**ELECTROCHEMISTRY**

In situ activation of Br-confined Ni-based metal-organic framework hollow prisms toward efficient electrochemical oxygen evolution

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Fundamental insights into the structural evolution of oxygen electrocatalysts under operating conditions are of substantial importance for designing efficient catalysts. Here, on the basis of operando x-ray absorption fine structure spectroscopy, we probe the in situ activation of Br-confined conductive Ni-based metal-organic framework (Br-Ni-MOF) hollow prisms toward an active oxygen electrocatalyst during the oxygen evolution reaction (OER) process. The successive structural transformations from pristine Br-Ni-MOF to a β-Ni(OH)2 analog then subsequently to a γ-NiOOH phase during OER are observed. This post-formed γ-NiOOH analog manifests high OER performance with a superior overpotential of 306 mV at 10 mA cm\(^{-2}\) and a high turnover frequency value of 0.051 s\(^{-1}\) at an overpotential of 300 mV, making Br-Ni-MOF one of the most active oxygen electrocatalysts reported. Density functional theory calculations reveal that the strong electronic coupling between Br and Ni atoms accelerates the generation of the key \(\text{O}\) intermediate toward fast OER kinetics.

**INTRODUCTION**

The increasing global energy demand and environmental degradation are calling for the urgent development of efficient, sustainable, and carbon-neutral energy conversion and storage technologies (1–5). Among them, alkaline-based electrolyzer cell is one of the vital and practical energy conversion devices, in which green hydrogen product can be facilely produced via electric-driven water splitting (5–7). To fulfill the industrial scaling up application of electrolyzer cells, highly active and cost-effective oxygen electrocatalysts with optimized compositions and well-defined architectures are required for the anode electrode in electrolyzer cells to effectively overcome the sluggish oxygen evolution reaction (OER) kinetics (8–10). It is well recognized that, due to the electrolyte effect and the strong driving force of applied electric field, the surface geometric and electronic structures of oxygen electrocatalysts usually experience a rapid reconstruction before efficiently catalyzing OER (11–13). Hence, a key point for rational design and optimization of targeted catalysts with desirable OER performance relies heavily on the comprehensive and fundamental insights into the nature of in situ formed active structure of catalysts under real conditions. To date, it is still a huge challenge to promptly and precisely determine the geometrical and electronic structure evolution of OER electrocatalysts during the catalytic process because of the complicated surface structure of catalysts and the technological limitation of in situ characterization technologies under aqueous conditions.

To effectively track in real time the structural evolution of electrocatalysts, one important prerequisite is to seek an efficient catalytic material with abundant, well-distributed, and structurally uniform active sites (12, 14–16). Recently, metal-organic framework (MOF)-based/derived functional nanomaterials, with plenty of well-dispersed active centers, have attracted intensive attentions as promising oxygen electrocatalysts working under acidic and/or basic conditions (17–19). As a key member of the MOF family, the currently emerging conductive MOF, formed by periodic \(\pi\)-conjugated coordination of planar metal nodes and aromatic-based organic ligands, offers an ideal platform with abundant and homogeneous active sites, high conductivity, large surface area, and abundant porosity for both catalytic activity improvement and catalytic mechanism investigation (20–23). By taking full advantage of its highly conductive property and intrinsic nanocavity feature, a tailored strategy of ion confinement has been theoretically predicted and experimentally substantiated for effectively manipulating the conductive MOF materials with appealing physicochemical properties toward efficient energy conversion and storage (24–26). Despite the improved activity for ion-confined conductive MOF, the structural evolution of active centers and the role of confined ions during the electrocatalytic process are still elusive due to the limited detectable signals derived from few surface active centers of bulk conductive MOF. To enable the accessibility of all potential active sites within conductive MOF to electrolyte, a well-designed architecture, such as hollow nanostructures, is hence required to substantially enlarge the surface area and improve the intrinsic porous structure for conductive MOF. This would guarantee an enormous amount of effective active sites involved in the catalytic reaction, which, in turn, strengthen the detectable in situ/operando spectroscopic signals during catalytic processes (27–29). However, because of the strong chelation and fast nucleation of metal ions and aromatic-based organic ligands, the precisely controlled direct synthesis of conductive MOF with well-designed hollow nanostructures is still very challenging, and the development of ion-confined conductive MOF-based hollow nanostructures as a promising oxygen electrocatalyst has been rarely explored.

Here, well-designed Br-confined conductive Ni-based MOF (designated as Br-Ni-MOF) hollow prisms are developed as a promising OER electrocatalyst through an etching and simultaneous ion confinement strategy. By using operando x-ray absorption fine structure (XAFS) spectroscopy, successive structural transformations of Br-Ni-MOF hollow prism electrocatalysts into the β-Ni(OH)\(_2\) and γ-NiOOH analogs during the OER process are promptly observed. Moreover, the confined Br atoms in Br-Ni-MOF catalysts...
are revealed to be useful promotors for the full formation of the active $\gamma$-NiOOH phase during the OER process. This in situ formed $\gamma$-NiOOH analog could exhibit excellent OER activity and long-term durability with a superior overpotential of 306 mV at 10 mA cm$^{-2}$, making it one of the most promising OER electrocatalysts reported so far. It is revealed by the density functional theory (DFT) calculation results that the strong electronic coupling between Br and Ni atoms could potentially accelerate the generation of the key $^*O$ intermediate over the active Ni centers during OER, thus greatly promoting the OER kinetics for the Br-Ni-MOF electrocatalyst.

