-based MOF (MoFe-NH₂-BDC) a 2D nanosheet and plate-like morphology, grown on NF via a one-step solvothermal method, is shown in Fig. 1a. This process effectively incorporates Mo into the Fe-NH2-BDC framework, resulting in MoFe-NH2-BDC with a well-defined 2D nanosheet and plates like structure supported on NF. The inclusion of Mo in the Fe and NH2-BDC mixture led to the formation of MoFe-NH₂-BDC. The structural analysis of catalyst was conducted using X-ray powder diffraction (XRD). The pristine Fe-NH₂-BDC exhibits two primary diffraction peaks at approximately 9.18° and 10.50°, closely aligning with the theoretical simulations of Fe-NH2-BDC as described in the crystallographic information file (CIF, Cambridge Crystallographic Data Centre no. 647646).¹⁸⁻²⁰ After Mo doping, the MoFe-NH₂-BDC retains a crystal structure similar to Fe-NH₂-BDC, indicating a low Mo doping load. However, as the Mo doping concentration increases, the diffraction peaks show a slight decrease in intensity, as observed in Fig. 1b, suggesting subtle structural changes with higher doping levels. The molecular structure and functional groups of the synthesized samples were analyzed using Fourier transform infrared (FTIR) spectroscopy (Fig. 1c). For MoFe-NH₂-BDC, the absorption peak at 3459 cm⁻¹ corresponds to the asymmetric stretching vibration of the -NH2 group. The peaks observed in the 1683-1380 cm⁻¹ range are attributed to the characteristic vibrations of the C=C, C=O, and -COO groups.^{21,22} A vibrational band at 1236 cm⁻¹ is associated with the C-N stretching mode. Additionally, the organic linker exhibits a C-H bending vibration at 760 cm⁻¹. Combination Fe ions with the organic ligands leads to metal-oxygen (M-O) vibrational bands observed in the range of 570-410 cm⁻¹.^{23,24} FTIR analysis confirms the successful incorporation of functional groups and the effective coordination between the metal

centers (Mo and Fe) and the organic ligands. The findings demonstrate that the MoFe-NH₂-BDC material maintains its structural integrity while integrating these components, ensuring the presence of essential functional groups for its potential OER applications.

The scanning electron microscopy (SEM) images reveal that both Fe-NH₂-BDC and Mo_{0.2}Fe-NH₂-BDC exhibit a distinct nanosheets and plates-like morphology, characterized by thin, smooth plates with sharp edges and a hierarchical, 2D-dimensional arrangement in a triangular shape (Fig. 2a and b).^{25,26} The morphology of MoFe-NH2-BDC is slightly similar to that of Fe-NH₂-BDC, indicating that the incorporation of Mo does not significantly alter the materials structural framework (Fig. S1[†]). However, addition Mo is expected to enhance the catalytic performance by introducing additional active sites. For the transmission electron microscopy (TEM) analysis, the Mo_{0.2}Fe-NH₂-BDC displays a similar 2D nanosheets and plateslike morphology as observed in SEM, with thin, smooth, and well-defined plates (Fig. 2c). The high transparency of the nanosheets and plates in the TEM image highlights their nanoscale thickness, further confirming their 2D structure. The morphology retains the structural framework and ensures a high surface area and accessibility to active sites, which is crucial for enhancing catalytic performance in electrocatalytic applications. High-resolution transmission electron microscopy (HR-TEM) image of Mo_{0.2}Fe-NH₂-BDC does not show clear lattice fringes, likely due to localized structural defects and the extreme sensitivity of MOFs to electron beam irradiation (Fig. 2d). MOF structures are highly susceptible to damage under HR-TEM conditions, often becoming amorphous during imaging, which limits the resolution to the materials beam stability rather than the capability of the microscope. Factors such as weak coordination between metal ions and ligands, hydrogen bonding, and structural flexibility further contribute to the difficulty in obtaining clear, highresolution images. This sensitivity is a common challenge when imaging beam-sensitive materials like MOFs.^{27,28} The selected area electron diffraction (SAED) pattern of the Mo_{0.2}Fe-NH₂-BDC 2D nanosheets and plates displays sharp and periodic diffraction spots (Fig. 2e), indicating the materials highly crystalline and single-crystalline nature.²⁹ The atomic force microscopy (AFM) image reveals the 2D morphology of Mo_{0.2}Fe-NH₂-BDC, with an average thickness of 31.20 nm, highlighting its thin and uniform nanoscale structure (Fig. 2f and g). This confirms the successful formation of 2D nanosheets and plates like morphology, which provide a high surface area and accessible surface features, making the material suitable for applications that benefit from its nanoscale dimensions and structural uniformity.

