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Electronic structure modulation with ultrafine Fe$_3$O$_4$ nanoparticles on 2D Ni-based metal-organic framework layers for enhanced oxygen evolution reaction

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ABSTRACT: Two-dimensional (2D) metal organic frameworks (MOFs) are emerging as low-cost oxygen evolution reaction (OER) electrocatalysts, however, suffering aggregation and poor operation stability. Herein, ultrafine Fe$_3$O$_4$ nanoparticles (diameter: 6 ± 2 nm) are homogeneously immobilized on 2D Ni based MOFs (Ni-BDC, thickness: 5 ± 1 nm) to improve the OER stability. Electronic structure modulation for enhanced catalytic activity is studied via adjusting the amount of Fe$_3$O$_4$ nanoparticles on Ni-BDC. The optimal Fe$_3$O$_4$/Ni-BDC achieves the best OER performance with an overpotential of
295 mV at 10 mA cm\(^{-2}\), a Tafel slope of 47.8 mV dec\(^{-1}\) and a considerable catalytic durability of more than 40 h (less than 5 h for Ni-BDC alone). DFT calculations confirm that the active sites for Fe\(_3\)O\(_4\)/Ni-BDC are mainly contributed by Fe species with a higher oxidation state, and the potential-determining step (PDS) is the formation of the adsorbed O* species, which are facilitated in the composite.

**Keywords:** Fe\(_3\)O\(_4\) nanoparticles; 2D Ni-BDC; Aggregation; Electronic structure modulation; Oxygen evolution reaction.

1. **Introduction**

With increasing concerns of fossil fuel related environmental crisis and global warming, there is an imperative demand for developing alternative green and sustainable energy conversion and storage technologies, such as batteries, fuel cells and water splitting [1–7]. As a crucial reaction of secondary metal-air batteries and electrochemical water splitting, oxygen evolution reaction (OER) plays an important role in the efficiency and operational stability of such systems [8–12]. High-performance electrochemical catalysts are thus urgently required to promote sluggish OER reaction kinetics, to provide low overpotential (\(\eta\)) and excellent catalytic stability. Considering the rarity and high cost of noble metal OER catalysts (e.g. Ir or Ru based materials) [13,14], earth-abundant and cost-effective transition-metal based electrocatalysts are clearly desired.

Metal-organic frameworks (MOFs) are a class of porous materials composed of organic linkers and metal nodes with covalent coordination [15]. MOFs and derived materials have been used in a wide range of fields, e.g. gas storage and separation, batteries and catalysis etc., benefiting from their high specific surface area, tuneable porosity and abundant active metal sites [16–21]. Two-dimensional (2D) MOFs based materials have attracted growing attention for OER catalysts with unique physicochemical features. 2D structure enables hydroxide units
in the electrolyte to easily reach the active site and fast dissociation of generated O$_2$, as well as shortening electron transfer pathway through the thin film to the conductive support [22–24]. 2D MOFs can also be engineered to possess a large number of coordinatively unsaturated metal atoms exposed as active sites [25,26]. Surface atom structure and bonding arrangement can be elaborately controlled to facilitate the interaction between the active site and the reaction intermediates for superior OER electrocatalysts [27,28]. However, 2D MOFs have a high tendency to aggregate with each other [29,30], leading to decreased effective surface area. Avoiding aggregation with high active surface area and improving the integral structural stability for superior OER catalysts are thus essential.

To tackle these issues, there are increasing reports demonstrating that the introduction of functional nanoscale components (nanosheets or nanoparticles etc.) in a MOF composite could prevent the aggregation and enhance the integral structural stability during operation [30,31]. Meanwhile, the electronic structure of metal units in the MOFs can be optimized by incorporation with heterogeneous metal containing groups for superior OER performance [30–35]. For example, Qiao and coworkers have synthesized 2D Ni-BDC/Ni(OH)$_2$ heterostructure, exhibiting a lower $\eta$ of 320 mV at 10 mA cm$^{-2}$ than that of Ni-BDC nanosheets, and a good catalytic durability of 20 h. The improved OER performance is attributed to the rational design of the composition and structure of the composite, and to the mitigation of aggregation of Ni-BDC by coupling with Ni(OH)$_2$ [30]. Similarly, Qin et al. have reported hybrids of Fe-Co polyphenolic network wrapped Fe$_3$O$_4$ nanocatalysts for enhanced OER with a $\eta$ of 260 mV at 10 mA cm$^{-2}$ and a durability over 24 h, taking advantage of strong metal-polyphenolic ligand complexation that ensures robust metal Co-Fe polyphenolic shells for prolonged operations [31]. Inspired by these reports, 2D Ni based MOFs could be promising
candidates for constructing hybrid electrocatalysts due to excellent surface structure and physicochemical features. Meanwhile, considering Fe$_3$O$_4$ nanoparticles with good electrical conductivity (>100 S cm$^{-1}$) and fast electron transfer between Fe$^{2+}$ and Fe$^{3+}$ in the crystals [31,36], the incorporation of Fe$_3$O$_4$ nanoparticles on the surface of 2D Ni based MOFs could be promising candidate to be used for OER.

