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Research Article

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Direct Visualization of Atomic Structure in Multivariate Metal-Organic Frameworks (MOFs) for Guiding Electrocatalysts Design

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The low-dose integrated differential phase contrast-scanning transmission electron microscopy (iDPC-STEM) technique is utilized to visualize the structure and resolve the lattice strain information of multivariate MOFs (MTV-MOFs) at an atomic level, providing

important guidance in the further design of MOFs for efficient OER, unlocking the iDPC-STEM technique as an effective tool in MOF design for electrocatalytic applications.

The direct utilization of metal--organic frameworks (MOFs) for electrocatalytic oxygen evolution reaction (OER) has attracted increasing interests. Herein, we employ the low-dose integrated differential phase contrast-scanning transmission electron microscopy (iDPC-STEM) technique to visualize the atomic structure of multivariate MOFs (MTV-MOFs) for guiding the structural design of bulk MOFs for efficient OER. The iDPC-STEM images revealed that incorporating Fe^{3+} or 2-aminoterephthalate (ATA) into Ni-BDC (BDC: benzenedicarboxylate) can introduce inhomogeneous lattice strain that weaken the coordination bonds, which can be selectively cleaved via a mild heat treatment to simultaneously generate coordinatively unsaturated metal sites, conductive Ni@C and hierarchical porous structure. Thus, excellent OER activity with current densities of 10 and 100 mA cm^{-2} are achieved over the defective MOFs at small overpotentials of 286 mV and 365 mV, respectively, which is superior to the commercial RuO_2 catalyst and most of the bulk MOFs.

Defect Engineering
Metal--Organic Frameworks
Multivariate MOFs
Oxygen Evolution Reaction
iDPC-STEM

Introduction

The oxygen evolution reaction (OER) plays a vital role in alternative energy conversion technologies, but currently suffers from the sluggish kinetics due to the multistep proton-coupled electron transfer process ($4\text{OH}^{\leftarrow\rightarrow} \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^{\leftarrow\rightarrow}$).^[1--3] Therefore, tremendous efforts have been devoted to developing novel efficient OER electrocatalysts by tuning the components and structures. Metal-organic frameworks (MOFs) are crystalline porous materials composed of metal/metal clusters and organic ligands.^[4] The unique structural characteristics of high porosity, diversity in building blocks, and flexible frameworks have endowed it various promising applications.^[5--29] In terms of electrocatalysis,

in addition to functioning as precursors for metal/carbon-based electrocatalysts via pyrolysis, increasing interests have been paid to the utilization of the intrinsic OER activity of MOFs, especially the few-layer MOFs.^[10--15] However, in spite of the exciting achievements, the few-layer MOFs have shortcomings of difficulties in sample preparation and easy restacking/aggregation during sample loading and catalytic process, greatly hindering their future applications. Therefore, strategies to enable the easily prepared bulk MOFs for efficient OER is highly desirable. The poor electrical conductivity, limited accessible active sites and low mass permeability are the bottlenecks of MOFs to achieve remarkable electrocatalytic performances. Ideal electrocatalysts require simultaneous optimization of all the above-mentioned factors, but it is quite challenging since improving any one of them usually compromises the others. The main obstacle to achieve this goal is the lack of an effective tool to direct the structure design at an atomic level.

The conventional methods for MOF characterizations, such as gas sorption method, crystallographic methods like the synchrotron single-crystal X-ray diffraction and X-ray absorption fine structure method, can only give an average structural information without real space details.^[30,^31] By contrast, transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM), which can offer the highest resolution in real space imaging, are able to directly visualize the local structures at the atomic scale. Unfortunately, due to the electron beam sensitive nature of MOFs, atomic-scale TEM/STEM analysis of MOFs with sufficiently high resolution has been precluded for a long time. This gap was recently filled by the development of low-dose high-resolution (HR) TEM/STEM by using the direct-detection electron-counting cameras.^[32--36] More recently, the low-dose STEM technique based on integrated differential phase contrast (iDPC) technique has also successfully achieved the atomic scale imaging of MOFs.^[37,^38]