The EDX spectrum and high-angle annular dark field (HAADF) image, combined with elemental mapping, confirm the successful synthesis, high purity, and structural integrity of the $Mo_{0.2}$ Fe-NH₂-BDC catalyst. Prominent peaks for C, O, and N correspond to the organic ligand framework, while distinct peaks for Fe and Mo validate their incorporation into the MOF structure (Fig. S2†). The elemental mapping (Fig. 2h–m)



Fig. 1 (a) Schematic diagram for the synthesis of MoFe-NH₂-BDC. (b) XRD patterns of Fe-NH₂-BDC and Mo_xFe-NH₂-BDC, along with simulated data from the Fe-NH₂-BDC crystal structure. (c) FTIR spectra of NH₂-BDC, Fe-NH₂-BDC, and Mo_xFe-NH₂-BDC.

highlights the uniform distribution of these elements throughout the 2D nanosheets and plates, confirming the absence of impurities and ensuring the materials high purity.³⁰ Additionally, the localized presence of Mo, observed in Fig. 2m, demonstrates the effectiveness of the doping process and its critical role in the catalyst's composition. These results collectively validate the materials composition, uniformity, doping efficiency, and reliability for OER applications.

The valence states of the surface metal species were analyzed using X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum of MoFe-NH₂-BDC confirms the presence of C, N, O, Fe, and Mo as shown in Fig. S3f,† indicating the successful incorporation of Mo into the structure. The highresolution C 1s spectrum (Fig. 3a and Fig. S3a†) reveals three distinct peaks corresponding to C=C/C-C (284.35 eV), C-N/C-O (285.48 eV), and C=O (288.23 eV).³¹⁻³³ In Fig. 3b, the highresolution XPS spectra of N 1s reveal distinct peaks corresponding to various nitrogen species. A peak at 397 eV is attributed to Mo-N coordination, confirming the successful incorporation of Mo into the structure and its interaction with nitrogen. Additionally, peaks at 398.56 eV, 399.82 eV, and 401.48 eV are assigned to C–N, N–H, and nitrogen oxide species, respect-

ively (Fig. S3b[†]).³⁴⁻³⁷ Notably, the C-N peak in Mo_{0.2}Fe-NH₂-BDC shifts to a lower binding energy compared to Fe-NH2-BDC, indicating electronic modulation caused by the introduction of Mo into the framework. This shift suggests that the interaction between Mo and the nitrogen alters the electronic environment of the C-N bond. In contrast, Fe-NH₂-BDC shows only C-N, N-H, and nitrogen oxide species without the Mo-N peak, further validating the specific interaction between Mo and the ligands in Mo_x Fe-NH₂-BDC. The deconvolution of the O 1s spectrum (Fig. 3c) shows three peaks at 530.43, 531.45, and 532.75 eV, which correspond to the M-O bond, O-C/C=O group, and adsorbed water molecules (H₂O_{ads}) (Fig. S3c†).^{38,39} The Fe 2p spectrum (Fig. 3d) shows two primary peaks and one satellite peak for both Fe-NH2-BDC and Mo0.2Fe-NH2-BDC at binding energies of 710.05 eV, 712.39 eV, and 715.50 eV, respectively.⁴⁰⁻⁴³ Notably, in the case of Mo doped Fe-NH₂-BDC, the Fe²⁺ peak experiences a slight shift to 710.21 eV, attributed to the electron density modification caused by the incorporation of Mo into the structure (Fig. S3d[†]). The presence of Mo in the framework alters the local electronic environment around the Fe centers, resulting in a redistribution of electron density and influencing the binding energy of



Fig. 2 SEM images of (a) Fe-NH₂-BDC and (b) $Mo_{0,2}$ Fe-NH₂-BDC. (c) TEM, (d) HR-TEM, (e) SAED pattern, (f) AFM, (g) corresponding height profiles, (h) HAADF-STEM, and (i-m) elemental mapping images of $Mo_{0,2}$ Fe-NH₂-BDC.