RESULTS

Synthesis and structural characterization

The synthetic approach of Br-Ni-MOF hollow prisms is schematically depicted in Fig. 1. Uniform Ni-based acetate hydroxide precursor (designated as Ni-precursor) prisms with an average length of about 1.7 $\mu$m are used to be the initial material (figs. S1 to S3). First, these solid Ni-precursor particles undergo a solvothermal reaction to grow a conductive Ni-MOF layer on their surface by using the ligand of 2, 3, 6, 7, 10, 11-hexahydroxytriphenylene (HHTP) molecules. In the solvothermal process, local dissolution of the Ni-precursor gradually occurs to release Ni cations, which undergo a rapid chelation reaction with the HHTP ligand on the surface, forming well-defined Ni-precursor@Ni-MOF (designated as Ni-pre@Ni-MOF) core-shell prisms. Afterward, the inner Ni-precursor core of Ni-pre@Ni-MOF prisms is facilely removed in a KBr aqueous solution, taking advantage of the high solubility of the Ni-precursor in water. Meanwhile, some Br$^-$ anions are simultaneously confined in the pores of the Ni-MOF shell owing to the ion diffusion effect during the etching process of the Ni-precursor core, finally generating well-defined Br-Ni-MOF hollow prisms.

Field-emission scanning electron microscopy (FESEM) images (Fig. 2, A and B), transmission electron microscopy (TEM) images (Fig. 2, C and D), and x-ray diffraction (XRD) analysis (fig. S4A) apparently show a layer of nanoparticle-assembled Ni-MOF fully supporting on the surface of Ni-precursor in Ni-pre@Ni-MOF core-shell prisms, contrary to a smooth surface of Ni-precursor (figs. S1 and S2). After the etching treatment in a KBr aqueous solution, these Ni-pre@Ni-MOF prisms are ultimately converted into Br-Ni-MOF hollow prisms. FESEM observations (Fig. 2, E and F, and fig. S5, A and B) exhibit uniformly distributed Br-Ni-MOF hollow prisms with an average length of about 1.6 $\mu$m and a rough surface. Moreover, TEM images (Fig. 2, G and H, and fig. S5, C and D) distinctly show a hollow structural feature of Br-Ni-MOF with a shell thickness of about 100 nm. XRD pattern (fig. S6A) and energy-dispersive x-ray (EDX) spectrum (fig. S6B) further reveal respectively the low crystalline feature of Br-Ni-MOF hollow prisms and the successful complete removal of the Ni-precursor core to give a Br:Ni molar ratio of about 0.16:1 in the final Br-Ni-MOF hollow.
prisms. The high-angle annular dark-field scanning TEM (HAADF-STEM) and corresponding EDX elemental mapping images (Fig. 2I) depict the homogeneous distribution of the Br element throughout the Br-Ni-MOF hollow prism. The specific surface area of Br-Ni-MOF hollow prisms is as high as 356 m² g⁻¹, which is attributed to their abundant mesopores mainly in the range of 3 to 10 nm (fig. S7). All the morphological and structural results mentioned above confirm the successful fabrication of the Br-Ni-MOF hollow prisms. In addition, Ni-MOF hollow prisms without confined Br⁻ ions are also fabricated as a reference sample (figs. S8 to S11).

XAFS characterizations were conducted to clarify the atomic structural configurations of Br-Ni-MOF hollow prisms (8, 31). The Ni K-edge $k^2\chi(k)$ oscillation curve of Br-Ni-MOF hollow prisms shows similar trends in oscillating frequency and shape to that of Ni-MOF hollow prisms in the entire $k$ range, and apparently differs from that of β-Ni(OH)₂ and NiO over the $k$ range of 2.0 to 9.0 Å⁻¹ (Fig. 3A). This result indicates a similar atomic configuration for the planar Ni nodes in both Br-Ni-MOF and Ni-MOF hollow prisms, which is quite different from that of Ni sites in β-Ni(OH)₂ and NiO. Moreover, the Fourier transform (FT) curves of extended XAFS (FT-EXAFS) at Ni K-edge are shown in Fig. 3B. As can be seen, the first dominant peak is positioned at 1.55 Å for Br-Ni-MOF hollow prisms, which is mainly originated from the contributions of Ni-O bonds in the nearest coordination shell (14, 32). This dominant peak of Ni-O bonds for Br-Ni-MOF hollow prisms seems to be similar in position and intensity to that of Ni-MOF hollow prisms, reflecting the indirect coordination between Ni nodes and confined Br atoms. The wavelet transform (WT) analyses of EXAFS (WT-EXAFS), with high resolution in both radial space and $k$ space, are used to further clarify the local structure around Ni nodes of the Ni-Br-MOF hollow prisms (Fig. 3C). It can be seen that, for β-Ni(OH)₂, the second dominant peak at 2.85 Å in Fig. 3B is mainly derived from the contribution of Ni-Ni bonds, which shows a maximum value of WT-EXAFS contour plots at about 6.5 Å⁻¹ in $k$ space (denoted by a dashed line in Fig. 3C). In comparison, the second dominant peak of 2.72 Å for Br-Ni-MOF is mainly related to the WT-EXAFS contour plot values at about 4 Å⁻¹ in $k$ space (Fig. 3, B and C), corresponding to a dominant contribution of Ni-C/O bonds (11, 12, 33).

