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Hybrid 2D Dual-Metal-Organic Frameworks for Enhanced Water Oxidation Catalysis

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Hybrid 2D Dual-Metal-Organic Frameworks for Enhanced Water Oxidation Catalysis

Abstract

Metal-organic frameworks (MOFs) and MOF-derived nanostructures are recently emerging as promising catalysts for electrocatalysis applications. Herein, 2D MOFs nanosheets decorated with Fe-MOF nanoparticles are synthesized and evaluated as the catalysts for water oxidation catalysis in alkaline medium. A dramatic enhancement of the catalytic activity is demonstrated by introduction of electrochemically inert Fe-MOF nanoparticles onto active 2D MOFs nanosheets. In the case of active Ni-MOF nanosheets (Ni-MOF at Fe-MOF), the overpotential is 265 mV to reach a current density of 10 mA cm⁻² in 1 M KOH, which is lowered by \approx 100 mV after hybridization due to the 2D nanosheet morphology and the synergistic effect between Ni active centers and Fe species. Similar performance improvement is also successfully demonstrated in the active NiCo-MOF nanosheets. More importantly, the real catalytic active species in the hybrid Ni-MOF at Fe-MOF catalyst are unraveled. It is found that, NiO nanograins (\approx 5 nm) are formed in situ during oxygen evolution reaction (OER) process and act as OER active centers as well as building blocks of the porous nanosheet catalysts. These findings provide new insights into understanding MOF-based catalysts for water oxidation catalysis, and also shed light on designing highly efficient MOF-derived nanostructures for electrocatalysis.

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Abstract: Metal-organic frameworks (MOFs) and MOF-derived nanostructures have recently been emerging as promising catalysts for electrocatalysis applications. Herein, two-dimensional (2D) MOFs nanosheets decorated with Fe-MOF nanoparticles are synthesized and evaluated as the catalysts for water oxidation catalysis in alkaline medium. A dramatic enhancement of the catalytic activity is demonstrated by introduction of electrochemically inert Fe-MOF nanoparticles onto active 2D MOFs nanosheets. In the case of active Ni-MOF nanosheets (Ni-MOF@Fe-MOF), the overpotential is 265 mV to reach a current density of 10 mA cm⁻² in 1 M KOH, which is lowered by ca. 100 mV after hybridization due to the 2D nanosheet morphology and the synergistic effect between Ni active centers and Fe species. Similar performance improvement is also successfully demonstrated in active NiCo-MOF nanosheets. More importantly, the real catalytic active species in the hybrid Ni-MOF@Fe-MOF catalyst are unraveled. We find that, NiO nanograins (~5 nm) are formed *in situ* during OER process and act as OER active centers as well as building blocks of the porous nanosheet catalysts. These findings provide new insights into understanding MOF-based catalysts for

water oxidation catalysis, and also shed light on designing highly efficient MOF-derived nanostructures for electrocatalysis.

Keywords: metal-organic frameworks, oxygen evolution reaction, nanosheets, electrocatalysis

1. Introduction

In view of the ever-growing concern about global warming and environmental crisis, there is urgent need for extensively utilizing clean and sustainable alternatives (e.g., solar energy, wind energy) to fossil fuels, which can be addressed by developing cost-effective and efficient energy conversion and storage technologies (e.g., fuel cells, batteries, water splitting).^[1-7] With regard to electrochemical water splitting and metal-air batteries, oxygen evolution reaction (OER) is undoubtedly deemed as one of the key processes for these applications. Highly efficient electrocatalysts are required to improve the sluggish reaction kinetics of OER, which is involved with multistep transfer of four electrons.^[8-11] Yet, the benchmark noble metal OER catalysts (e.g., RuO₂ or IrO₂) can hardly satisfy the scale-up applications due to their scarcity and high cost.^[12-13] Therefore, extensive efforts have been devoted to search of low-cost and highly efficient alternatives, such as transition metal-based oxides, hydroxides, and carbonaceous materials.^[14-20] Among them, Ni-based OER catalysts including hydroxides, oxides, sulfides and phosphides, have demonstrated outstanding OER catalytic activities in alkaline electrolytes.^[21-27] In particular, Fe incorporation in Ni-based compounds usually results in further enhanced electrocatalytic performance.^[28-30]

More recently, metal-organic frameworks (MOFs) have been receiving increasing attention for energy-related applications, benefiting from their tunable porosity, high specific surface area as well as diversity in functional species of metal centers and organic linkers.^[31] Notably, MOFs are emerging as precursors for preparing various metal compounds/porous carbon nanocomposites via pyrolysis or chemical reactions toward catalysis applications.^[32-35] However, the active sites and intrinsic structures of MOFs-derived electrocatalysts can be

easily sacrificed due to loss of organic ligands during calcination at high temperatures. Hence, directly adopting MOFs as efficient electrocatalysts for OER still remains a challenge. Benefitting from the tunable structural merits of MOFs, catalytic active sites have been modified by introducing heteroatom/ligands or creating unsaturated coordination environment for enhanced electrocatalytic activities.^[36-40] Nevertheless, more efforts are required to focus on further revealing the structure-performance relationships in addition to theoretical models and calculations. Very recently, converting traditional bulk MOFs crystals into two-dimensional (2D) nanosheets has also contributed to improved OER performance.^[41] This can be readily ascribed to desirable merits of 2D nanomaterials such as high percentages of exposed active atoms to guarantee high catalytic activity as well as nanometer thickness to ensure rapid mass transport and charge transfer.^[42-44] Furthermore, some strategies focusing on MOF-involved hybridization with secondary conductive phase, such as self-supported substrates (Ni foam),^[45] graphene,^[46] and MXenes,^[47] have also been reported to accelerate the water oxidation reaction. However, the stability of MOFs during OER as well as the actual catalytic mechanism is rarely studied and needs to be further elucidated.

In this work, 2D MOFs nanosheet-based hybrids were for the first time prepared via facile stepwise synthesis at room temperature and were evaluated as catalysts for water oxidation catalysis. The catalytic performance of the active MOFs nanosheets was substantially improved by depositing electrochemically inert Fe-MOF nanoparticles onto the MOFs nanosheets. Meanwhile, the real active species in the hybrid Ni-MOF@Fe-MOF catalyst were also unraveled based on the *ex-situ* transmission electron microscopy (TEM) and Raman spectra results.