Fig. 3 High-resolution XPS spectra and thermal characterization of Fe-NH₂-BDC and Mo_{0.2}Fe-NH₂-BDC. (a) C 1s, (b) N 1s, (c) O 1s, (d) Fe 2p, (e) Mo 3d and (f) Relative distribution of Fe²⁺ and Fe³⁺ species (g and h) TG/DTG curves of Fe-NH₂-BDC and Mo_{0.2}Fe-NH₂-BDC.

Fe²⁺. This shift highlights the interaction between Mo and Fe, which modulates the electronic structure and enhances catalytic properties. Additionally, the relative content of Fe species (Fig. 3f) further illustrates the impact of Mo incorporation. In Fe-NH₂-BDC, the Fe²⁺ content is 26.04%, while the Fe³⁺ content is 43%. After Mo doping, the Fe^{2+} content increases to 34.12%, and Fe³⁺ rises to 47.84%, indicating an overall increase in the proportion of Fe³⁺ species. This shift suggests that the presence of Mo enhances the oxidation state of Fe, which could be critical in facilitating OER activity by increasing the availability of Fe³⁺ active sites. For Mo_{0.2}Fe-NH₂-BDC, the Mo 3d spectrum reveals two distinct sets of peaks (Fig. 3e) indexed to Mo 3d_{5/2} and Mo 3d_{3/2}, respectively. The peaks centered at 231.04 eV and 234.09 eV, are attributed to Mo⁴⁺. These peaks are associated with the Mo-O bonding environment. On the other hand, the peaks observed at 231.97 eV and 235.18 eV correspond to $Mo^{6+.44,45}$ The coexistence of both Mo^{4+} and Mo⁶⁺ suggests the presence of mixed-valence states of Mo in Mo_rFe-NH₂-BDC (Fig. S3e[†]). The XPS analysis of Mo_rFe-NH₂-BDC reveals key insights into its structural and electronic properties, which are crucial for OER electrocatalysis. These findings highlight the materials enhanced catalytic potential, driven by the synergistic interactions between Mo, Fe, and nitrogen-containing ligands, making Mo_xFe-NH₂-BDC a promising candidate for efficient OER performance. The thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) highlight significant differences in the thermal behaviors of Fe-NH₂-BDC and Mo_{0.2}Fe-NH₂-BDC (Fig. 3g and h). For Fe-NH₂-BDC, an initial weight loss (10.01%) occurs around 113 °C due to the removal of adsorbed moisture, followed by decomposition of the organic linker (10.97%) around 222 °C, and a major weight loss (53.18%) around 290 °C indicating rapid structural degradation. In comparison, Mo_{0.2}Fe-NH₂-BDC exhibits a reduced initial weight loss (2.47%), suggesting lower moisture retention, and a much smaller weight loss (16.47%) occurring at a significantly higher temperature of approximately 390 °C.46,47 This shift highlights the improved thermal stability of the Mo-doped material, likely due to stronger interactions between Mo and the organic framework. The enhanced decomposition temperature and lower overall weight loss in Mo_{0.2}Fe-NH₂-BDC suggest that Mo incorporation reinforces the structural integrity, making it more suitable for OER electrocatalysis, where thermal robustness is crucial.

3.2. OER electrocatalytic efficiency

The OER performance of the synthesized catalysts was evaluated in 1.0 M KOH using a standard three-electrode configuration consisting of a working electrode, a counter electrode, and a reference electrode. All potentials were calibrated to the reversible hydrogen electrode (RHE) and fully 100% *iR*-compensated to ensure accuracy. As illustrated in Fig. 4a, the linear sweep voltammetry (LSV) curves highlight the outstanding OER activity of $Mo_{0.2}$ Fe-NH₂-BDC, requiring only 254 mV, 301 mV and 323 mV to achieve current densities of 20, 100, and 200 mA cm⁻², respectively (Fig. S5†). This performance surpasses the other catalysts tested, showcasing its superior

electrocatalytic efficiency. To further investigate the OER kinetics, Tafel slopes were calculated from the polarization curves (Fig. 4b). The Mo_{0.2}Fe-NH₂-BDC catalyst exhibits a Tafel slope of 66 mV dec⁻¹, which is significantly lower than that of Fe- NH_2 -BDC (86 mV dec⁻¹) and even surpasses the benchmark RuO_2 (73 mV dec⁻¹). This lower Tafel slope indicates that introducing Mo into the Fe-NH2-BDC structure effectively improves the catalytic kinetics, facilitating faster reaction rates for OER. The enhanced activity can be attributed to improved charge transfer efficiency and the catalysts synergistic effects between Mo and Fe. Fig. 4c demonstrates that Mo_{0.2}Fe-NH₂-BDC consistently exhibits a smaller ratio compared to Fe-NH2-BDC across various current densities. This observation further validates the improved reaction kinetics of Mo_{0.2}Fe-NH₂-BDC, highlighting its superior catalytic efficiency and enhanced charge transfer capabilities during the OER process.