Herein, we have successfully prepared ultrasmall Fe$_3$O$_4$ nanoparticles that are uniformly immobilized on 2D Ni based MOFs (Fe$_3$O$_4$/Ni-BDC). The functionalized Fe$_3$O$_4$ nanoparticles (6 ± 2 nm) with abundant surface hydroxide groups are initially synthesized, and then either added directly during the synthesis of 2D Ni-BDC layers (4 ± 1 nm) or alternatively mixed with pre-synthesized 2D Ni-BDC. We have investigated morphology changes and electronic structure modulation to tackle the aggregation issue for OER via tuning the amount of Fe$_3$O$_4$ immobilized on the 2D Ni-BDC layers. The optimized Fe$_3$O$_4$/Ni-BDC-4 composite demonstrates significantly enhanced OER performance with a $\eta$ of 295 mV at 10 mA cm$^{-2}$, a Tafel slope of 47.8 mV dec$^{-1}$ and an excellent catalytic durability over 40 h. DFT calculations are further conducted to identify the active site and help to understand how the valance state of transition metals affects the OER performance.

2. Experimental

2.1 Chemicals and Reagents

Iron (III) chloride hexahydrate (FeCl$_3$·6H$_2$O, 97%), sodium bicarbonate (NaHCO$_3$, ≥99.7%), L-ascorbic acid, terephthalic acid (1, 4-BDC, 98%), N,N-dimethylformamide (DMF, 99.8%), Nafion solution (10 wt%) were bought from Sigma-Aldrich. Triethylamine (TEA, 99%) was purchased from Merck (Germany). Nickel (II) chloride hexahydrate (NiCl$_2$·6H$_2$O, 98%) was from BDH Chemicals Ltd Poole England. All chemicals were used as received without further
purification. Ultrapure water (≥ 18.25 MΩ·cm, Sartorius arium® pro, Germany) was used to prepare all the aqueous solutions.

2.2 Synthesis of Fe\textsubscript{3}O\textsubscript{4}/Ni-BDC composites

Water-soluble Fe\textsubscript{3}O\textsubscript{4} nanoparticles were synthesized as in a previous report [37]. Briefly, a 20 mL aqueous solution of 1 mM L-ascorbic acid was added into a 60 mL mixture aqueous solution of 6 mM FeCl\textsubscript{3}·6H\textsubscript{2}O and 18 mM NaHCO\textsubscript{3}, under stirring for 20 min. The mixture was transferred to a 150 mL Teflon-lined stainless-steel autoclave, which was kept at 150 °C for 6 h. The product was separated using a magnet, washed with ultrapure water more than three times, leading to water-soluble Fe\textsubscript{3}O\textsubscript{4} nanoparticles that could be re-dispersed in water for further using.

Ni-BDC was grown with or without the presence of water-soluble Fe\textsubscript{3}O\textsubscript{4} for Fe\textsubscript{3}O\textsubscript{4}/Ni-BDC composites. 63 mg 1,4-BDC was first dissolved in a mixed solvent of DMF (15 mL), ethanol (1 mL), and ultrapure water (1 mL), into which 90 mg NiCl\textsubscript{2}·6H\textsubscript{2}O and a certain volume of water or water-soluble Fe\textsubscript{3}O\textsubscript{4} solution were added subsequently and under ultrasonication for 10 min, followed by a quick injection of 0.50 mL TEA. To optimize the ratio of Fe\textsubscript{3}O\textsubscript{4} and Ni-BDC in the composite, different volumes of water-soluble Fe\textsubscript{3}O\textsubscript{4} solution (12 mg mL\textsuperscript{-1}; 1, 2, 3, 4 or 5 mL) were used. The above mixture was sealed and continuously ultra-sonicated for 6 h at room temperature. Finally, the precipitates were centrifuged and washed with ethanol three times, dried in a vacuum oven at 60 °C for 12 h. The obtained composites were collected and labelled as Fe\textsubscript{3}O\textsubscript{4}/Ni-BDC-\textit{n} (\textit{n} = 1, 2, 3, 4 and 5).