2. Results and Discussion

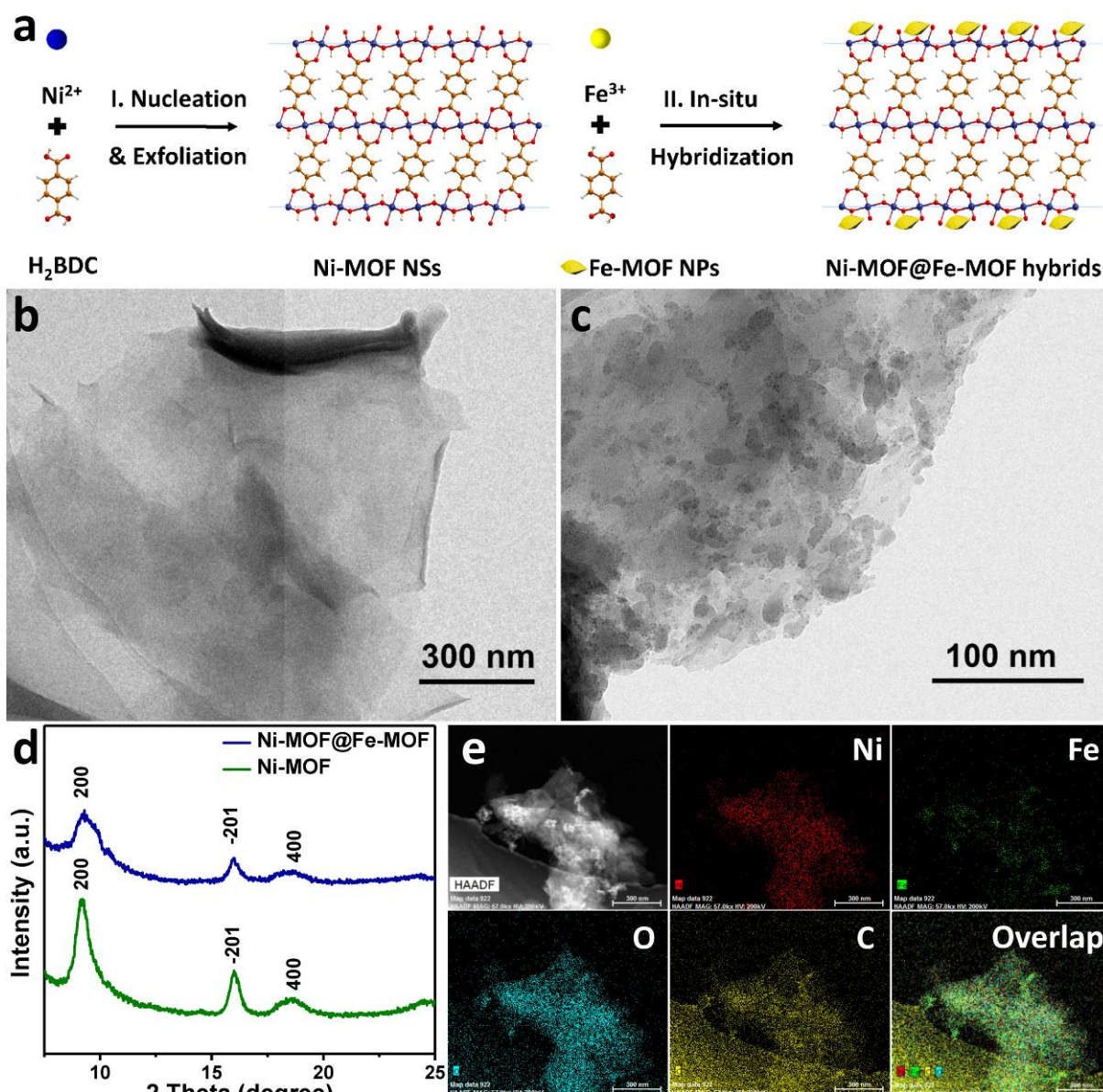


Figure 1. (a) Schematic illustration of synthesis of Ni-MOF@Fe-MOF hybrid nanosheets. TEM images of (b) Ni-MOF and (c) Ni-MOF@Fe-MOF hybrid. (d) XRD patterns of Ni-MOF and Ni-MOF@Fe-MOF hybrid. (e) HAADF-STEM image and corresponding EDS elemental mapping images of Ni-MOF@Fe-MOF hybrid.

2D Ni-MOF@Fe-MOF hybrid nanosheets were prepared via a facile ultrasonication-assisted stepwise synthesis process at room temperature as illustrated in **Figure 1a**. Typically, pristine Ni-MOF nanosheets were firstly prepared via the liquid exfoliation method under ultrasonication. As can be seen from the transmission electron microscopy (TEM) image shown in Figure 1b, Ni-MOF possesses flexible ultrathin nanosheet morphology with lateral size in microscale. The thickness of the Ni-MOF nanosheet is determined to be ca. 5.0 nm or 6.0 nm by atomic force microscopy (AFM) as shown in Figure S1 (Supporting Information),

corresponding to approximately 5-6 coordination structural layers (4.95 or 5.94 nm). Endowed with their ultrathin morphology and good dispersivity in the mixed N,N-dimethylformamide (DMF)/ethanol/H₂O solvent system, the 2D Ni-MOF nanosheets can be further decorated with Fe-MOF nanoparticles via the *in-situ* coordination of surface-anchored Fe(III) and H₂BDC ligand (Figure 1c). Bare Fe-MOF nanoparticles synthesized without the presence of Ni-MOF nanosheets are severely agglomerated together (Figure S2, Supporting Information). As characterized by X-ray diffraction (XRD), both the hybrid Ni-MOF@Fe-MOF and pristine Ni-MOF share the same crystal phase with peaks assigned to (200), (-201) and (400) planes of a monoclinic structure (Figure 1d). As seen from the illustrated crystal structure (Figure S3, Supporting Information), Ni atoms are coordinated by six O atoms (μ_3 -OH and O in carboxylate) forming slightly distorted NiO₆ octahedra, which are further corner/edge connected with each other in the (200) planes resulting in 2D metallic layers separated by BDC ligands.^[48] In contrast, no distinct diffraction peaks can be observed for bare Fe-MOF, suggesting its amorphous nature (Figure S4, Supporting Information). High-angle annular dark field scanning TEM (HAADF-STEM) coupled with energy dispersive spectroscopy (EDS) elemental mapping reveal the highly uniform distribution of Ni, O and C throughout the nanosheets (Figure 1e). Meanwhile, Fe species are well dispersed on the nanosheet, confirming the successful hybridization of Fe-MOF with Ni-MOF. In addition, the atom ratio of Ni/Fe is determined to be about 3.5/1 based on inductively coupled plasma optical emission spectrometer (ICP-OES) analysis.