Furthermore, the exceptional OER performance of Mo_{0.2}Fe-NH2-BDC outperforms Fe-NH2-BDC and RuO2 and exceeds most recently reported OER catalysts, as shown in Fig. 4d and detailed in Table S1.† Electrochemical impedance spectroscopy (EIS) was conducted to evaluate the charge-transfer efficiency of the catalysts. As shown in Fig. 4e, Mo_{0.2}Fe-NH₂-BDC exhibits a significantly lower charge transfer resistance $(R_{\rm ct} = 1.82 \ \Omega)$ compared to Fe-NH₂-BDC $(R_{\rm ct} = 5.62 \ \Omega)$ and RuO₂ (R_{ct} = 3.58 Ω). This lower R_{ct} value indicates that Mo_{0.2}Fe-NH2-BDC facilitates faster charge transfer and exhibits enhanced electrical conductivity. The significant reduction in charge transfer resistance is attributed to Mo doping, which alters the local electronic environment around Fe centers, thereby promoting more efficient electron transport.48,49 Furthermore, Mo introduces synergistic effects that improve the adsorption and activation of OER intermediates, collectively accelerating interfacial charge transfer kinetics.^{50,51} The electrochemical double-layer capacitance (C_{dl}) , which is directly proportional to the electrochemical surface area (ECSA), was measured using cyclic voltammetry (CV) in the non-faradaic region at various scan rates (Fig. S4a-d⁺). $Mo_{0.2}$ Fe-NH₂-BDC demonstrated a significantly higher C_{dl} value of 3 mF cm⁻² compared to its counterparts, including Mo_{0.1}Fe-NH₂-BDC, Mo_{0.3}Fe-NH₂-BDC, and Fe-NH₂-BDC, as shown in Fig. 4f. This elevated C_{dl} value reflects a considerably larger ECSA of 75 cm² for Mo_{0.2}Fe-NH₂-BDC, as illustrated in Fig. 4g, which is notably higher than those of the other tested catalysts. The large ECSA suggests that Mo_{0.2}Fe-NH₂-BDC offers more electrochemically active sites, essential for facilitating the OER. This enhanced surface area not only promotes better interaction with the electrolyte but also improves the accessibility of catalytic active sites, thereby contributing to its superior catalytic performance. The durability tests for Mo_{0.2}Fe-NH₂-BDC demonstrated exceptional long-term stability during OER under both moderate and high current densities. At a constant current density of 20 mA cm⁻², the catalyst exhibited a minimal decline of only 3.94% in current density after 100 h of continuous operation (Fig. 4h), highlighting its stability under standard conditions. Moreover, at a high current density of 100 mA cm⁻², Mo_{0.2}Fe-NH₂-BDC maintained



Fig. 4 OER performance of various electrocatalysts in 1.0 M KOH solution. (a) LSV polarization curves of the catalysts. (b) Corresponding Tafel slopes. (c) The overpotential (η) ratio to $\log |j|$ at different current densities. (d) Comparison of the overpotential and Tafel slope with previously reported OER catalysts. (e) Electrochemical impedance spectroscopy. (f) Double-layer capacitance (C_{dl}) plots. (g) Comparison of the electrochemical active surface area (ECSA). (h) Long-term stability test of the catalyst at 20 and 100 mA cm⁻², with the inset showing the polarization curves before and after 3000 CV cycles.

robust performance for 80 h, indicating its potential for practical applications in water-splitting technologies. Additional durability assessments through multi-cycle CV further underscored its resilience. After 3000 CV cycles, the polarization curves showed negligible shifts (inset Fig. 4h), confirming the structural and electrochemical stability of the catalyst over extended cycling. These findings highlight Mo_{0.2}Fe-NH₂-BDC as an efficient and durable catalyst for OER, capable of delivering exceptional long-term performance under both standard and demanding conditions. The comprehensive evaluation reveals its outstanding electrocatalytic properties, including low overpotentials, a small Tafel slope, excellent charge transfer efficiency, and a large electrochemical surface area. Additionally, the catalyst demonstrates remarkable stability over extended operation, maintaining its structural and electrochemical integrity even during prolonged testing. The incorporating Mo into the Fe-NH2-BDC framework is crucial in enhancing its activity and durability, making Mo_{0.2}Fe-NH₂-

BDC a promising candidate for water-splitting applications and sustainable energy technologies.