2.3 Materials characterization
The crystalline structure was characterized by X-ray diffraction (XRD, D8 Advance X-Ray diffractometer (Huber)). X-ray photoelectron spectroscopy (XPS) was performed by drop-casting samples onto silicon substrates with a Thermo-Scientific system (Al-Kα radiation, 1484.6 eV). Fourier transform infrared spectroscopy (FTIR) measurements were performed on an Alpha-P FTIR spectrometer (Bruker) in the range of 4,000 - 400 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\). The specific surface area was estimated by a Surface Area & Pore Size Analyzer (ASAP 2020, Micromeritics). Elemental analysis was performed by inductively-coupled plasma optical emission spectrometry (ICP-OES). Microstructure and composition characterization were conducted with scanning electron microscopy (SEM, Quanta FEG 200 ESEM, 15 kV), atomic-force microscopy (AFM, Agilent Technology 5500, tapping mode, a mica sheet as the substrate), and transmission electron microscopy (TEM, Tecnai G2 T20, 200 kV).

### 2.4 Electrochemical measurements

In order to prepare catalyst inks, 4 mg of active materials (Fe\(_3\)O\(_4\)/Ni-BDC-\(n\), Ni-BDC or Fe\(_3\)O\(_4\)), 4 mg of carbon black (Alfa Aesar™) and 25 μL of Nafion solution (10 wt%) were mixed with 0.75 mL of 2-propanol and 0.25 mL of ultrapure water for a uniform ink after 1 h sonication. Prior to use, rotating disk electrodes (RDE) using glassy carbon electrodes (GCEs, \(d = 5.0\) mm, \(A = 0.19625\) cm\(^2\)) and rotating ring disk electrodes (RRDEs, \(d_{\text{disk}} = 5.61\) mm, \(A_{\text{disk}} = 0.2472\) cm\(^2\), \(d_{\text{ring}}\) (inner) = 6.25 mm, \(d_{\text{ring}}\) (outer) = 7.92 mm, \(A_{\text{ring}} = 0.1859\) cm\(^2\)) with a GCE disk and a Pt ring were polished on a polishing pad with Al\(_2\)O\(_3\) slurries with decreasing particle diameters (1.0, 0.3 and 0.05 μm). Afterwards, 10 μL of the catalyst ink was drop-cast onto the surface of GCEs, leading to a mass loading of 0.398 mg cm\(^{-2}\) and dried under room temperature. Electrochemical tests were carried out in a typical three-electrode setup with 1.0 M KOH solution as the electrolyte on an electrochemical workstation (Autolab PGSTAT12) with a
graphite rod as the counter electrode and a Ag/AgCl (sat. KCl) as the reference electrode. Rotation of RDE and RRDE were controlled on a Pine Instruments rotating system. The applied potentials were compensated with the solution resistance $R_s$ and current $I$ via: $E_{\text{Ag/AgCl-corr}} = E_{\text{Ag/AgCl}} - IR_s$ [38], where the uncompensated Ohmic solution resistance ($R_s$) in the high-frequency region was measured by electrochemical impedance spectroscopy (EIS) in a frequency range from 100 kHz to 0.1 Hz at 1.525 V vs. RHE. All measured potentials were calibrated to reversible hydrogen electrode (RHE) potential according to the following equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl-corr}} + 0.197 + 0.059 \times \text{pH}$. To maintain the $\text{O}_2/\text{H}_2\text{O}$ equilibrium at 1.23 V versus RHE, oxygen gas ($\text{O}_2 \geq 99.995\%$) flow was kept in the electrolyte during the test. The $\eta$ for OER was defined as: $\eta = E_{\text{RHE} \ -1.23 \text{ V}}$. For OER test, working electrodes were initially scanned for 10 cycles using cyclic voltammetry (CV) to obtain stable signals. Then, linear sweep voltammetry (LSV) curves were obtained at a slow scan rate of 5 mV s$^{-1}$ at a rotational speed of 1,600 rpm to decrease capacitive currents and interference from generated gas bubbles. The electrode durability was evaluated by chronopotentiometry at a current density of 10 mA cm$^{-2}$. Tafel slope ($b$) was calculated based on the Tafel equation [39,40]:

$$\eta = a + b \cdot \log j \quad (2.1)$$

and compared to $b = 2.303RT/\alpha nF$, where $j$ is current density of samples from the LSV test, $\alpha$ the charge transfer coefficient, $n$ the number of transferred electrons during the redox reaction, $F$ the Faraday constant (96485 C mol$^{-1}$), $R$ the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $T$ the temperature (K).

The electrochemical double-layer capacitance ($C_{dl}$) was tested by using CVs in a narrow potential range of 1.223-1.323 V vs. RHE, with scan rates of 40, 60, 80, 100, and 120 mV s$^{-1}$. The plot of $\Delta j = (j_a - j_c)$, where $j_a$ and $j_c$ are the anodic and cathodic current, respectively, at
1.24 V vs. RHE (no faradaic reaction occurring) against the scan rate had a linear relationship, whose slope was twice of $C_{dl}$. The electrochemically active surface area (ECSA) relative to GCE and GCE-normalized current density were calculated according to the equations [41]:

$$ECSA = \frac{C_{dl, samples}}{C_{dl, GCE}}$$  \hspace{1cm} (2.2)

$$j_{ECSA, normalized} = \frac{j}{ECSA}$$  \hspace{1cm} (2.3)

Herein, $C_{dl, GCE}$ is the specific capacitance for a plane surface in the range of 20-60 $\mu$F cm$^{-2}$, and $C_{dl, GCE} = 40$ $\mu$F cm$^{-2}$ was used [32]. To investigate the reaction mechanism for OER, RRDE voltammograms were recorded to determine the OER reaction pathway by measuring the $HO_2^-$ formation, with the ring potential held at 1.50 V vs. RHE at 1,600 rpm, and linearly scanning the potential of the disk in O$_2$-saturated 1.0 M KOH solution.

### 2.5 Computational details

Spin-polarized density functional theory (DFT) calculations were performed using the Vienna $ab$-$initio$ simulation package (VASP) [42,43]. The Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximations (GGA) was used to account for exchange correlation effects. The projector-augmented wave method was used to represent the core-valence electron interaction. The valence electronic states were expanded in plane-wave basis sets with energy cutoff at 450 eV, and the force convergence criterion in the structure was set to be 0.05 eV/Å. The transition states were searched using a constrained optimization scheme [44–48]. The Hubbard $U$ approach was used to correct Ni and Fe 3$d$ orbitals with $U_{eff} = 3.8$ eV [49-52]. The zero-point energies (ZPE) and entropy corrections to the free energies at room temperature (298.15 K) were applied. DFT-D3 method with Becke-Johnson (BJ) damping
was employed to describe Van der Waals interaction [53,54]. The free energy of gas-phase O₂ molecule is discussed in Supporting Information.

2.6 Structure models

On the basis of our XRD characterization (Fig. 1a and Fig. S1) and previous report [52], the (200) surface of Ni-BDC was constructed and used to study the interactions between catalysts and adsorbates. A $p(2\times1)$ Ni-BDC catalytic surface system was modelled with two metal oxide layers separated by one BDC layer (Fig. S22). A (5×5×1) k-point was used for geometry optimization with quasi-Newton algorithm. For the structure of Fe₃O₄, the XRD data shows the (311) plane to be the main surface facet and thus was constructed to model the active surface, exposing five-coordinated Fe sites, two-coordinated and three-coordinated O sites (Fig. S23). Four stoichiometric layers of Fe₃O₄(311) on the Ni-BDC(200) surface was created to model a Fe₃O₄/Ni-BDC compositied structure. A (1×5×2) k-mesh was used for geometry optimization. While there could be residual surface groups from the hydroxide groups and DHAA, the models used for DFT focus on the possible interaction in this Fe₃O₄/Ni-BDC compositied structure.