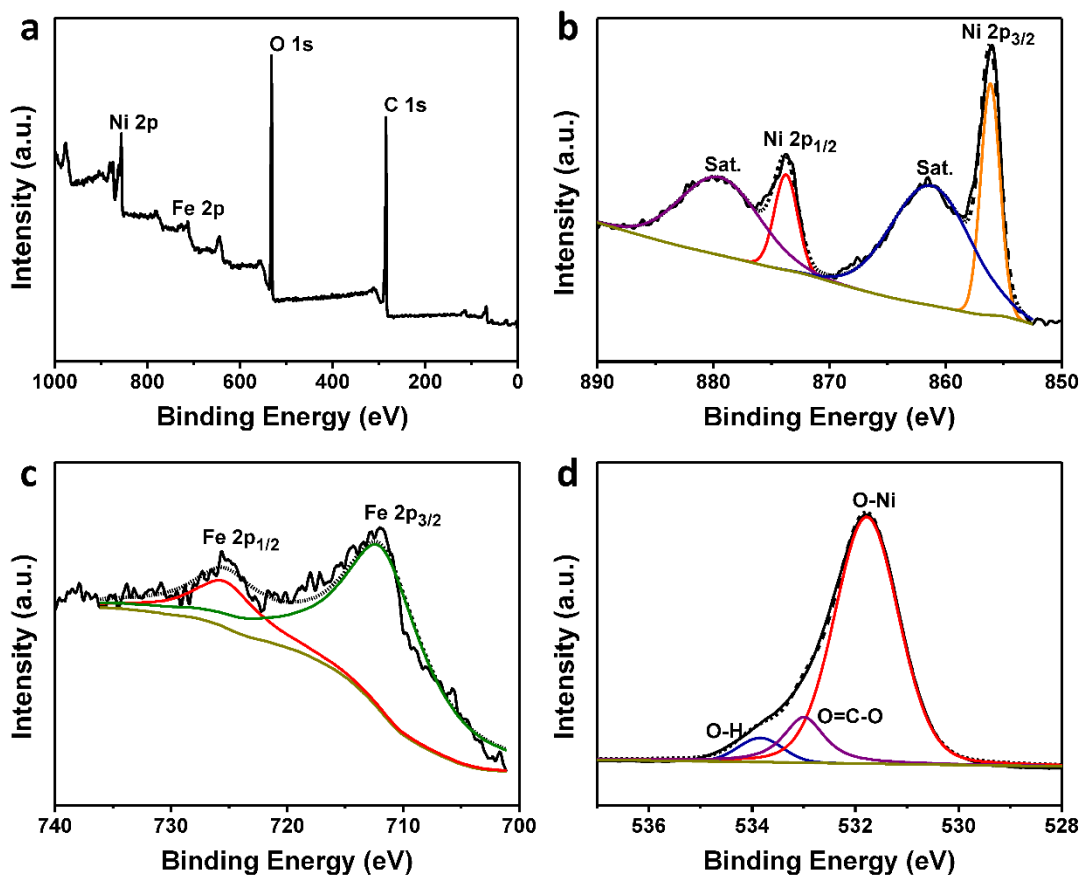


Figure 2. XPS spectra of Ni-MOF@Fe-MOF hybrid. (a) survey spectrum, (b) Ni 2p, (c) Fe 2p, and (d) O 1s.

The chemical composition and oxidation states of the as-obtained Ni-MOF@Fe-MOF hybrid nanosheets were also examined by X-ray photoelectron spectroscopy (XPS) analysis, as shown in **Figure 2**. The full survey spectrum demonstrates the co-existence of Ni, Fe, O and C elements (Figure 2a). The presence of Ni²⁺ can be demonstrated by the high-resolution Ni 2p region (Figure 2b), where typical peaks at 856.1 eV and 873.8 eV can be assigned to Ni 2p_{2/3} and Ni 2p_{1/2} electronic configurations, respectively.^[41] As compared to pristine Ni-MOF (Figure S5, Supporting Information), negligible shift of binding energy can be observed, suggesting that the coordination environment of Ni active centers is barely modified after depositing Fe-MOF. Moreover, Fe 2p spectrum (Figure 2c) deconvoluted into Fe 2p_{2/3} (725.8 eV) and Fe 2p_{1/2} (712.4 eV) is consistent with the characteristics of typical MIL-type Fe-MOF.^[36] In addition, the fitted peak at 531.8 eV of O 1s region can be attributed to Ni-O bond forming the NiO₆ octahedra in Ni-MOF, while another two peaks at higher binding energies

can be assigned to the oxygen components (O=C-O) on terephthalate linkers and possibly μ_3 -OH or absorbed water molecules (Figure 2d).^[49]