3.3. Integrated *operando* spectroscopic techniques for elucidating the OER mechanism

The dynamic reconstruction of catalysts during OER electrocatalysis is primarily driven by the redox electrochemistry of metal species within catalytic systems. This reconstruction process facilitates structural transformations and form highly active sites. These *in situ* generated active sites are essential for optimizing catalytic activity and enhancing the overall efficiency of the OER process. *In situ* electrochemical impedance spectroscopy (EIS) measurements were carried out to monitor the dynamic evolution of the catalysts and elucidate the charge transfer processes occurring at the catalytic surface. As the applied potential increases, the phase angle shifts significantly, as shown in Fig. 5a and b, indicating enhanced reaction kinetics and improved adsorption of reactants. The $Mo_{0.2}Fe-NH_2-BDC$

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Fig. 5 In situ electrochemical and spectroscopic analysis. (a) Bode plots of $Mo_{0,2}Fe-NH_2-BDC$ at different potentials (vs. RHE). (b) Bode plots of Fe-NH₂-BDC at varying potentials (vs. RHE). (c) Response of the phase angle to the applied potential for $Mo_{0,2}Fe-NH_2-BDC$ and $Fe-NH_2-BDC$. (d) Potential-dependent *in situ* Raman spectra of $Mo_{0,2}Fe-NH_2-BDC$ at different potentials (vs. RHE). (e) In situ ATR-FTIR spectra of $Mo_{0,2}Fe-NH_2-BDC$ at different potentials. (f) Schematic diagram of the dynamic surface reconstruction process and active FeOOH site formation in a KOH environment. (g) Proposed stepwise OER mechanism for $Mo_{0,2}Fe-NH_2-BDC$.

catalyst demonstrates a pronounced decrease in phase angle across the potential range compared to Fe-NH₂-BDC, suggesting that Mo doping improves the charge transfer rate and facilitates surface activation of the catalyst. Notably, the complete transition for Mo_{0.2}Fe-NH₂-BDC occurs at 1.50 V, whereas for Fe-NH₂-BDC, the transition is delayed, occurring around 1.55 V, highlighting the enhanced kinetics of the Mo_{0.2}Fe-NH₂-BDC catalyst.52,53 Moreover, the EIS-derived Bode plots, as depicted in Fig. 5c, provide deeper insights into the interfacial dynamics of the electrocatalysts and the OER process, showcasing the variation of phase angles at different applied potentials. The peak in the high-frequency region $(10^2 - 10^5 \text{ Hz})$ corresponds to the oxidation of Fe species, while the peak in the low-frequency region $(10^{-2}-10^{1} \text{ Hz})$ is associated with the OER process.⁵⁴ The smaller phase angles observed for Mo_{0.2}Fe-NH₂-BDC compared to Fe-NH₂-BDC across the same potential range indicate that the Mo doping facilitates more efficient electron transfer (Fig. S6[†]). This improved electron mobility accelerates the reaction kinetics and enhances the OER performance. These results collectively highlight the dynamic processes and the critical role of the Mo_{0.2}Fe-NH₂-BDC 2D nanosheets and plates in achieving superior OER catalytic activity.

To further investigate the surface reconstruction process, in situ electrochemical Raman spectroscopy was employed to analyze the structural evolution of the Mo_{0.2}Fe-NH₂-BDC catalyst in the potential range of 1.10-1.50 V (vs. RHE). As shown in Fig. 5d, no significant changes were observed in the Raman features of the catalyst at lower potentials (1.10-1.30 V), indicating the stability of the Mo and Fe coordination at these stages. The Raman peak observed at approximately 944 cm⁻¹ in the potential range from OCP to 1.30 V (vs. RHE) is attributed to the terminal Mo=O stretching mode, characteristic of Mo⁶⁺ oxo species. As the applied potential increases beyond 1.30 V, this Mo=O peak gradually diminishes, indicating a structural transformation of the Mo environment.55,56 Notably, at 1.30 V, a new distinct peak emerges at 894 cm⁻¹, which is assigned to bridging Mo-O-Mo vibrations.^{57,58} This shift reflects the condensation of Mo=O units into polymerized Mo-O networks, signifying the active involvement of Mo in the electrochemical restructuring process. However, upon increasing the potential to 1.40 V (vs. RHE), new Raman peaks emerge at 474 $\rm cm^{-1}$ and 554 $\rm cm^{-1},$ attributed to the $\rm E_g$ bending and A1g stretching vibrations of Fe-O in FeOOH, signifying the surface oxidation and transformation of Fe