3. Results and discussion

3.1 Structural and component characteristics

Fe₃O₄/Ni-BDC composites are synthesized through a two-step procedure as illustrated in Scheme 1. Water-soluble Fe₃O₄ nanoparticles are initially prepared with a modified hydrothermal method [37]. Dehydroascorbic acid (DHAA) is oxidized from the ascorbic acid, serving as a stabilizer and capping ligand on surfaces of Fe₃O₄ nanoparticles interacted by carbonyl groups, ensuring a good dispersibility of Fe₃O₄ nanoparticles in aqueous solution.
During the subsequent sonication process, functionalized Fe$_3$O$_4$ nanoparticles are homogenously dispersed in an alkaline solution (pH ~ 10), immobilized on 2D Ni-BDC. Triethylamine (TEA) serves as the deprotonating agent and the modulator to promote the nucleation of pristine Ni-BDC for monodisperse film with the controllable orientation [57]. Introducing the Fe$_3$O$_4$ nanoparticles solution into the synthetic process of Ni-BDC leads to lower TEA concentration, restraining the continuous nucleation of Ni-BDC layers. As a consequence, smaller Ni-BDC layers with more defects and edges are obtained, and with Fe$_3$O$_4$ nanoparticles immobilized, leading to Fe$_3$O$_4$/Ni-BDC composites.

**Scheme 1.** Schematic illustration of the synthesis of Fe$_3$O$_4$/Ni-BDC composite. Inset shows two-dimensional Ni-BDC layer immobilized ultrasmall Fe$_3$O$_4$ nanoparticles with ball and stick mode: nickel (pink), oxygen (red), carbon (grey), hydrogen (white) and iron (blue). Not drawn to real scale.

The water-soluble Fe$_3$O$_4$ nanoparticles (Fig. 1a) were characterized by XRD analysis, showing peaks matching well with the standard Fe$_3$O$_4$ phase (JCPDS no. 89-0688), with peaks at 18.3°,
30.0°, 35.4°, 43.0°, 56.9° and 62.5° fitting well with (111), (220), (311), (400), (511) and (440) planes of magnetite, respectively. The diffraction peaks of pure Ni-BDC (Fig. 1a) can be assigned based on Ni-BDC composites in literature [27,52]. The main diffraction peaks at 8.8°, 15.7° and 17.9° are ascribed to the (200), (201) and (-201) planes of Ni-BDC, respectively. Fe$_3$O$_4$/Ni-BDC-\(n\) composites with various amount of Fe$_3$O$_4$ are successfully synthesized, and XRD patterns of Fe$_3$O$_4$/Ni-BDC-4 (Fig. 1a) confirm the co-existence of the crystalline phases of Fe$_3$O$_4$ and Ni-BDC. Similar diffraction peaks are also observed on those of Fe$_3$O$_4$/Ni-BDC-1, 2, 3 or 5 (Fig. S1). It can be observed that the diffraction peaks of Ni-BDC become weaker with the increase of Fe$_3$O$_4$ content, a phenomenon due to the process that Fe$_3$O$_4$ nanoparticles limit the growth of Ni-BDC layers. In addition, FTIR spectra of Fe$_3$O$_4$, Ni-BDC and Fe$_3$O$_4$/Ni-BDC-4 are shown in Fig. 1b. The band at 553 cm$^{-1}$ is assigned to the Fe-O stretching vibration of Fe$_3$O$_4$ [58], with the bands in the range of 600-1300 cm$^{-1}$ attributed to out-of-plane vibrations of the BDC linker [59]. The strong bands at 1373 and 1564 cm$^{-1}$ are ascribed to the stretching modes of the coordinated carboxylate (-COO$^-$) of the terephthalate linker of Ni-BDC, indicative of the presence of both Fe$_3$O$_4$ and Ni-BDC [59]. The absorption band at 1647 cm$^{-1}$ is regarded as the coordination between O atom of the carbonyl group (C=O) from DHAA and Fe units from the surfaces of Fe$_3$O$_4$ nanoparticles [37]. The broad band at 3315 cm$^{-1}$ is attributed to the strong stretching mode of hydroxyl groups (-OH) [37,59,60].
Fig. 1. XRD patterns (a) and FT-IR spectra (b) of Ni-BDC, Fe$_3$O$_4$ and Fe$_3$O$_4$/Ni-BDC-4. (c) High-resolution Ni 2p XPS spectra of Ni-BDC and Fe$_3$O$_4$/Ni-BDC-4. (d) High-resolution Fe 2p XPS spectra of Fe$_3$O$_4$ and Fe$_3$O$_4$/Ni-BDC-4. (e) High-resolution O 1s XPS spectra of Ni-BDC, Fe$_3$O$_4$ and Fe$_3$O$_4$/Ni-BDC-4. (f) Typical nitrogen adsorption-desorption isotherms of Fe$_3$O$_4$/Ni-BDC-4 composites; inset is the corresponding pore-size distribution.