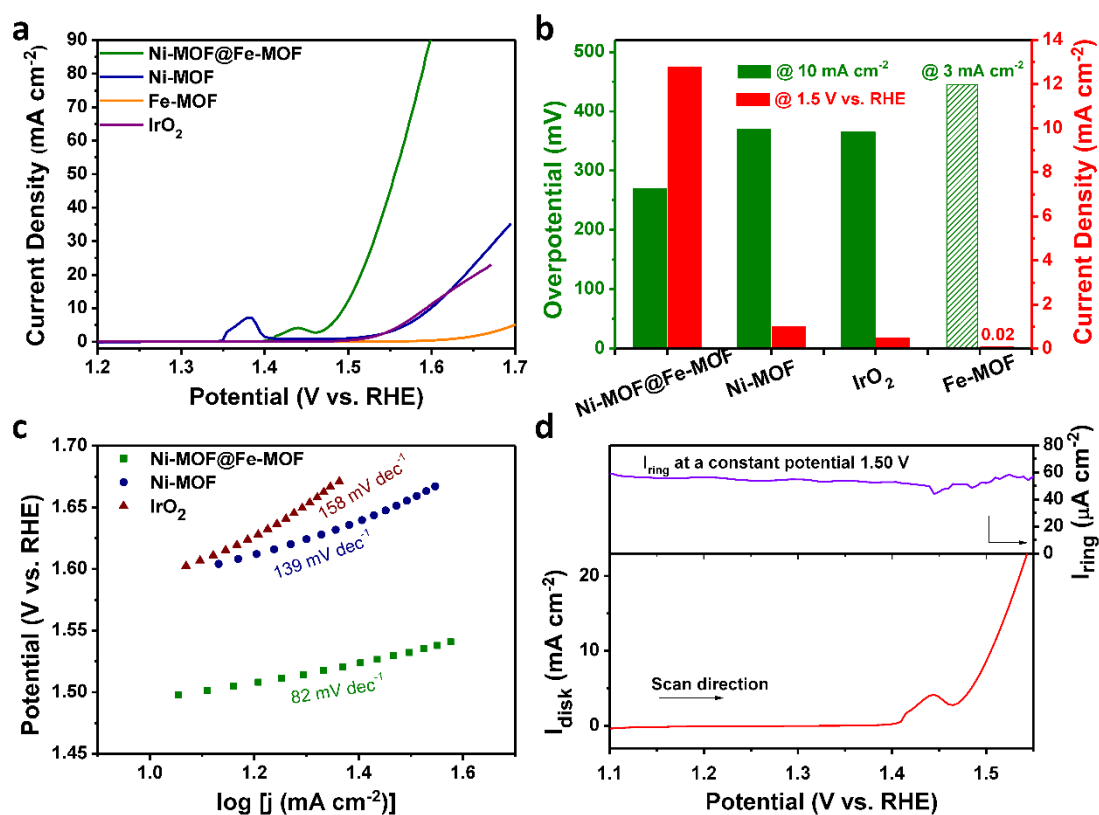


Figure 3. (a) Linear sweep voltammetry (LSV) polarization curves toward OER in O_2 -saturated 1 M KOH with a scan rate of 5 mV s^{-1} . (b) Corresponding overpotential and current density of different catalysts at 10 mA cm^{-2} and 1.50 V vs. RHE , respectively. (c) Corresponding Tafel plots derived from LSV curves. (d) RRDE measurement of 2D Ni-MOF@Fe-MOF hybrid in O_2 -saturated 1 M KOH at a rotation speed of 1600 rpm with the ring potential fixed at 1.50 V vs. RHE .

Impressively, the 2D Ni-MOF@Fe-MOF hybrid nanosheets can be directly used to catalyze OER without annealing treatment. The electrocatalytic activity of Ni-MOF@Fe-MOF hybrid was investigated in 1 M KOH in a conventional three-electrode cell. For comparison, the catalytic performance of bare Ni-MOF, Fe-MOF and IrO_2 was also examined with an equal mass loading on glassy carbon (GC) electrode (0.2 mg cm^{-2}). Polarization curves are obtained by employing linear sweep voltammetry at a scan rate of 5 mV s^{-1} as presented in **Figure 3a**. A typical anodic peak ranging from 1.40 to 1.47 V vs. the reversible hydrogen electrode (RHE) can be observed for Ni-MOF@Fe-MOF hybrid, which can be attributed to oxidation of Ni^{2+} to Ni^{3+} .^[50-51] Notably, a positive shift of the anodic peak as

compared to bare Ni-MOF can be ascribed to the incorporation of Fe, which phenomenon is typically observed for Fe modified Ni-based OER catalysts.^[52] Here, the catalytic activity of Ni-MOF@Fe-MOF hybrid varies with different Ni/Fe atom ratios (Figure S6, Supporting Information). The optimal catalytic performance can be achieved at a Ni/Fe atom ratio of 3.5/1 with the lowest overpotential of 265 mV at a current density of 10 mA cm⁻², which is superior to the state-of-the-art OER catalysts IrO₂ (365 mV). It is worth mentioning that bare Fe-MOF is inert to the water oxidation reaction, whereas the hybridization with Fe-MOF significantly decreases the overpotential of Ni-MOF (370 mV) by ca. 100 mV. At a potential of 1.50 V vs. RHE, Ni-MOF@Fe-MOF hybrid delivers a high current density of 12.8 mA cm⁻², which is over 10 times higher than that of bare Ni-MOF (1 mA cm⁻²) (Figure 3b). Furthermore, the corresponding Tafel slope for Ni-MOF@Fe-MOF hybrid (82 mV dec⁻¹) is also lower than that of Ni-MOF (139 mV dec⁻¹) and IrO₂ (158 mV dec⁻¹), indicating substantially enhanced catalytic reaction kinetics after hybridization (Figure 3c). In addition, rotating ring-disk electrode (RRDE) technique was employed to investigate the reaction mechanism. The potential of Pt ring electrode was fixed at 1.5 V to oxidize the peroxide intermediates formed at the Ni-MOF@Fe-MOF hybrid surface during OER (Figure 3d). The detected ring current density ($\mu\text{A cm}^{-2}$) is 3 orders of magnitude lower as compared to the disk (mA cm⁻²), indicating negligible formation of hydrogen peroxide and thus a desirable four-electron pathway for water oxidation ($4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4e^-$).^[17, 53] Meanwhile, a continuous OER (disk)-ORR (ring) process can be carried out to verify that the detected disk current results from oxygen evolution rather than other side reactions. By applying a constant disk current (200 μA), O₂ molecules generated on the surface of Ni-MOF@Fe-MOF hybrid catalyst are swept across the surrounding Pt ring electrode and then reduced. A ring current of about 50.7 μA (Figure S7, Supporting Information) can be obtained, corresponding to a high Faradaic efficiency of 99.1%.