Herein, we employ the low-dose iDPC-STEM approach to directly visualize the atomic structure of multivariate MOFs (MTV-MOFs) at the atomic level, for directing the design and further optimization of the MOFs-based electrocatalysts for efficient OER. A set of MTV-MOFs are prepared and our atomic-resolution iDPC-STEM images reveal that, incorporating Fe^{3+} and 2-aminoterephthalate (ATA) into Ni-BDC (BDC: benzenedicarboxylate) can generate remarkable inhomogeneous local lattice strain in these MTV-MOFs. The presence of lattice strain variation not only improves the OER activity, but more importantly, weakens the local bonding in MOFs, which facilitates further structure engineering. With the multifold aims of simultaneously enhancing electrical conductivity, increasing active sites and promoting mass permeability, a mild heat treatment over the MTV-MOFs with strain variation is carried out to selectively cleave the weaker bonds, resulting in the formation of defective hierarchical porous MOFs with evenly distributed conductive Ni@C embedded. The improved conductivity, presence of unsaturated metal sites and mesopores of the defective MOFs result in an excellent OER activity, with current densities of 10 and 100 mA cm^{-2} reached at small overpotentials of 286 mV and 365 mV, respectively, which is superior to the commercial RuO_2 and most of the bulk MOFs.

Results and Discussion

Figure¹a-b provide the structure of Ni-MOF and a schematic illustration for the preparation of the MTV-MOFs ($\text{Fe}_x\text{Ni-BA}_y$, where x and y represent the percentage of feeding Fe and ATA). The obtained $\text{Fe}_{10}\text{Ni-BA}_{0.7}$ shows similar XRD diffraction patterns as Ni-BDC, indicating that incorporation of Fe^{3+} and ATA has little influence on the long-range order of the frameworks (Figure¹c). The slightly decreased diffraction intensity implies the presence of structural distortion. Scanning electron microscopy (SEM) and TEM images reveal that $\text{Fe}_{10}\text{Ni-BA}_{0.7}$ features similar morphology with Ni-BDC, which is composed of stacked nanosheets to form nanostructures with dimension of several

micrometers (Figure^{S1--2}). The well inherited morphology of Fe₁₀Ni-BA_{0.7} from Ni-BDC without any new moieties appearing on the surface or anywhere of the nanosheets proves that both ATA and Fe³⁺ have been well incorporated into the framework of MOFs. Energy dispersive spectroscopy (EDS) mapping images reveal the homogeneous distribution of both Fe³⁺ and ATA in Fe₁₀Ni-BA_{0.7} (Figure^{S2d}).

The iDPC-STEM technique is then employed to characterize the MOFs at higher resolution. The low atomic number elements could be easily visualized via iDPC-STEM technique.^[37,38] As such, the carbon and oxygen atomic columns in MTV-MOF can be distinctly shown in the images. The atomic structures of the MOFs are acquired in Cs-corrected STEM with segmented annular detectors. The electron-beam current was reduced <1 pA by unfiltered monochromator and the combination of the electron dose is <808^{e⁻}M⁻² Å^{M->2} to maintain adequate imaging quality without beam damage on samples. To exclude the possibility of drifting, the iDPC-STEM images of Ni-BDC were acquired from different scanning directions (0°, 30°, 60°, and 90°) with slightly optimized conditions with the dose <1010^{e⁻} Å^{M->2}, showing negligible image distortion under different scanning directions even under higher dose (Figure^{S3}), ensuring that the obtained images could reflect the real state of the samples. The iDPC-STEM image of Ni-BDC shows the Ni-O 2D layers separated by BDC molecules, matching well with the projected structural model (Figure^{1<xfgr1>d}). There is no structural damage during the beam dwell time (5^{μs}) as confirmed by the well-preserved structure without noticeable defects.