species.^{59–61} The *in situ* Raman highlights the dynamic and synergistic roles of Mo and Fe during the surface reconstruction process, where Mo facilitates the structural transformation, and Fe contributes to the formation of active FeOOH species, eventually enhancing the catalytic activity of the $Mo_{0,2}$ Fe-NH₂-BDC catalyst for the OER.

Understanding the OER pathway relies on identifying the intermediates formed during the reaction. To achieve this, operando attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was employed to monitor the oxygen species generated on the Mo_{0.2}Fe-NH₂-BDC catalyst under alkaline OER conditions. This technique offers critical experimental insights into the reaction mechanism by tracking the evolution of key intermediates in real time. The in situ ATR-FTIR spectra reveal key insights into forming intermediates during the OER. At the open circuit potential (OCP), no significant absorption peaks are detected, indicating the absence of active intermediates on the catalyst surface (Fig. 5e). However, as the applied voltage enters the OER region, distinct peaks appear at 1176 cm⁻¹, corresponding to *OOH species, and 1282 cm⁻¹, attributed to O-O bond vibrations.62-64 These intermediates are integral to the adsorbate evolution mechanism (AEM), where surface-bound oxygen species (*OH, *OOH, and O₂) form sequentially. The increasing intensity of these peaks with higher voltages signifies the accumulation and active involvement of these intermediates in the OER process, further confirming the stepwise nature of the reaction mechanism on the Mo_{0.2}Fe-NH₂-BDC catalyst.

The SEM images shown in Fig. S7a-d† illustrate the surface morphology of the Mo_{0.2}Fe-NH₂-BDC catalyst after the stability test. The slight textural changes observed suggest surface activation and reconstruction, characteristic of catalysts under prolonged operational conditions.^{65,66} After the CP stability test, the XPS results provide strong evidence for the dynamic surface reconstruction and electronic modulation of the Mo_{0.2}Fe-NH₂-BDC catalyst during OER. After the OER stability test, a positive shift in the O 1s XPS peak was observed, suggesting a change in the surface chemical environment. This shift is consistent with the formation of FeOOH, as the higher binding energy corresponds to hydroxylated oxygen species typically associated with Fe3+ in oxyhydroxide structures (Fig. S8a and b⁺).⁶⁷ The leaching of N and Mo species after the OER CP test is attributed to the chemical instability of their coordination environments under prolonged electrochemical conditions. Nitrogen atoms, coordinated through amino-functionalized linkers, are prone to de-coordination or oxidative cleavage under high anodic potentials, especially in the presence of reactive oxygen species, leading to their gradual release into the electrolyte. For molybdenum, leaching occurs due to its tendency to form soluble molybdate species (MoO_4^{2-}) in alkaline media, particularly when present in higher oxidation states such as Mo⁶⁺. The combination of oxidative conditions and strong hydroxide interaction facilitates the dissolution of Mo-O units from the catalyst surface.⁶⁸⁻⁷⁰ These processes are facilitated by the strongly oxidative and alkaline environment during OER, resulting in surface reconstruction and compositional changes at the electrode electrolyte interface. The diminished signals in the N 1s and Mo 3d spectra (Fig. S8c and d[†]) further support the occurrence of leaching and highlight the dynamic nature of these elements during catalysis. The shift in the Fe 2p spectra to higher binding energies indicates the formation of highly active FeOOH species, signifying the oxidation of Fe^{2+} to Fe^{3+} , which is critical for catalytic activity (Fig. S8e and f⁺). This transformation highlights the dynamic surface reconstruction of the catalyst, enabling enhanced adsorption and conversion of oxygen intermediates (*OH, *O, *OOH) during the OER process.^{71,72} Mo is actively involved in stabilizing FeOOH sites and facilitating electron transfer during the reaction. Despite this leaching, the Fe-based active centers remain dominant, as supported by in situ Raman spectra showing Fe-O vibrational modes associated with FeOOH.