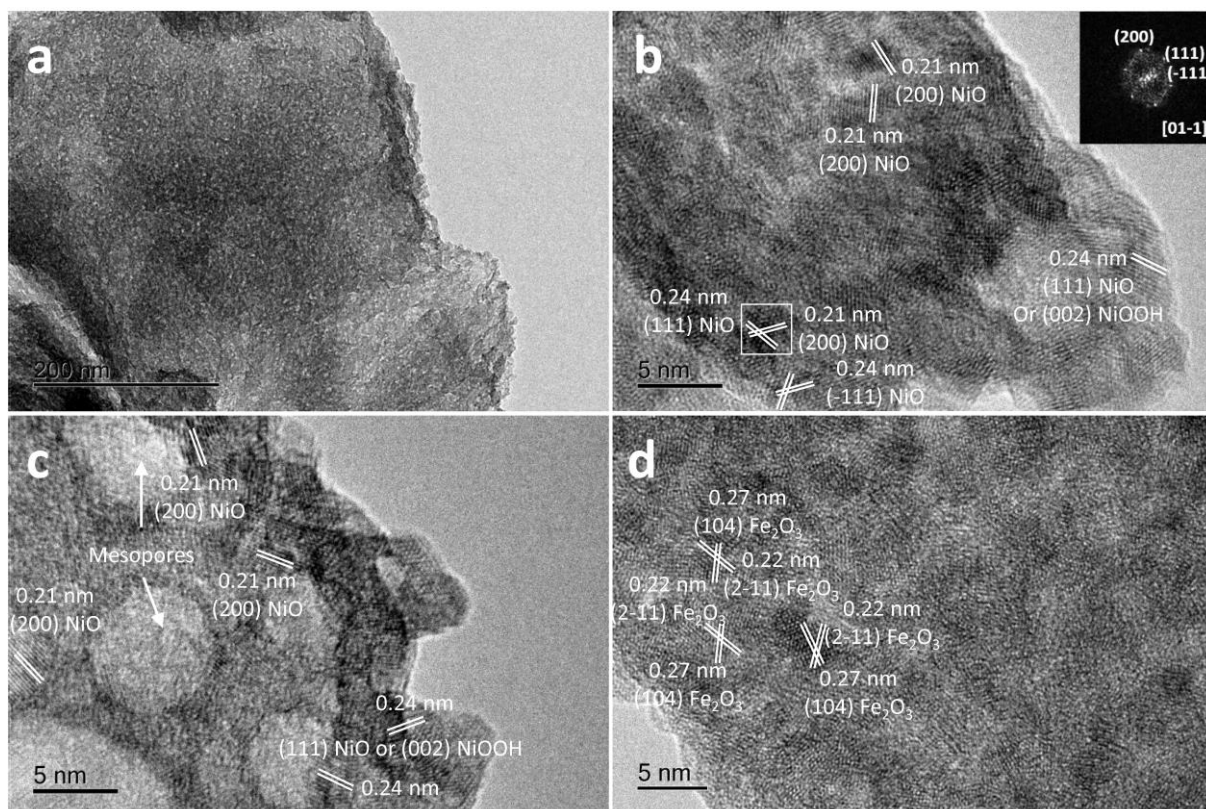


Figure 4. (a) TEM and (b) HRTEM images of Ni-MOF@Fe-MOF hybrid after OER testing for 20 CV cycles. Inset of (b): FFT pattern for the selected square region. (c) HRTEM image of Ni-MOF@Fe-MOF hybrid after 50 CV cycles. (d) HRTEM image of bare Fe-MOF after 20 CV cycles.

There have been plenty of reports on Ni-based OER catalysts with impressive performance. The generation of nickel oxide/hydroxide during water oxidation was constantly confirmed and considered as veritable active species for OER. Yet, the substantial composition variation of Ni-MOF based catalysts during OER process has not been clearly uncovered. Herein, Ni-MOF@Fe-MOF hybrid was further characterized after OER measurement with a series of techniques. As revealed by TEM analysis, the nanosheets morphology can still be maintained with the lateral size of hundreds of nanometers after CV cycles (**Figure 4a**). Notably, well-defined lattice fringes are revealed by HRTEM image (**Figure 4b**), demonstrating apparently distinct morphology profile from pristine Ni-MOF@Fe-MOF hybrid. In particular, uniformly distributed domains (ca. 5 nm) throughout the porous nanosheets can be well attributed to cubic NiO nanograins. The lattice spacing of 0.21 and 0.24 nm with an angle of 55° can be assigned to the (200) and (111) crystal planes of NiO, respectively. The fast Fourier transform

(FFT) result for selected regions (inset) also demonstrates the good crystallinity of the *in-situ* generated NiO nanograins. Basically, NiOOH is probably formed during the oxidation process and thus some lattice fringes with a spacing of 0.24 nm could also be ascribed to (002) facet of hexagonal NiOOH.^[54-57] In addition to the characteristic lattice fringes of NiO nanograins, TEM and HRTEM images for Ni-MOF@Fe-MOF hybrid after 50 cycles clearly exhibits well-defined mesopores ranging from 5 to 10 nm (Figure 4d and Figure S8, Supporting Information). This can be ascribed to the structural shrinkage of MOFs accompanied with the damage of organic ligands during water oxidation. With the presence of interconnected NiO active species and homogeneously distributed mesopores, enhanced electrocatalytic performance can be thus favored by abundant active centers as well as desirable mass transport. With regard to Fe species (Figure S9, Supporting Information), the *ex-situ* HRTEM image of Fe-MOF after CV cycles provides solid evidence for the formation of Fe₂O₃ nanograins (Figure 4d). On the basis of the aforementioned discussion, it can be concluded that Ni-Fe oxides, e.g., NiO nanograins with increased activity promoted by neighboring Fe₂O₃,^[52, 58] should be the real active species of Ni-MOF@Fe-MOF hybrid catalysts during water oxidation.