The obtained MTV-MOFs show similar structures as Ni-BDC, proving their isostructural to Ni-BDC (Figure^{1<xfgr1>e--g}). The spatial resolution of STEM images for these MTV-MOFs (Figure^{1<xfgr1>e-g}) is usually lower than that of pristine MOFs (Figure^{1<xfgr1>d}) because of the enhanced lattice distortion and disorders. The strain mapping by geometric phase analysis (GPA) reveals that incorporation of either Fe³⁺ or ATA

can lead to remarkable variation in E_{xx} (normal strain in direction perpendicular to 2D layers), E_{yy} (normal strain in direction close to parallel with 2D layers) and E_{xy} (shear strain) (Figure¹d-g). Notably, the FeNi-B and FeNi-BA samples (Figure¹f-g) exhibit much higher variation in E_{yy} than Ni-BDC and Ni-BA samples (Figure¹d-e). These strain variations reach as local as 1-2 nm scale. This is possibly due to the different coordination strength of ATA or Fe^{3+} and BDC or Ni^{2+} , resulting in the weakening of the interlayer bonding, and the local shrinkage in E_{yy} direction. The generation of these lattice strain variations in the MTV-MOFs might cause the loss of localized stability, as confirmed by the density functional theory (DFT) simulations. As shown in Figure², the -C-NH_2 group on ATA affects the coordination around Ni^{2+} , and the bonding strength of ATA-Ni and Ni-C-OH in Ni-BA is significantly weakened by 0.15 and 0.09 eV than that in Ni-BDC. Similar trends are also found in the case of FeNi-B. Although the Ni-C-O bonds become a little stronger after Fe^{3+} incorporation due to the higher oxidation state of Fe^{3+} , the dissociation energies of the BDC-Fe or OH-C-Fe bonds decrease by 0.15 and 0.27 eV (Figure², S4), which can be attributed to the prolonged bond length of Fe-C-O (Figure⁵). Such localized stability loss provides rich opportunities for further functional design and tailoring of the catalytic properties.

Destruction of MOFs by external stimuli is one of the key methods to optimize the properties of MOFs.^[39,40] In view of the bottlenecks of MOFs-based electrocatalysts, a subsequent thermal treatment is performed over these MTV-MOFs for controllable molecular cleavage. Thermogravimetric analysis (TGA) shows that Ni-BDC starts to decompose at around 377 °C, while the decomposition temperature shifts slightly to lower values after incorporating ATA or Fe^{3+} (Figure⁶⁻⁷). Accordingly, the thermal treatment temperature is carefully set at 370 °C with the aim of selective cleavage at the labile domains, whilst keeping the overall framework intact. As expected, the XRD diffraction pattern of $\text{Fe}_{10}\text{Ni-BA}_{0.7}$ is maintained in the thermalized $\text{Fe}_{10}\text{Ni-BA}_{0.7}$ ($\text{Fe}_{10}\text{Ni-BA}_{0.7}\text{-T}$) (Figure¹c).

Two insignificant peaks at 44.4° and 52.2° corresponding to the metallic Ni appear in Fe₁₀Ni-BA_{0.7}-T, implying the occurrence of selective bonds cleavage during thermal treatment. The generation of Ni⁰ is also confirmed by the XPS spectrum with the appearance of a signal at 852.1 eV (Figure S8a). The absence of Fe⁰ in Fe₁₀Ni-BA_{0.7}-T indicates that Fe³⁺ remains in the MOF framework (Figure S8b). In the Raman spectrum of the nanoparticles separated from the acid digested Fe₁₀Ni-BA_{0.7}-T, typical signals of the D band and G band of sp² carbon at 1359 cm⁻¹ and 1597 cm⁻¹ are observed (Figure S9a).^[41] This is in accordance with the color change of the MOFs from light yellow to black after thermolysis (Figure S9b). It is noted that these collected nanoparticles can be well dispersed in ethanol without precipitation after 24 h, suggesting their ultra-small size and the uniform distribution in Fe₁₀Ni-BA_{0.7}-T (Figure S9c). ¹H NMR spectra shows the disappearance of the ATA signal after thermolysis, manifesting that ATA in Fe₁₀Ni-BA_{0.7} is selectively carbonized during the heating process, in line with the gradually decreased thermal stability after ATA incorporation (Figure S7a, S10). These results firmly prove that thermal treatment over Fe₁₀Ni-BA_{0.7} leads to selective Ni-C-O bonds cleavage and results in the formation of conductive Ni⁰ and ATA derived carbon species.