Furthermore, the detailed electronic structure of Br-Ni-MOF hollow prisms is characterized by x-ray photoelectron spectroscopy (XPS) (Fig. 3, D and E, and fig. S12). From the deconvoluted results of Ni 2p in Fig. 3D, there is a dominant peak at 855.6 eV for Br-Ni-MOF hollow prisms, which belongs to 2p½ of Ni²⁺ species (8, 28). From the Br 3p XPS spectrum in Fig. 3E, the dominant peak at about 182 eV is originated from contributions of both free Br⁻ ions and Br-C bonds with a molar ratio of about 4:1, indicating that the confined Br atoms within Br-Ni-MOF hollow prisms mainly exist in a free ionic state (34–36). Accordingly, on the basis of the XAFS and XPS analyses, free Br⁻ ions with strong electronegativity are evidently confined in Br-Ni-MOF hollow prisms, which could synergistically promote high catalytic activity of Br-Ni-MOF hollow prisms through the Coulomb interaction between Br⁻ anions and positively charged Ni nodes during the OER process.

**Evaluation of electrocatalytic performance**

Electrochemical OER measurements were conducted to evaluate the electrocatalytic performance of Br-Ni-MOF hollow prisms in alkaline solution, along with Ni-MOF hollow prisms and a commercial RuO₂ catalyst as two references. To fully activate the electrocatalysts, an activation process of 20-min chronoamperometric operation was conducted for both Br-Ni-MOF and Ni-MOF hollow prisms. The samples of Br-Ni-MOF and Ni-MOF hollow prisms in the preactivation stage are marked as Br-Ni-MOF(P) and Ni-MOF(P), respectively.

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**Fig. 3. XAFS and XPS measurements.** (A to C) The $k^2\chi(k)$ oscillation curves (A), Fourier transform (FT) curves (B), and wavelet transform (WT) contour plots (C) of Ni K-edge EXAFS spectra for NiO, β-Ni(OH)₂, Ni-MOF, and Br-Ni-MOF hollow prisms. (D and E) Ni 2p XPS spectrum (D) and Br 3p XPS spectrum (E) of Br-Ni-MOF hollow prisms. a.u., arbitrary units.
respectively, while those after the activation process are labeled as Br-Ni-MOF(A) and Ni-MOF(A), respectively. Linear sweep voltammetry (LSV) curves in Fig. 4 (A and B) depict a great enhancement in OER activity for both Br-Ni-MOF and Ni-MOF hollow prism catalysts after the activation process, indicating the possible existence of structural activation during OER for both Br-Ni-MOF and Ni-MOF catalysts. Impressively, a small overpotential ($\eta_{10}$) of 306 mV is needed for the Br-Ni-MOF(A) catalyst to achieve a current density of 10 mA cm$^{-2}$, substantially outperforming that of both Ni-MOF(A) (356 mV) and RuO$_2$ (348 mV). As can be seen from fig. S13A, the OER performance of both Br-Ni-MOF(A) and Ni-MOF(A) is much superior to that of HHTP ligand and carbon paper, suggesting that Ni metal sites are the main contributor for the high intrinsic OER activity of Br-Ni-MOF(A) and Ni-MOF(A) electrocatalysts. Moreover, the Tafel slope of the Br-Ni-MOF(A) catalyst is only 79.1 mV dec$^{-1}$ (Fig. 4C), clearly superior to that of Ni-MOF(A) (108.9 mV dec$^{-1}$) and RuO$_2$ (86.2 mV dec$^{-1}$), indicating accelerated OER kinetics after confinement of Br$^-$ ions. For the OER process in alkaline medium, the formation of *O intermediates over the active sites of catalysts, via deprotonation of adsorbed *OH, may give a Tafel slope of 60 mV dec$^{-1}$ from previous studies (37, 38). Considering a Tafel slope of 79.1 mV dec$^{-1}$ for the Br-Ni-MOF(A) catalyst, which is close to 60 mV dec$^{-1}$, it can be speculated that the formation of key *O intermediates at Ni sites may be the rate-determining step (RDS) during the OER process for the Br-Ni-MOF(A) catalyst. Notably, the Br-Ni-MOF(A) catalyst presents substantially enhanced turnover frequency (TOF) values over the whole applied potential range in comparison with Ni-MOF(A) and RuO$_2$ (Fig. 4D), where a high TOF value of 0.051 s$^{-1}$, five times that of Ni-MOF(A) (0.010 s$^{-1}$), is achieved for the Br-Ni-MOF(A) catalyst at the overpotential of 300 mV.