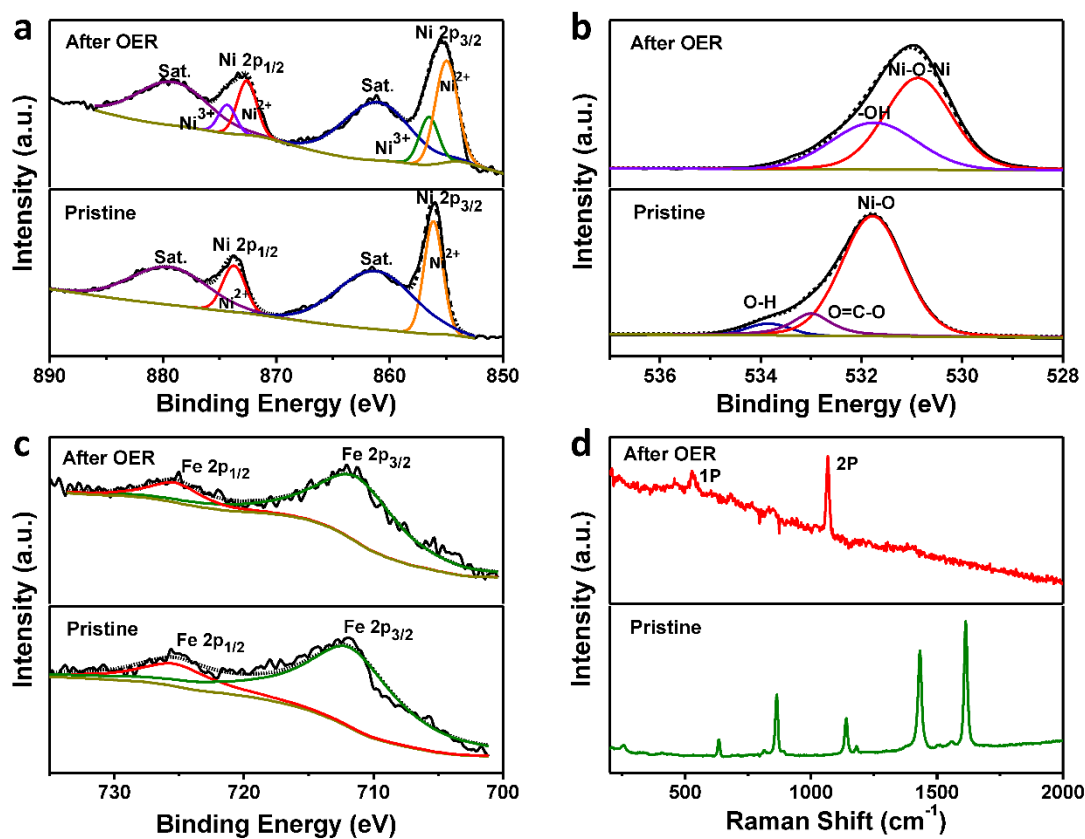


Figure 5. High-resolution XPS spectra of (a) Ni 2p region, (b) O 1s region and (c) Fe 2p region and (d) Raman spectra for Ni-MOF@Fe-MOF hybrid before and after OER testing.

Comparison of the high-resolution Ni 2p XPS spectroscopy further reveals the phase transformation of Ni-MOF@Fe-MOF hybrid after OER cycling (**Figure 5a**). The negative shift of binding energy (0.9 eV) for Ni 2p_{3/2} and 2p_{1/2} can be ascribed to altered local electronic structure of Ni atom after the degradation of organic ligands. Specifically, fitted peaks for Ni²⁺ species (centered at 849.9 and 872.5 eV) along with their satellite can be attributed to the presence of NiO.^[59] While increased electron density of Ni conduction electrons lost to oxygen-containing ligand groups results in higher binding energy of Ni 2p for Ni-MOF, decreased binding energy for Ni-MOF derived NiO can be ascribed to increased electrostatic shielding of nucleus due to the replacement by bare O atom. Besides, the minor peaks assigned to Ni³⁺ (emerged at 856.4 and 874.1 eV) are readily related to the formation of NiOOH during water oxidation.^[60-61] The structural reorganization of Ni-MOF@Fe-MOF hybrid during OER is also evidenced by the distinct shift of the dominant peak in O 1s, which

can be deconvoluted into lattice oxygen of NiO and hydroxyl groups from remaining NiOOH on the surface of the catalyst, respectively (Figure 5b). Fe 2p spectrum is nearly identical to the pristine one before OER (Figure 5c), in spite of the formation of Fe₂O₃ nanograins. Furthermore, *ex-situ* Raman analysis was carried out to confirm the restructuring of Ni-MOF@Fe-MOF hybrid into NiO (Figure 5d). Typical Raman peaks originating from the vibrational modes from organic component of pristine Ni-MOF@Fe-MOF hybrid are no longer detected after OER cycling. Instead, first-(1P) and second-order phonon (2P) scattering of NiO can be detected. This result suggests the complete transformation of Ni-MOF into NiO, rather than merely the superficial region as reported for other Ni-based catalysts.^[21, 62-63] It is worth noting that the chemical environment of Ni-based active centers barely changed (still bonded to six O atoms in NiO), as well as 2D nanosheet morphologies as discussed above. With phase transformation proceeding progressively during cycling, no significant degradation of the catalytic performance was observed. A desirable overpotential of 280 mV at 10 mA cm⁻² is reached after 500 CV cycles, while an overpotential of 290 mV can be still obtained after 1000 CV cycles when the catalyst is fully transformed (Figure S10, Supporting Information).