The chemical bonding states of Fe$_3$O$_4$, Ni-BDC and Fe$_3$O$_4$/Ni-BDC composites are investigated by XPS. All signals originating from expected elements (Ni, Fe, O or C) are recorded in the survey spectra (Fig. S2). The high-resolution Ni 2p spectra (Fig. 1c) are deconvoluted into two satellite peaks and a couple of peaks for Ni$^{2+}$ (854.8/872.5 eV for Fe$_3$O$_4$/Ni-BDC-4 and 860.2/878.5 eV for Ni-BDC) [27]. In addition, in high-resolution Fe 2p spectra (Fig. 1d), a spin-orbit doublet at 709.2/722.6 eV and 709.4/723.0 eV is assigned to the Fe$^{2+}$ in Fe$_3$O$_4$/Ni-BDC and Fe$_3$O$_4$, respectively [61]. Peaks at 712.2/725.9 eV and 712.2/725.9 eV are belong to the Fe$^{3+}$ in Fe$_3$O$_4$/Ni-BDC and Fe$_3$O$_4$, respectively [34]. High-resolution Ni 2p (Fig. 1c) and Fe 2p (Fig. 1d) spectra indicate the Ni 2p$_{3/2}$ (856.7 eV for Ni-BDC) and Fe 2p$_{3/2}$ (710.4 eV for Fe$_3$O$_4$) shift to lower and higher binding energies (Fig. 1c, d and S3; Ni 2p$_{3/2}$ and Fe 2p$_{3/2}$ of Fe$_3$O$_4$/Ni-
BDC-4), respectively [52,62]. The detailed binding energy data are summarized in Table S1. Binding energy level of Ni 2p\textsubscript{3/2} decreases and while Fe 2p\textsubscript{3/2} increases slightly with the amount of Fe\textsubscript{3}O\textsubscript{4} nanoparticles among the five composites. This indicates that there is change in the bond strength of both Fe and Ni to varying degree in the different Fe\textsubscript{3}O\textsubscript{4}/Ni-BDC composites.

The typical O 1s spectrum of Fe\textsubscript{3}O\textsubscript{4}/Ni-BDC-4 (Fig. 1e) indicates peaks at 533.4, 532.4 and 531.6 eV, that are assigned to O-H, O=C-O and Ni-O bonding, respectively, originating from the terephthalate linker and NiO\textsubscript{6} octahedra in Ni-BDC [27]. Other peaks at 531.2, 530.7 and 529.8 eV are assigned to O-H, O=C and Fe-O bonding, respectively, attributed to the surface hydroxyl and carbonyl groups from the DHAA and internal Fe-O units of the water-soluble Fe\textsubscript{3}O\textsubscript{4} [61,63]. To quantify the specific surface area and pore sizes of Fe\textsubscript{3}O\textsubscript{4}/Ni-BDC-4, the typical adsorption–desorption isotherm is recorded using nitrogen adsorption–desorption measurements (Fig. 1f). The specific surface area is determined to be 136 m\textsuperscript{2} g\textsuperscript{-1}, which is attributed to the slit-like structure formed by aggregation of Fe\textsubscript{3}O\textsubscript{4}/Ni-BDC-4 [52]. The pore size distributions of the composite are mainly centered at 40 nm. Besides, the pore size distribution indicates the presence of micropores (<2 nm), mesopores (2-50 nm) and macropores (>50 nm), confirming a hierarchical porous structure for Fe\textsubscript{3}O\textsubscript{4}/Ni-BDC-4, which is beneficial for mass transport for OER. Finally, ICP-OES is conducted to check the metallic components of various Fe\textsubscript{3}O\textsubscript{4}/Ni-BDC composites (Table S2). It verified that proportional Fe in the composite increases with the added amount of Fe\textsubscript{3}O\textsubscript{4}. Fe\textsubscript{3}O\textsubscript{4}/Ni-BDC-4 is composed of 24.7 at% Ni and 75.3 at% Fe.