The electrochemical double-layer capacitance ($C_{dl}$), closely related to the amounts of surface active sites, is evaluated to give the electrochemically active surface area (ECSA) of Br-Ni-MOF(A) (5, 8). As shown in Fig. 4E and fig. S14, Br-Ni-MOF(A) exhibits a moderate $C_{dl}$ value of 1.08 mF cm$^{-2}$, slightly superior to Ni-MOF(A) (0.72 mF cm$^{-2}$). Moreover, the normalized LSV curves (fig. S15A) present intrinsic higher OER activity for Br-Ni-MOF(A) relative to Ni-MOF(A). The electrochemical impedance spectroscopy (EIS) results (fig. S15B) depict much smaller charge transfer resistance during OER for Br-Ni-MOF(A), which indicates that the improved OER kinetics may account for the high intrinsic OER activity of Br-Ni-MOF(A). Note that both Br-Ni-MOF(A) and Ni-MOF(A) exhibit excellent OER durability in alkaline conditions, with negligible increase of potential or slight decay of the initial current density after a long-term OER operation for 100 hours (Fig. 4F and figs. S16 and S17), while an apparent increase of above 30 mV in potential is observed for the RuO$_2$ catalyst after the similar OER operation (Fig. 4F). On the basis of the aforementioned electrocatalytic performance results, the Br-Ni-MOF hollow prisms manifest excellent OER performance with a low $\eta_{10}$, a small Tafel slope, and high TOF values after an in situ activation process, serving as one of the most efficient MOF-based or MOF-derived (oxy)hydroxide OER electrocatalysts in alkaline solution (table S1) and being comparable with the most active transition metal sulfide/phosphide OER electrocatalysts reported so far (11, 32, 39–48).

Fig. 4. Electrocatalytic performance evaluation. (A and B) LSV plots (A) and the corresponding overpotential at 10 mA cm$^{-2}$ (B) for Ni-MOF and Br-Ni-MOF hollow prisms in the pre- and post-activation stages. (C and D) Tafel slopes (C) and TOF values (D) of RuO$_2$, Ni-MOF(A), and Br-Ni-MOF(A). (E) Capacitive current density ($\Delta J/2$) at 1.05 V versus RHE against the scan rate for Ni-MOF(A) and Br-Ni-MOF(A). (F) Potential-time curves at the current density of 10 mA cm$^{-2}$ for RuO$_2$, Ni-MOF(A), and Br-Ni-MOF(A).
Operando XAFS characterization

Operando XAFS spectroscopy, including x-ray absorption near-edge structure (XANES) and EXAFS analyses, was used to promptly monitor the local structural evolution of metal centers in Br-Ni-MOF hollow prisms during the OER process. As shown in operando Ni K-edge $k^2\chi(k)$ oscillation curves in Fig. 5A, the oscillation curves of Br-Ni-MOF hollow prisms under increasing potentials are quite different in shape and intensity from the ex situ one without applied potential, indicating that there are potential-induced local atomic rearrangements around Ni nodes during OER. In particular, two different sets of oscillating shape and frequency over the $k$ range of 5 to 10 Å$^{-1}$ are discerned before and after the applied potential of 1.35 V versus RHE. This result indicates that there are two major structural transformations for Br-Ni-MOF hollow prisms in the two periods of precatalytic stage (1.10 to 1.35 V) and catalytic OER stage (1.45 to 1.55 V) during the catalytic process. Moreover, the FT curves of operando EXAFS at Ni K-edge in Fig. 5B present a red shift of the first and second dominant peaks from 1.55 and 2.72 Å to 1.66 and 2.85 Å, respectively, after applying a potential of 1.10 V. This observation suggests that the initial reconstruction of Ni nodes in Br-Ni-MOF hollow prisms takes place at relatively low applied potentials. Notably, as the potential increases to 1.35 V, the second major peak at about 2.85 Å undergoes a split into two peaks, which may be an indicator of further structural rearrangement of Ni nodes in Br-Ni-MOF hollow prisms. Notably, when higher potentials of 1.45 and 1.55 V are applied, the first and second dominant peaks of Br-Ni-MOF hollow prisms show a blue shift by about 0.19 and 0.31 Å relative to those at 1.10 V (Fig. 5B and fig. S18), inferring the formation of final active structure of Ni centers in the catalytic OER stage toward efficient oxygen evolution.