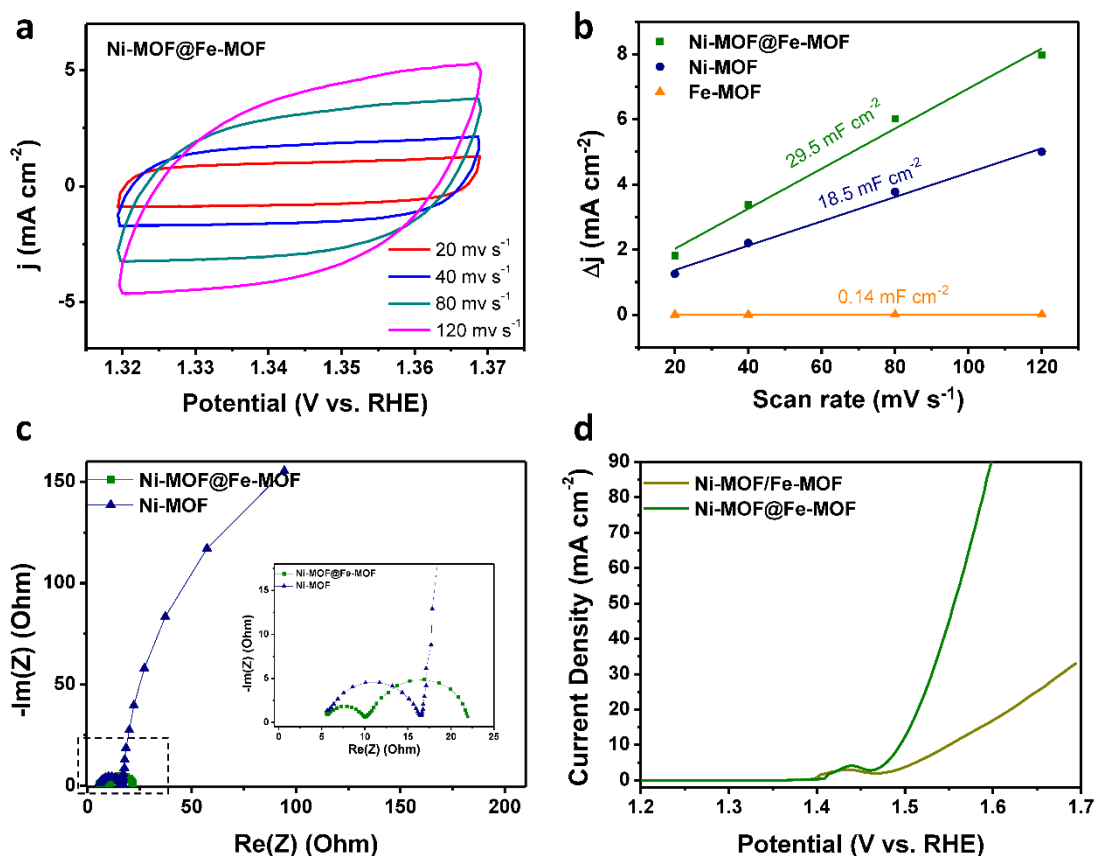


Figure 6. (a) CV curves in a potential range of 1.32-1.37 V vs. RHE of Ni-MOF@Fe-MOF hybrid. (b) Current density difference at 1.35 V plotted against scan rate in a non-Faradaic range. (c) Electrochemical impedance spectra at 1.50 V vs. RHE. Inset: enlarged image for the marked area. (d) OER polarization curves of *in-situ* hybridized Ni-MOF@Fe-MOF and physically mixed Ni-MOF/Fe-MOF.

Possible factors affecting the catalytic performance were carefully explored for gaining further insights into understanding the OER activity enhancement. The electrochemically active surface areas (ECSAs) of different catalysts were estimated by calculating the double-layer capacitance (C_{dl}) based on CV test in a non-Faradaic region (Figure 6a and Figure S11, Supporting Information). As expected, Ni-MOF@Fe-MOF hybrid shows an enlarged C_{dl} than bare Ni-MOF (Figure 6b). The presence of Fe-MOF particles shall inhibit the restacking of Ni-MOF nanosheets and thus facilitate the exposure of more active sites at the solid-liquid interface. To gain a better understanding of OER kinetics, electrochemical impedance spectra (EIS) measurement were conducted at controlled potentials. As seen from Figure 6c, the Nyquist plots of both Ni-MOF@Fe-MOF hybrid and bare Ni-MOF consist of two semicircles corresponding to the possible ionic resistance (R_i) in the higher frequency region and the

charge transfer resistance (R_{ct}) in the low frequency region, which were fitted by the RC circuit as shown in Figure S12 (Supporting Information). R_i related to the double-layer capacitance barely changes ($\sim 5 \Omega$), while R_{ct} varies with increasing overpotentials for Ni-MOF@Fe-MOF, which is considered to be associated with the electrochemical reaction kinetics (Figure S13, Supporting Information).^[64-65] Evidently, Ni-MOF@Fe-MOF hybrid exhibited a prominently decreased R_{ct} (11.1 Ω) compared to that of bare Ni-MOF (up to 363.5 Ω), demonstrating improved charge transfer kinetics after the hybridization with Fe-MOF (Table S1, Supporting Information). Moreover, the Ni-MOF@Fe-MOF hybrid resulting from *in-situ* deposition of Fe-MOF nanoparticles on Ni-MOF nanosheets apparently exhibits superior OER performance than the simple mixture of both MOFs (Figure 6d), suggesting crucial interaction between Ni and Fe species. The synergistic effect between Ni and Fe undoubtedly contributes to enhanced catalytic activity of hybrid MOF-based catalysts, which is consistent with other reports on NiFe-based catalysts.^[52, 66-68] In addition, the electrocatalytic performance of Ni-MOF@Fe-MOF is among the best reported NiFe-based OER catalysts under the similar measurement conditions (Table S2, Supporting Information). This can be attributed to not only the desirable formation of mesopores throughout nanosheets after electrochemical activation to facilitate mass transport, but also the presence of carbon-based frameworks in MOFs to likely inhibit the agglomeration of active Ni-Fe oxides nanoparticles.

Compared to previously reported strategies to obtain MOF-based composites, the present method is free of high-temperature reactions (e.g., hydrothermal, microwave, calcination, etc.), easy to operate and generic to be adapted for multiple MOF-based systems. As indicated by TEM images (Figure S14, Supporting Information), the incorporation of Fe-MOF was also successfully demonstrated on 2D NiCo-MOF nanosheets. STEM-EDS mapping suggests the uniform distribution of Ni, Co, Fe, C and O in the 2D NiCo-MOF@Fe-MOF hybrid (Figure S15, Supporting Information). When evaluated as OER catalysts in 1 M KOH (Figure S16,

Supporting Information), NiCo-MOF@Fe-MOF hybrid delivers substantially lower overpotential and Tafel slope (275 mV at 10 mA cm⁻², 54 mV dec⁻¹), in comparison to bare NiCo-MOF (375 mV at 10 mA cm⁻², 118 mV dec⁻¹). Evidently, it is demonstrated that introducing Fe-MOF nanoparticles on ultrathin NiCo-MOF nanosheets can also significantly promote water oxidation catalysis, shedding light on developing hybrid MOFs-related 2D nanostructures for energy applications.

3. Conclusion

In summary, hybrid Ni-based MOFs nanosheets decorated with Fe-MOF nanoparticles were synthesized under mild conditions. As a proof-of-concept demonstration, a dramatic enhancement of the catalytic activity towards water oxidation catalysis was achieved by introduction of electrochemically inert Fe-MOF nanoparticles onto active 2D MOFs nanosheets. In addition to the 2D nanosheet morphology and synergistic effect between Ni active centers and Fe species, the hybrid MOFs were converted *in situ* into oxides nanoparticles during OER, acting as real active centers as well as building blocks of porous nanosheet catalysts. Similar performance improvement was also successfully demonstrated in active NiCo-MOF nanosheets. This work provides new insights into understanding MOF-based catalysts for water oxidation catalysis, and also opens a new avenue for developing highly efficient MOF-derived nanostructures for electrocatalysis.