The dynamic surface reconstruction and mechanistic insights gathered through in situ analyses and XPS strongly support the AEM pathway for OER on the Mo_{0.2}Fe-NH₂-BDC catalyst. Furthermore, Fig. 5f shows the dynamic surface reconstruction and the AEM that govern the OER on the Mo_{0.2}Fe-NH₂-BDC catalyst. The insights from in situ Raman confirm the dynamic transformation of Fe species into FeOOH active sites at higher applied potentials, a process facilitated by Mo doping that stabilizes the structure and enhances charge transfer. Raman spectra reveal the formation of Fe-O vibrational modes associated with FeOOH and a reduction in Mo-O-Mo vibrations, indicating Mo role in supporting structural reconstruction. Similarly, in situ ATR-FTIR provides evidence of the stepwise formation of reaction intermediates, such as *OH, *OOH, and O-O species, with distinctive absorption peaks corresponding to these intermediates. These in situ analyses support AEM pathway. The OER on the FeOOH active sites proceeds through a stepwise AEM, as illustrated in Fig. 5g. Initially, hydroxide ions (OH⁻) are adsorbed onto the active FeOOH sites, forming *OH intermediates through an electron transfer process. In the second step, the *OH intermediates are oxidized, releasing water and forming *O species. These *O species then react with additional hydroxide ions (OH⁻) in the third step, leading to the formation of *OOH intermediates, which are crucial intermediates in the OER pathway. Finally, in the fourth step, the *OOH species release molecular oxygen (O_2) and regenerate the active FeOOH site, completing the catalytic cycle. This sequential mechanism highlights the transformation of oxygen-containing intermediates (*OH, *O, *OOH) and the regeneration of active sites, which are critical for sustaining efficient and stable OER performance.⁷³⁻⁷⁵ The in situ analyses validate the dynamic surface reconstruction and directly correlate it with the catalytic process. Mo enhances charge transfer and stabilizes the FeOOH active sites, while the FeOOH structure facilitates intermediate formation and transformation, as demonstrated by Raman study. The stepwise mechanism is confirmed by the ATR-FTIR peaks corresponding to *OOH and O-O bond vibrations. The synergy between Mo and Fe, coupled with dynamic surface reconstruction and the AEM pathway, ensures superior OER performance. Mo facilitates charge transfer and structural stabilization, while FeOOH active sites enable efficient intermediate adsorption and transformation, delivering excellent catalytic activity and durability for the $Mo_{0.2}$ Fe-NH₂-BDC catalyst.

3.4. Overall water splitting

The two-electrode water splitting experiment is a key benchmark to determine whether a catalyst holds potential for commercialization in overall water splitting applications. As illustrated in Fig. 6a, the electrolyzer was constructed using Mo_{0.2}Fe-NH₂-BDC as the anode and commercial Pt/C as the cathode. This configuration provides a robust system for evaluating the catalysts efficiency and durability. The setup ensures efficient oxygen evolution at the anode and hydrogen evolution at the cathode, forming a complete water splitting system. The performance of the electrolyzer is shown in the inset of Fig. 6b, where it achieves a cell voltage of only 1.49 V to drive a current density of 20 mA cm⁻², which is significantly lower than the benchmark $RuO_2^{(+)}||Pt/C^{(-)}$ system that requires 1.57 V for the same current density, also surpassing other previously reported catalysts (Table S2[†]). This demonstrates the superior efficiency of the Mo_{0.2}Fe-NH₂-BDC catalyst in reducing the energy barrier for oxygen evolution. Fig. 6c compares the cell voltage of $Mo_{0.2}$ Fe-NH₂-BDC with other reported twoelectrode water splitting systems. The results show that this catalyst achieves one of the lowest cell voltages among the systems tested, further emphasizing its superior performance for overall water splitting. This comparison highlights the competitive advantage of $Mo_{0.2}$ Fe-NH₂-BDC in terms of energy efficiency and practicality for water splitting applications. Additionally, Fig. 6d highlights the excellent stability of the system, maintaining steady performance for 85 h at 20 mA cm⁻² without voltage degradation, underscoring the durability of the catalyst.