SEM images show that Fe₁₀Ni-BA_{0.7}-T exhibits similar morphology as Fe₁₀Ni-BA_{0.7}, indicating the little influence of the mild heating process on the overall structure (Figure S11). More detailed structural information obtained from TEM images reveals that, different from the smooth surfaces of Fe₁₀Ni-BA_{0.7}, numerous nanoparticles coated by sp² carbon shells are uniformly embedded in the nanosheets of Fe₁₀Ni-BA_{0.7}-T, and the MOF nanosheets show hierarchical porous structures with the formation of mesopores around the Ni@C nanoparticles (Figure S12). HRTEM image shows the lattice fringe of 2.01 Å in the nanoparticles (Figure S12 inset), corresponding to the (111) planes of metallic Ni, in agreement with the XRD and XPS results.

To confirm that Ni@C is intrinsically present in Fe₁₀Ni-BA_{0.7}-T, rather than generated by electron beam irradiation during TEM measurement, Fe₁₀Ni-BA_{0.7}-T is rinsed by acid to remove the MOF framework, and the remaining precipitate is collected. TEM images of the separated nanoparticles showed similar Ni@C core-shell structure, proving their generation during the heating process (Figure[^]S13). Although some Ni nanoparticles are also formed in Ni-BDC-T, the amount is quite small with sparse dispersion and no mesopores can be observed, which is possibly due to the removal of some encapsulated metastable coordination species during MOF preparation process (Figure[^]S14).^[42--44] The heat treatment is also performed over Fe₁₀Ni-B and Ni-BA_{0.7}. Similar hierarchical porous structures with well dispersed Ni@C nanoparticles are generated in both Fe₁₀Ni-B-T and Ni-BA_{0.7}-T (Figure[^]S15--18). These results clearly reveal that such unique hierarchical porous structure with well dispersed Ni@C in Fe₁₀Ni-BA_{0.7}-T could be a result of heat treatment over the disordered structures introduced by both Fe³⁺ and ATA.

The partial structure decomposition certainly leads to formation of defects. Both missing ligand and missing cluster defects can be possibly generated, which however is difficult to be distinguished by other characterizations except for high resolution TEM/STEM. The iDPC-STEM technique is thereby employed to elucidate the detailed defect information in the thermalized MTV-MOFs. Ni-BDC-T shows clearly distinguished metal atoms and ligands that match well with the projected structure model without any noticeable defect, confirming that it is stable during heat treatment (Figure[^]3<figr3>a--c). In contrast, apparent missing ligand defects are observed in FeNi-BA-T as confirmed by the iDPC-STEM images and the line profile analysis, due to the removal of ATA (Figure[^]3<xfigr3>d--f, Figure[^]S19a). Those coordination unsaturated metal atom sites can function as active catalytic sites for OER,^[10,^12,^13] while the well distributed carbon-based species and the enlarged pores can improve the conductivity and promote mass transfer for boosting catalytic activity. No missing cluster defect is observed because when the metal species are released

from the MOF framework, the dangling ligands are readily carbonized and capture the metal species, as confirmed by the formation of Ni@C and mesopores. In addition, lower lattice strain variation is generated after thermal treatment, owing to the removal of ligands in the distorted regions (Figure[^]S19b). Thus, we show that the lattice strain introduced by ATA and Fe³⁺ incorporation can be further utilized for active site engineering by selective thermal treatment. The density of the coordination unsaturated Ni sites, conductive Ni@C nanoparticles and mesopores in the FeNi-BA-T can be well controlled by simply changing the amount of either Fe³⁺ or ATA for facile optimization of the electrocatalytic activity (Figure[^]S20--23).