4. Experimental Section

Materials and Reagents: Nickel(II) chloride hexahydrate (NiCl₂·6H₂O, 98%) was purchased from Alfa Aesar. Iron(III) chloride (FeCl₃, 97%), Cobalt(II) chloride hexahydrate (CoCl₂·6H₂O, 98%), terephthalic acid (1, 4-BDC, 98%), triethylamine (TEA, 99%), N,N-Dimethylformamide (DMF, 99.8%), Nafion solution (5 wt%) were bought from Sigma-Aldrich. All chemicals were used as received without further purification.

Synthesis of Ni-MOF: Pure Ni-MOF was synthesized according to a previously reported method with modifications.^[41] 1, 4-BDC (125 mg) was first dissolved in a mixed solution of

DMF (30 mL), ethanol (2 mL) and DI water (2 mL) under vigorous stirring. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (180 mg) was then added, followed by a quick injection of TEA (1 mL) into the above solution. Subsequently, the mixture was stirred for 10 min to form a uniform colloidal suspension, sealed and continuously ultrasonicated for 8 h at room temperature. Finally, the precipitates were collected via centrifugation, washed with ethanol for three times and dried at 60 °C for 12 h.

Synthesis of Ni-MOF@Fe-MOF: In a typical procedure, Ni-MOF (70 mg) was first dispersed in a mixed solution of DMF (30 mL), ethanol (2 mL) and DI water (2 mL) with ultrasonication for 3 h. 1, 4-BDC (60 mg), FeCl_3 (12 mg) and TEA (1 mL) were then added into the above-mentioned homogenous suspension in sequence under vigorous stirring. The reaction mixture was further sealed and ultrasonicated for 8 h at room temperature. Finally, the precipitates were collected via centrifugation, washed with ethanol for three times and dried at 60 °C for 12 h.

Synthesis of Fe-MOF: The preparation process of pure Fe-MOF was same as that of Ni-MOF, except that $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was replaced by FeCl_3 (120 mg).

Synthesis of NiCo-MOF: The preparation process of pure NiCo-MOF was same as that of Ni-MOF, except that $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was replaced by $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (90 mg) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (90 mg).

Synthesis of NiCo-MOF@Fe-MOF: The preparation process of NiCo-MOF@Fe-MOF was same as that of Ni-MOF@Fe-MOF, except that Ni-MOF was replaced by NiCo-MOF (70 mg).

Materials characterization: The morphology and microstructures of the samples were characterized using transmission electron microscopy (TEM, JEM-2010) at 200 kV. Scanning transmission electron microscopy (STEM) characterization was conducted utilizing a probe-corrected JEOL ARM-200F at 200 kV equipped with an energy dispersive X-ray spectroscopy (EDS) detector. Powder X-ray diffraction (XRD) was carried out on GBC MMA

X-ray diffractometer with a Cu K α irradiation source ($\lambda = 1.54056 \text{ \AA}$) at a low scanning speed of 0.1° per min. X-ray photoelectron spectroscopy (XPS) was performed on an X-ray photoelectron spectrometer (Thermo ESCALAB 250). Raman spectra were collected using a JY HR800 Raman spectrometer equipped with a 633 nm laser as the excitation source. The contents of Ni and Fe were obtained by inductively coupled plasma optical emission spectrometer (ICP-OES) measurement using an Optima 7300 DV instrument. Atomic force microscopy (AFM) measurements were done on a Asylum MFP-3D instrument.

Electrochemical measurements: The catalyst ink was first prepared by dispersing catalysts (2 mg) in a mixed solution containing Nafion solution (16 μL), DI water (384 μL), and isopropanol (100 μL) followed by ultrasonication for 2 h. Then, 10 μL of the catalyst ink was uniformly cast onto the polished glassy carbon (GC) disk electrode and dried at room temperature, which was then used as the working electrode with a loading of 0.2 mg cm^{-2} . The electrochemical measurements were performed in a three-electrode setup (Pine Research Instruments) with a Hg/HgO electrode and Pt mesh as reference and counter electrodes, respectively. An O₂-saturated 1 M KOH aqueous solution was used as the electrolyte. All potentials measured were calibrated to the reversible hydrogen electrode (RHE) using the following equation: $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 \text{ V} + 0.059\text{pH}$. During the oxygen evolution reaction (OER) measurements, the working electrode was constantly rotated at 1600 rpm. Cyclic voltammetry (CV) for the working electrode was first conducted from 1.1 to 1.6 V vs. RHE at 30 mV s^{-1} to well activate the catalysts. Linear sweep voltammetry (LSV) was then recorded at 5 mV s^{-1} to obtain the polarization curves. All LSV curves were corrected with 95% iR compensation. The impedance spectra were recorded at 1.5 V vs. RHE in the frequency range of 0.1-100k Hz (BioLogic Science Instrument).

To investigate the reaction mechanism for OER, rotating ring-disk electrode (RRDE) voltammograms were conducted consisting of a GC disk electrode and a Pt ring electrode. For determination of the OER reaction pathway by detecting the HO₂⁻ formation, the ring

potential was held at 1.5 V versus RHE with a rotation rate of 1600 rpm in the O₂-saturated 1 M KOH. On the other hand, to calculate the Faradaic Efficiency (FE) of the system, the ring potential was held at 0.4 V versus RHE in the N₂-saturated 1 M KOH with a rotation rate of 1600 rpm. The FE was obtained according to the equation:

$$FE = \frac{I_{ring}}{I_{disk} \times C_e} \times 100\%$$

where I_{ring} is the collection current on the Pt ring electrode, I_{disk} is the given current on the disk electrode, and C_e is the oxygen collection coefficient (25.6%) for this type of electrode configuration.

Supporting Information

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

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A highly efficient 2D MOF-based hybrid electrocatalyst for oxygen evolution reaction (OER) is demonstrated by *in-situ* deposition of electrochemically inert Fe-MOF nanoparticles onto active Ni-MOF nanosheets. This work provides new insights into understanding MOF-based catalysts for water oxidation catalysis, and sheds light on developing MOF-derived nanostructures for electrocatalysis.

Electrocatalysis

Kun Rui, Guoqiang Zhao, Yaping Chen, Yue Lin, Qian Zhou, Jiayi Chen, Jixin Zhu*, Wenping Sun*, Wei Huang, Shi Xue Dou

Hybrid Two-dimensional Dual-Metal-Organic Frameworks for Enhanced Water Oxidation Catalysis

ToC figure