To evaluate the performance of the electrolyzer under more demanding conditions, high current density tests were conducted, as shown in Fig. 6b. The $Mo_{0.2}Fe-NH_2-BDC^{(+)}||Pt/C^{(-)}$ system required only 1.58 V and 1.87 V to drive current densities of 100 mA cm⁻² and 500 mA cm⁻², respectively (Fig. S9†). Impressively, the system demonstrated exceptional stability even under these challenging conditions, with no noticeable voltage increase after 85 h at 100 mA cm⁻², as depicted in Fig. 6d. This excellent performance under high current densities, coupled with long-term stability, under-



Fig. 6 Overall water splitting performance of the $Mo_{0.2}Fe-NH_2-BDC$ catalyst in 1.0 M KOH. (a) Schematic illustration of overall water splitting in a two-electrode system. (b) Polarization curves of the electrolytic cells with $Mo_{0.2}Fe-NH_2-BDC^{(+)}||Pt/C^{(-)}$ and the reference cell with $RuO_2^{(+)}||Pt/C^{(-)}$. (c) Comparison of the cell voltages with previously reported water electrolyzers. (d) Chronopotentiometry curves at 20 and 100 mA cm⁻² for 85 h (inset: experimental phenomenon during the catalyst stability test).

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scores the potential of this catalyst for practical water splitting applications. Together, these results demonstrate that $Mo_{0.2}$ Fe-NH₂-BDC is a highly efficient and durable catalyst, achieving competitive performance compared to state-of-the-art systems and highlighting its promise for practical and sustainable water splitting.

3.5. Mechanistic insights and performance factors

The exceptional OER electrocatalytic activity, stability, and overall water splitting performance of the Mo_{0.2}Fe-NH₂-BDC catalyst are attributed to the following key factors: (1) The unique 2D nanosheets and plates-like morphology maximizes active site exposure, accelerates electrolyte diffusion, and facilitates efficient gas evolution. (2) The incorporation of Mo into the Fe-NH2-BDC framework enhances charge transfer efficiency through electronic interactions between Mo and Fe, as revealed by in situ EIS measurements. (3) In situ Raman and ATR-FTIR analyses confirm a dynamic surface reconstruction process that transforms Fe species into FeOOH active sites, which are essential for adsorbing and converting oxygen intermediates. (4) XPS results show shift in the Fe 2p binding energies, indicating the oxidation of Fe²⁺ to Fe³⁺ and the formation of highly active FeOOH species, with Mo playing a critical role in stabilizing these sites. (5) The strong electronic interactions between Mo and Fe help optimize the adsorption energies of intermediates, reduce activation energy, and enhance catalytic efficiency. Collectively, these factors ensure the high catalytic activity and stability of Mo_{0.2}Fe-NH₂-BDC, making it a promising candidate for practical water splitting applications.

4. Conclusion

The experimental findings strongly support the role of Mo incorporation in significantly enhancing the OER performance of Fe-based MOFs. Structural characterization confirmed the successful formation of a 2D nanosheet and plate-like morphology, ensuring high surface area and increased accessibility to active sites. Electrochemical evaluations revealed that Mo_{0.2}Fe-NH₂-BDC achieves an overpotential of 254 mV at 20 mA cm⁻², outperforming conventional RuO₂ catalysts while maintaining exceptional stability over 100 h. Key insights from in situ Raman and ATR-FTIR spectroscopy indicate that the catalytic mechanism follows an AEM. Mo facilitates the formation of FeOOH active sites through dynamic surface reconstruction. This transformation significantly improves intermediate adsorption and charge transfer efficiency, as evidenced by EIS and XPS analyses. The two-electrode system further confirmed the catalysts superior performance, achieving a low cell voltage of 1.58 V at 100 mA cm^{-2} , demonstrating excellent long-term stability (85 h) at high current densities. These findings establish Mo_{0.2}Fe-NH₂-BDC as a promising candidate for OER electrocatalysis, highlighting the impact of Mo doping in optimizing electronic structure and catalytic stability. The study provides a comprehensive framework for designing next-generation MOF-based electrocatalysts, with significant implications for energy storage, water splitting, and hydrogen production applications.

Author contributions

Sheraz Muhammad: writing – original draft, investigation, conceptualization. Bowen Yao: investigation. Aling Zhou: data curation. Zhiyang Huang: formal analysis. Sumayya Khan: data curation. Fengli Wei: conceptualization. Zuyang Luo: methodology. Tayirjan Taylor Isimjan: writing – review & editing. Xiulin Yang: writing – review & editing, supervision.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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