The OER activity of the as-obtained samples is studied via a three-electrode system in 1.0[^]M KOH aqueous solution. As shown in Figure[^]S24, pristine carbon paper is almost inactive for OER and the activity of Ni-BDC is quite poor. Increased OER performance is observed in Fe₁₀Ni-BA_{0.7}, which could be attributed to the modified electronic structure of Ni. More importantly, thermal treatment lead to further enhanced OER performance (Figure[^]S25). Significantly improved OER activity is achieved in Fe₁₀Ni-BA_{0.7}-T with a small overpotential of 290[^]mV at a current density of 10[^]mA^{cm⁻²}, which is much smaller than that of Fe₁₀Ni-BA_{0.7} (320[^]mV) (Figure[^]S25d). In addition, Fe₁₀Ni-BA_{0.7}-T delivers the current density of 100[^]mA^{cm⁻²} at a small overpotential of 385[^]mV. In contrast, a large overpotential of 477[^]mV is needed for Fe₁₀Ni-BA_{0.7}. At a potential of 1.65[^]V (vs RHE), Fe₁₀Ni-BA_{0.7}-T exhibits a high current density of ≈150[^]mA^{cm⁻²}, which is ca. 2.5[^]times that of Fe₁₀Ni-BA_{0.7} (≈59[^]mA^{cm⁻²}). Fe₁₀Ni-BA_{0.7}-T also shows superior OER activity as compared with Fe₁₀Ni-B-T (303[^]mV and 433[^]V @ 10 and 100[^]mA^{cm⁻²}), Ni-BA_{0.7}-T (370[^]mV @ 10[^]mA^{cm⁻²}, unable to reach 100[^]mA^{cm⁻²} in the test range), Ni-BDC-T (370[^]mV @ 10[^]mA^{cm⁻²}, unable to reach 100[^]mA^{cm⁻²} in the test range) and the commercial RuO₂ (329[^]mV @ 10[^]mA^{cm⁻²}, unable to reach 100[^]mA^{cm⁻²} in the test range) (Figure[^]4<figr4>a--c). The Ni@C

collected from the acid digested Fe₁₀Ni-BA_{0.7}-T has negligible OER activity, excluding its role as active sites (Figure⁴S26). Thus, the enhanced OER activity of Fe₁₀Ni-BA_{0.7}-T should be originated from the MOF frameworks.

The OER activity can be further optimized by simply changing the amount of Fe³⁺ and ATA in FeNi-BA, and the best performance was achieved in Fe₁₀Ni-BA_{7.0}-T, which shows a decreased overpotential of 286 mV @ 10 mA cm⁻² and 365 mV @ 100 mA cm⁻², and a highly improved current density of 200 mA cm⁻² @ 1.65 V (vs RHE) (Figure⁴a, Figure²⁷⁻²⁸ and Table¹S1). Such excellent performance of Fe₁₀Ni-BA_{7.0}-T has exceeded most bulk MOFs and is comparable with some thin MOF nanosheets in previous reports (Table²S2).

The OER kinetics analyzed by Tafel plots show that Fe₁₀Ni-BA_{7.0}-T has the smallest Tafel slop of 45.3 mV dec⁻¹ as compared to Fe₁₀Ni-BA_{0.7}-T (50.6 mV dec⁻¹), Fe₁₀Ni-B-T (57.0 mV dec⁻¹), Ni-BA_{0.7}-T (94.3 mV dec⁻¹), Ni-BDC-T (105.1 mV dec⁻¹) and commercial RuO₂ (57.4 mV dec⁻¹), indicating the fastest reaction kinetics (Figure⁴d). In addition, electrochemical impedance spectroscopy (EIS) obtained at a potential of 1.65 V shows the smallest semicircular diameter of Fe₁₀Ni-BA_{7.0}-T, suggesting the fastest charge-transfer process (Figure⁴e). The Fe₁₀Ni-BA_{7.0}-T is stable during OER test as confirmed by XRD, XPS and TEM analyses (Figure²⁹⁻³⁰). Besides, the chronoamperometric (i-t) measurement over Fe₁₀Ni-BA_{7.0}-T at a current density of 10 mA cm⁻² shows negligible density decay after 16000 s, further manifesting the high durability of Fe₁₀Ni-BA_{7.0}-T during OER test (Figure⁴f).