To further clarify the structural evolution of Ni nodes in Br-Ni-MOF hollow prisms during OER, the in situ formed (oxy)hydroxide phase might also be helpful for enabling the Br-Ni-MOF electrocatalyst with increasing applied potentials were provided, which is helpful for discriminating the backscattering atoms around central metal sites and then evidently determining the exact active structure. As seen from Fig. 5C, upon the applied potential of 1.10 V, a maximum value of WT-EXAFS contour plots is obtained at about 6.5 Å$^{-1}$ in $k$ space for Br-Ni-MOF hollow prisms (denoted by a dashed line in Fig. 5C), which is well consistent with the location of Ni-Ni scattering and is similar to that of $\beta$-Ni(OH)$_2$ (11, 49). This might indicate the formation of $\beta$-Ni(OH)$_2$ analogs derived from the pristine Br-Ni-MOF at a relatively low potential in the precatalytic stage, which can also be verified by the FT-EXAFS results in fig. S18. In particular, this maximum value of WT-XAFS contour plots at 6.5 Å$^{-1}$ disappears when the potential increases to 1.35 V and then reemerges at a higher potential of 1.55 V, inferring further structural transformation from hydroxides into oxyhydroxides in the catalytic OER stage. It is well known that two types of NiOOH, $\beta$- and $\gamma$-NiOOH, are reported as the real active phase of Ni-based OER electrocatalysts in the previous works, where $\gamma$-NiOOH is a metastable phase with a Ni valence state higher than +3 relative to the stable $\beta$-type phase with main Ni$^{3+}$ species (50–52). The XANES analyses in Fig. 5 (D and E) distinctly show an average metal valence state of Ni$^{3.3+}$ in Br-Ni-MOF hollow prisms at 1.55 V, indicating that the in situ formed $\gamma$-NiOOH analog is responsible for the intrinsic high OER activity of the Br-Ni-MOF catalyst. Furthermore, when the applied potential is turned back to 1.10 V from 1.55 V, this in situ formed active $\gamma$-NiOOH structure can be quickly converted into a $\beta$-Ni(OH)$_2$ analog (fig. S18), which is known to be less active for catalyzing OER. This interesting observation again confirms that the potential-dependent metastable $\gamma$-NiOOH analog is the real highly active structure for Br-Ni-MOF hollow prisms during OER. Moreover, this in situ formed (oxy)hydroxide phase might also be helpful for enabling the Br-Ni-MOF electrocatalyst with increasing applied potentials.
high activity and robust durability under relatively high operating potentials (50, 51).

Note that a substantial increase of Ni valence state from about +2.0 (corresponding to the ex situ state) to +2.8 is observed when a relatively low potential of 1.10 V is applied on the Br-Ni-MOF hollow prisms (Fig. 5, D and E). This indicates the possible formation of strong coordination interactions between confined Br atoms and Ni sites during the initial structural transformation process in the precatalytic stage, which is helpful for promoting the full formation of the active $\gamma$-NiOOH phase at a low potential of 1.45 V (Fig. 5, A and B). In comparison, without the confined Br atoms, a mixed phase of hydroxide/(oxy)hydroxide analogs is obtained for the Ni-MOF catalyst even under the relatively high potentials of 1.55 to 1.75 V (fig. S19). Moreover, a hierarchical hollow architecture, with abundant ultrathin nanosheets fully covering the surface of hollow prisms, is observed for the Br-Ni-MOF catalyst after a long-term OER operation (fig. S20). These in situ formed ultrathin nanosheets, with a thickness of about 2 nm, are shown to be Ni-based hydroxides according to the high-resolution TEM image and XRD pattern results shown in fig. S21, which is well consistent with the operando XAFS analyses in Fig. 5 and fig. S18. From the elemental mapping images in fig. S22, some C elements are still observed in the Br-Ni-MOF catalyst after the OER test, which again suggests that certain part of MOF structures remains untransformed during the OER process. It appears that most of the Br atoms are still retained in the Br-Ni-MOF catalyst after a long-term OER operation, with an atomic ratio of about 0.11:1 for Br:Ni (fig. S23). To clarify the influence of Fe impurity in the electrolyte, the electrochemical measurements of Br-Ni-MOF and Ni-MOF electrocatalysts are also conducted in a purified KOH electrolyte as references (53). It can be seen that the Br-Ni-MOF electrocatalyst shows similar OER activity in fresh and purified KOH electrolytes (fig. S13B), and there is no detectable Fe impurity in Br-Ni-MOF electrocatalysts after the activation process based on the XPS characterization results shown in fig. S24. These results highlight the important role of confined Br atoms on the high intrinsic OER activity of the Br-Ni-MOF electrocatalyst.

**DISCUSSION**

The in-depth DFT calculations were performed for Br-Ni-MOF hollow prisms to rationalize the role of confined Br$^-$ ions in efficiently boosting the OER activity. As revealed by operando XAFS analyses in Fig. 5, the Ni-based (oxy)hydroxide analog is undoubtedly determined to be the real active phase for Br-Ni-MOF(A) during OER. Hence, the structures of NiOOH with and without Br dopants are selected as the computational models for Br-Ni-MOF(A) and Ni-MOF(A) catalysts, respectively (fig. S25). As seen from Fig. 6A and fig. S26A, the calculated partial density of state (PDOS) shows that both Ni 3d and Br 4p of Br-Ni-MOF(A) have substantial DOS over the range of −4 to 0 eV, inferring the strong electronic coupling between Ni and Br atoms. Furthermore, with the introduction of Br atoms, an evident upshifting of Ni d band center is observed for Br-Ni-MOF(A) relative to Ni-MOF(A), from about −2.41 to −2.25 eV (Fig. 6B). The upshifting of Ni d band center toward the Fermi level for Br-Ni-MOF(A) could effectively regulate the electronic structure of Ni sites with more antibonding states and higher valence states, which would enable Ni centers stronger binding ability with reactive intermediates toward efficient oxygen electrocatalysis. As can be seen from Fig. 6C and fig. S26B,