Ni species are usually recognized as the OER active sites in the FeNi-based catalytic systems, whose electronic structure is highly critical to the reaction. Ni species with high valence state has been proved positive in promoting the OER process.^[14,45,46] To identify the

origin of the excellent OER activity of Fe₁₀Ni-BA_{7.0}-T, the electronic structures of the samples are analyzed by XPS analyses. As shown in Figure⁵a, the binding energy of Ni in the samples follows the order of Fe₁₀Ni-BA_{7.0}-T > Fe₁₀Ni-BA_{0.7}-T > Fe₁₀Ni-B-T > Ni-BA_{7.0}-T > Ni-BDC-T, which agrees with their OER performances. The formation of high-valence Ni in Fe₁₀Ni-BA_{7.0}-T should be related to the Fe³⁺ and ATA incorporation.^[8,14,45,47] Since the electron-electron repulsion is dominated in the Ni²⁺<C->O<C->Ni²⁺ units (Figure⁵b top), substitution of Ni²⁺ by Fe³⁺ to form the Ni²⁺<C->O<C->Fe³⁺ units will trigger partial charge transfer from Ni²⁺ to Fe³⁺ (Figure⁵b middle). When BDC is further replaced by the labile ATA, the interaction between Ni²⁺ and ligands is weakened, which result in stronger interaction between Ni²⁺ and Fe³⁺ bridged by O for charge balance. The strengthened Ni²⁺<C->O<C->Fe³⁺ interaction and the electron-electron repulsion between Ni²⁺ and the bridging O lead to further charge flow from Ni²⁺ to Fe³⁺ (Figure⁵b bottom). This has been confirmed by the gradually increased binding energy of Ni in the order of Ni-BA_{0.7} < Fe₁₀Ni-BA_{0.7} < Fe₁₀Ni-BA_{7.0} (Figure⁵c). Heat treatment to convert Fe₁₀Ni-BA_{7.0} to Fe₁₀Ni-BA_{7.0}-T leads to the increased electron density around Ni²⁺ with a shift of the binding energy to a lower value, which could be due to its partial reduction by the ATA derived carbon that in close proximity to Ni²⁺ (Figure⁵d). It is noted that although the Ni in Fe₁₀Ni-BA_{7.0} shows higher valence state than that in Fe₁₀Ni-BA_{7.0}-T, Fe₁₀Ni-BA_{7.0} exhibits much inferior OER performance as compared with Fe₁₀Ni-BA_{7.0}-T (Figure^{S31}), indicating that in addition to the high-valence Ni, the thermal generated conductive Ni@C and the hierarchical porous structure in Fe₁₀Ni-BA_{7.0}-T also play important roles in the catalytic performance. Benefiting from the presence of well dispersed Ni@C, Fe₁₀Ni-BA_{7.0}-T shows much smaller electrical resistance as compared with Fe₁₀Ni-BA_{7.0} (Figure^{S32a}). In addition, a markedly stronger Ni redox feature peak between 1.3--1.5 V is observed in Fe₁₀Ni-BA_{7.0}-T as compared with Fe₁₀Ni-BA_{7.0}, while the Ni@C has negligible CV signal in this region, suggesting that the OER active

$\text{Ni}^{3+}/\text{Ni}^{4+}$ can be more easily generated in $\text{Fe}_{10}\text{Ni-BA}_{7.0}\text{-T}$ (Figure^{^S32b--c}). The electrochemically active surface areas (ECSAs) evaluated from the double-layer capacitance (C_{dl}) reveal that $\text{Fe}_{10}\text{Ni-BA}_{7.0}\text{-T}$ shows a C_{dl} value more than twice that of $\text{Fe}_{10}\text{Ni-BA}_{7.0}$, revealing the higher amount of accessible active sites in $\text{Fe}_{10}\text{Ni-BA}_{7.0}\text{-T}$ (Figure^{^S32d--f}).

In addition to Ni, the contribution of the coordinatively unsaturated Fe sites to OER cannot be ignored. DFT calculations are carried to elucidate the role of Fe sites (Figure^{^6<figr6>}). Our DFT calculations reveal that the pristine Ni-BDC shows the predicted limiting overpotential (η) of 1.06^{^V}, in accordance with its lower experimental OER performances (Figure^{^6<xfigr6>c}). The OER intermediate energy profile with the bare Ni as reactive sites shows that the conversion of OH^* to O^* is the rate determining step (RDS). Ni atoms become thermodynamically more favorable with the intermediates adsorption after doping with Fe atoms, with the η decreased by 0.02--0.06^{^V}. It is noted that when Fe is used as the active sites, the η decreases to 0.69^{^V} for OER and the RDS changes to be the O^* to OOH^* , which can be attributed to the much stronger O^* binding strength (1.27 vs 2.89^{^eV}) on Fe compared to that on Ni. Thus, it is clear that after doping with Fe, the η decreases on both Ni and Fe reactive sites in different ways, which agrees with our experimental measurements. These results unambiguously reveal that the excellent OER performance of FeNi-BA-T is a synergistic result of the presence of coordinatively unsaturated metal sites, and the easy accessibility of these active sites promoted by the well dispersed conductive Ni@C and the hierarchical structure.

Conclusion

In summary, we use the low-dose iDPC-STEM technique to directly visualize the structure of MTV-MOFs at the atomic scale, which allows us to unveil the localized lattice strain upon introducing Fe^{3+} or ATA into Ni-BDC for guiding the subsequent optimization of electrocatalytic activities. The mild heat treatment break the weakened bonds in the MTV-

MOFs and leads to the formation of hierarchical porous MOFs with evenly distributed conductive Ni@C and missing ligand defects, as distinguished by the iDPC-STEM images. As a result of the improved conductivity, the presence of coordinatively unsaturated metal sites and mesopores, excellent OER activity with current densities of 10 and 100 mA cm⁻² is achieved at small overpotentials of 286 mV and 365 mV, respectively, outperforming the commercial RuO₂ and most of the bulk MOFs. This work highlights the iDPC-STEM technique as an effective tool to unlock the design of MOFs at the atomic scale for novel electrocatalysts.

Experimental Section

Detailed experimental procedures including the materials preparation, characterizations, catalytic activity test and theoretical calculation are described in Supporting Information.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Figure¹ a) Projected structure model of Ni-BDC. b) Schematic illustration for the preparation of FeNi-BA-T. c) XRD diffraction patterns of Ni-BDC, Fe₁₀Ni-BA_{0.7} and Fe₁₀Ni-BA_{0.7}-T. The iDPC-STEM and derived strain mapping images of d) Ni-BDC e) Ni-BA f) FeNi-B and (g) FeNi-BA. Figure^{1d--g} were acquired under the same magnification of 5.60 Mx.

Figure² The structures of Ni-BDC, Ni-BA and FeNi-B with labels of dissociation energies of chemical bonds. Dissociation energies for BDC and OH groups are colored in green and red, respectively.

Figure³ The iDPC-STEM images of a) Ni-BDC-T b) enlarged image of the blanket in (a), and c) the projected structural model of Ni-BDC-T. The iDPC-STEM images of

d) FeNi-BA-T, e) enlarged image of the blanket in (d) showing the missing ligand defect, and (f) the projected structural model of FeNi-BA-T.

Figure 4 a) Polarization curves and b) current density @ 1.6 V and overpotential @ 10 mA cm^{-2} of Fe₁₀Ni-BA_{7.0}-T, Fe₁₀Ni-BA_{0.7}-T, Fe₁₀Ni-B-T, RuO₂, Ni-BA_{0.7}-T, Ni-BDC-T and carbon paper. c) Overpotential @ 100 mA cm^{-2} of Fe₁₀Ni-BA_{7.0}-T, Fe₁₀Ni-BA_{0.7}-T and Fe₁₀Ni-B-T. d) Tafel slop and e) EIS of Fe₁₀Ni-BA_{7.0}-T, Fe₁₀Ni-BA_{0.7}-T, Fe₁₀Ni-B-T, RuO₂, Ni-BA_{0.7}-T and Ni-BDC-T. f) Chronoamperometric curves of Fe₁₀Ni-BA_{7.0}-T.

Figure 5 a) XPS spectra of different FeNi-BA-T samples in Ni 2p region. b) Schematic representation of the electronic coupling among Ni and Fe in Ni-BDC (top), FeNi-B (middle) and FeNi-BA (bottom). c) XPS spectra of Ni-BA_{0.7}, Fe₁₀Ni-BA_{0.7} and Fe₁₀Ni-BA_{7.0}. d) XPS spectra of Fe₁₀Ni-BA_{7.0} before and after heat treatment.

Figure 6 a) Structural models of the FeNi-BA-T with different coordinated metal sites. b) The primitive steps of OER process. c) Energy profiles of different structural models for OER.