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**Fig. 6. DFT simulation.** (A) Calculated partial density of states (PDOS) for Br-Ni-MOF(A). (B) Calculated DOS of Ni 3d for Ni-MOF(A) and Br-Ni-MOF(A). (C) Free energy diagram of OER for Ni-MOF(A) and Br-Ni-MOF(A). (D) Schematics of the OER catalytic mechanism for Br-Ni-MOF(A), where M means the active centers of Br-Ni-MOF(A).
the free energy diagram of Ni-MOF(A) shows the largest energy barrier (1.91 eV) for the formation of the *O intermediate during the multistep OER process, indicating that the *O generation is the RDS for Ni-MOF(A) \(^{(35, 55)}\). In contrast, the free energy of the *O formation is obviously reduced to 1.72 eV for Br-Ni-MOF(A) after Br incorporation as shown in Fig. 6D, accounting for the promoted OER energetics on Br-Ni-MOF(A). This means a theoretical overpotential of 0.49 V for Br-Ni-MOF(A), which is close to that widely reported for NiFeOOH catalysts (typically in the range of 0.26 to 0.48 V) \(^{(37, 55)}\). Therefore, it can be expected that Br-Ni-MOF(A) may serve as a promising OER electrocatalyst. Moreover, the free energy change of the \(\text{O}_2\) gas releasing step from the Br-Ni-MOF(A) catalyst is only 0.78 eV (Fig. 6D), which is obviously superior to that of Ni-MOF(A) (1.09 eV), again indicating improved OER kinetics after the Br incorporation. The above theoretical calculations explicitly reveal that the introduced Br atoms will form strong electronic coupling with Ni centers in Br-Ni-MOF(A) through Br-Ni bonding. This could effectively regulate and optimize the electronic structure of Ni centers in Br-Ni-MOF(A), thus contributing to thermodynamically favorable generation of the *O intermediate toward fast oxygen catalytic kinetics for efficient OER.

On the basis of the experimental and theoretical results discussed above, confined Br\(^{-}\) ions play an important role on the structural evolution and the high intrinsic OER activity of the Br-Ni-MOF catalyst during the OER process. In the precatalytic stage, robust coordination interactions between confined Br and Ni sites occur during the initial structural transformation, which contributes to a substantial increase of Ni valence state in the Br-Ni-MOF catalyst (Fig. 5, D and E). Because of the strong electronegativity of Br atoms, the electronic structure of adjacent Ni sites could be effectively regulated, which is then very helpful for promoting the further local structural transformation of Ni centers in the Br-Ni-MOF catalyst. Relative to the Ni-MOF catalyst, an active \(\gamma\)-NiOOH analog is easily and completely observed for the Br-Ni-MOF catalyst when a relatively low potential of 1.45 V is applied (Fig. 5, A and B, and fig. S19). This result reveals that the confined Br\(^{-}\) ions are useful promoters for the structural evolution of Br-Ni-MOF catalysts toward the formation of the active \(\gamma\)-NiOOH phase during OER. Furthermore, because of the strong electronic coupling between Ni and Br atoms, an evident upshifting of Ni d band could be theoretically expected in Br-Ni-MOF(A), which results in more antibonding states and higher valence states of Ni species for Br-Ni-MOF(A) (Fig. 6B). These active Ni sites with improved electronic structures would enable Br-Ni-MOF(A) a stronger binding affinity to key oxo-contained intermediates, thus reducing greatly the thermodynamic barrier of RDS during oxygen electrocatalysis toward faster OER kinetics.

In summary, rationally designed Ni-based MOF hollow prisms with confined Br\(^{-}\) ions (Br-Ni-MOF) have been in situ activated as an efficient oxygen evolution electrocatalyst. The successive structural evolution of Br-Ni-MOF hollow prisms during OER is promptly observed at the atomic level through the operando synchrotron radiation spectroscopic technology. During the structural transformation process, the \(\beta\)-Ni(OH)\(_2\) analog is first formed in the precatalytic stage followed by the generation of the metastable highly active \(\gamma\)-NiOOH analog in the catalytic OER stage. Theoretical calculations rationalize the important role of confined Br\(^{-}\) ions on the improved OER performance of Br-Ni-MOF hollow prisms. Specifically, the electronic structure of Ni nodes in the Br-Ni-MOF catalyst can be properly regulated via strong electronic coupling between Ni and Br atoms, contributing to the thermodynamically facilitated formation of key *O intermediate over Ni centers toward fast OER kinetics. These findings can provide constructive insights into the nature of in situ formed active structure of oxygen electrocatalysts and may spark some new inspirations on the rational design of efficient electrocatalysts for sustainable energy storage and conversion.

### MATERIALS AND METHODS

#### Synthesis of Ni-precursor supported Ni-MOF (Ni-pre@Ni-MOF) core-shell prisms

Typically, 2 mg of Ni-precursor prisms is dispersed into 8 ml of \(N,N'\)-dimethylformamide (DMF) solution by ultrasonication. Afterward, 4 mg of the 2, 3, 6, 7, 10, 11-HHTP ligand is dissolved into 2 ml of DMF, which is subsequently added into the former solution containing Ni-precursor prisms. After stirring for 3 min, this resultant solution is put into a preheated oil bath and then remained under a temperature of 120°C for 2 hours. After cooling down to room temperature under stirring, the product is centrifuged and washed with DMF and ethanol several times to get the Ni-pre@Ni-MOF core-shell prisms.

#### Synthesis of Br-Ni-MOF hollow prisms

In a typical preparation, the dispersion of 2 mg of Ni-pre@Ni-MOF core-shell prisms into 4 ml of DMF is realized by ultrasonication. After that, the resultant solution is quickly injected into 4 ml of aqueous solution containing 40 mg of KBr and then kept under stirring at room temperature for 1 hour. The product is centrifuged and then washed with deionized (DI) water and ethanol for several times to obtain the final Br-Ni-MOF hollow prisms.

#### Synthesis of Ni-MOF hollow prisms

The Ni-MOF hollow prisms are synthesized in a similar way to that of Br-Ni-MOF hollow prisms, where the suspension solution of Ni-pre@Ni-MOF is quickly added into 4 ml of DI water without KBr.

#### Materials characterizations

FESEM (JEOL-6700) and TEM (JEOL-6700) are used to record the morphology of the samples. XRD (Bruker D2 Phaser XRD) with Cu K\(_{\alpha}\) radiation is used to examine the crystal structure of the samples. The XRD pattern of conductive Ni-MOF is theoretically simulated by using diffraction analysis software of Mercury 4.1.0. The FESEM equipment with an EDX spectroscopy is used to analyze the compositions of the samples. TEM (JEOL, JEM-2100F) equipped with an EDX spectroscopic detector is used to record the elemental mapping images of the samples. The nitrogen adsorption-desorption isothermal curves are recorded by a 3Flex Surface characterization Analyzer (Micromeritics) at the temperature of 77 K for the samples. The detailed electronic structure of the samples is measured by XPS (PHI Quantum 2000), where the binding energy of 284.6 eV for the
adventitious carbon (C 1s) is used as the reference. The molar ratio of various surface components in samples can be reasonably determined by directly calculating the fitting peak area ratio of those components based on the deconvolution analyses of corresponding XPS spectra. In this work, the deconvoluted results of Br 3p3/2 peak in Fig. 3E reveal a fitting peak area ratio of 697.5:175.3 for free Br− ions to Br−C bonds, giving a molar ratio of about 4:1 for free Br− ions to Br−C bonds in Br-Ni-MOF catalysts. FT infrared spectroscopy (Thermo Smart iTR) is used to study the surface functional groups of the samples. The operando and ex situ XAFS spectroscopy results of Ni K-edge are collected at the 1W1B station of the Beijing Synchrotron Radiation Facility (BSRF), China, and at the X-ray absorption fine structure for catalysis (XAFCA) beamline of the Singapore Synchrotron Light Source (SSLS), Singapore, respectively. A nickel foil is used to calibrate the energy. During the operando XAFS measurements, the method of constant potential is applied. To monitor the changes of electrodes during the OER process, anodic voltages from 1.10 to 1.55 V or 1.75 V versus RHE are applied for Br-Ni-MOF or Ni-MOF catalysts, respectively. For each XAFS spectroscopy collection, the selected constant potential is first applied to the electrodes in 1 M KOH electrolyte for 10 min as the pretreatment step. Subsequently, the XAFS spectra of electrocatalysts are collected through a fluorescence mode within 30 min. It would take about 40 min for the XAFS measurement under each constant potential applied. FT of $k^2\chi(k)$ oscillation curves is conducted on the basis of the IFEFFIT software packages. WT of $k^2\chi(k)$ oscillation curves is carried out on the basis of Morlet wavelets.

**Electrochemical measurements**

A three-electrode configuration workstation (CHI 760E) is used to record the electrochemical measurements for the samples without $iR$ compensation, where the counter and reference electrodes are graphite rod and Hg/HgO, respectively. To avoid the contamination of Fe impurity, a high-purity KOH reagent (semiconductor grade, 99.99% trace metals basis) was used elaborately to prepare the KOH electrolyte (designated as fresh KOH) for the electrochemical measurements, unless stated otherwise. An activation process of chronoamperometric measurement is conducted for both pristine Br-Ni-MOF and Ni-MOF catalysts before the OER performance tests. In detail, the LSV measurement is first carried out for the pristine electrocatalysts to determine suitable potential parameters for the chronoamperometric measurement of the activation process. The potential at a catalytic current density of 1 mA cm$^{-2}$ is used as the initial potential parameters for the chronoamperometric measurements, which are determined to be about 1.48 and 1.53 V versus RHE for pristine Br-Ni-MOF and Ni-MOF catalysts, respectively. After that, the chronoamperometric measurement of the activation process is performed under the corresponding potentials in 1 M KOH solution for 20 min to fully activate the Br-Ni-MOF and Ni-MOF catalysts. For the preparation of the catalyst ink, full dispersion of 5 mg of catalyst into a mixed solution of 0.25 mL of water, 0.70 mL of ethanol, and 0.05 mL of 0.5 weight % Nafion solution is achieved by 30-min ultrasonication. After that, to prepare the working electrode, 20 µL of catalytic ink is loaded onto one end of a piece of carbon paper (1 cm × 3 cm), with a loading area of 1 cm × 1 cm, and then dried naturally at room temperature. During the electrochemical measurements, only the part of carbon paper loaded with catalysts (with an area of 1 cm × 1 cm) is elaborately immersed into the KOH solution. LSV curves are measured in alkaline (1.0 M KOH) solutions by a forward scan with a scan rate of 5 mV s$^{-1}$. A pH value of 13.75 is determined for this 1.0 M KOH solution by a basic pH meter (PB-10, Sartorius). On the basis of the Nernst equation, $E_{RHE} = E_{H_2/O_2} + 0.098 + 0.059 \times pH$, all potentials in this work are calculated relative to the RHE potential. Moreover, the overpotential ($\eta$) during OER is estimated on the basis of the following formula: $\eta = E_{RHE} - 1.23$ V. The evaluation of the ECSA for the samples is based on the $C_d$ results measured in the potential range of 1.0 to 1.1 V versus RHE. The EIS test of the samples is measured under an amplitude of 5 mV in a frequency range of 0.1 to 10$^5$ Hz. For the 4e− OER process, the TOF values for the samples are estimated on the basis of the following formula: TOF = ($j < A$) / ($4 \times F \times m$), where $j$, $A$, $F$, and $m$ are the current density under the given potential, the electrode surface area, the faradaic constant, and the molar number of active metal for the electrode, respectively ($11$). The inductively coupled plasma optical emission spectroscopy (Agilent 720) is used to measure the content of active metal components of the catalytic electrodes. TOF values estimated here are related to the created oxygen molecules per second for the total metal active sites in catalysts. To rule out the influence of Fe impurity in the electrolyte, the fresh KOH electrolyte is further purified (designated as purified KOH) based on the method reported by Boettcher’s group ($53$). On the basis of the inductively coupled plasma mass spectroscopy (Agilent 7700s) analyses, the Fe impurity in the fresh and purified KOH solution is about 17.9 and 2.8 parts per billion, respectively.

**DFT calculations**

Theoretical calculations are carried out on the basis of the first-principles DFT calculations by using the DMol 3 package equipped in the Materials Studio Program. To describe the exchange-correction potential, the generalized gradient approximation of Perdew-Burke-Emrzerhof functional is used. To calculate the catalytic activity of Ni-MOF catalysts, three consecutive O-Ni-O sandwich slabs, created from NiOOH crystal, were used as the calculated model, with a 15-Å vacuum space along the z direction. This model includes a total number of 60 atoms for Ni, O, and H. For Br-Ni-MOF catalysts, its computational model is similar in structure to that of Ni-MOF, except the replacement of a surface oxygen atom with one Br atom. The free energy change, ΔG(ad), of the OER intermediates (e.g., *OH, *O, and *OOH) was calculated by the following equation ($54$)

$$\Delta G(ad) = \Delta E(ad) + \Delta ZPE(ad) - T \Delta S(ad)$$

where “ad” means the adsorbed intermediate and ΔE(ad), ΔZPE(ad), and ΔS(ad) denote the electronic energy change, zero-point energy difference, and entropy difference, respectively. Especially, ΔE(ad) for key intermediates is calculated on the basis of the following equations

$$\Delta E(*OH) = E(*OH) + 0.5 \times E(H_2) - E(H_2O) - E(model)$$

$$\Delta E(*O) = E(*O) + E(H_2) - E(H_2O) - E(model)$$

$$\Delta E(*OOH) = E(*OOH) + 1.5 \times E(H_2) - 2 \times E(H_2O) - E(model)$$

where $E(*OH), E(*O), E(*OOH), E(model), E(H_2),$ and $E(H_2O)$ represent the energies of adsorbed *OH, *O, *OOH, the surface...
model, H₂, and H₂O molecules, respectively. ΔZPE(ad) and ΔS(ad) are calculated by frequency analyses. The free energy changes for each OER step could be depicted as follows

\[
\Delta G_1 = \Delta G(*OH) \\
\Delta G_2 = \Delta G(*) - \Delta G(*OH) \\
\Delta G_3 = \Delta G(**OH) - \Delta G(*) \\
\Delta G_4 = 4.92 \text{ eV} - \Delta G(**OH)
\]

Accordingly, the theoretical overpotential (η_{DFT}) can be estimated on the basis of the following equation: \( \eta_{DFT} = \max(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4/e - 1.23 \text{ V} \), where \( \max(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4) \) means the maximum value of the free energy changes during OER and \( e \) is the electron.

**SUPPLEMENTARY MATERIALS**

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