3.2 Morphology and microstructure

The morphologies of Ni-BDC, Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{3}O\textsubscript{4}/Ni-BDC are performed by SEM and TEM. SEM images of pure Ni-BDC (Fig. 2a, Fig. S4a and b) show a hierarchical-layer structure comprised
of aggregated 2D nanosheets. After immobilizing different amounts of Fe$_3$O$_4$ nanoparticles (Fig. 2b, Fig. S4c and d), the generated Fe$_3$O$_4$/Ni-BDC composites show changes in morphology and microstructures. With increasing the ratio of Fe$_3$O$_4$, the Fe$_3$O$_4$/Ni-BDC (Fig. 2c, Fig. S4e and f, Fig. S5) turns from a layered structure to a smoother structure with smaller Ni-BDC grains. Likely caused by Fe$_3$O$_4$ nanoparticles anchoring Ni-BDC on their surface hindering extended growth of Ni-BDC layers. As a control to assess if any leaching Fe from could cause MOF formation, samples following the same synthetic route of Fe$_3$O$_4$/Ni-BDC-4 without the addition of NiCl$_2$·6H$_2$O are also fabricated, but were difficult to purify and separate from solution. SEM images and the corresponding EDS spectrum (Fig. S6) indicate that the control sample is the water-soluble Fe$_3$O$_4$ nanoparticles with no formation of Fe based MOF. This further confirms the importance of Ni source (NiCl$_2$·6H$_2$O) in the formation of Fe$_3$O$_4$/Ni-BDC composites. TEM image of pure Ni-BDC (Fig. 2d) clearly demonstrates a two-dimensional hierarchical-layer structure. The AFM image (Fig. S7) of partial Ni-BDC samples further indicates the thickness of Ni-BDC nanosheets is 5 ± 1 nm. TEM image of Fe$_3$O$_4$ (Fig. 2e) obviously shows ultrafine nanoparticles with a particle size of 6 ± 2 nm. The interplanar spacing of the lattice (Fig. 2f) is measured to be 0.485 nm, matching well with the (111) plane of magnetite Fe$_3$O$_4$ (JCPDS no. 89-0688) [64]. When the mass ratio of Fe$_3$O$_4$ is low, the high-resolution TEM image of Fe$_3$O$_4$/Ni-BDC-1 (Fig. S8) clearly shows the boundary between Fe$_3$O$_4$ and Ni-BDC. Fe$_3$O$_4$ nanoparticles are tightly anchored on the Ni-BDC layers, originating from the strong coupling effects between them. With a higher mass ratio of Fe$_3$O$_4$, the typical TEM images of Fe$_3$O$_4$/Ni-BDC-4 (Fig. 2g-h and S9) show that ultrafine Fe$_3$O$_4$ nanoparticles are homogenously immobilized on the Ni-BDC layers. The high-resolution TEM image of Fe$_3$O$_4$/Ni-BDC-4 (Fig. 2i) demonstrates a crystalline interplanar spacing of 0.297 nm, in accordance with the (220) plane of magnetite Fe$_3$O$_4$ (JCPDS no. 89-0688) [65]. The STEM-EDS elemental
mapping images corresponding to a fragment of Fe\textsubscript{3}O\textsubscript{4}/Ni-BDC-4 (Fig. 2j-n) suggests the homogeneous distribution of nickel (cyan), iron (red), oxygen (green) and carbon (purple) elements, confirming that Fe\textsubscript{3}O\textsubscript{4} nanoparticles are uniformly distributed on Ni-BDC sheets. Linear elemental distribution of Fe\textsubscript{3}O\textsubscript{4}/Ni-BDC-4 composite (Fig. S10) further verifies that ultrasmall Fe\textsubscript{3}O\textsubscript{4} nanoparticles distributes on the surface of Ni-BDC.

Fig. 2. SEM images of (a) Ni-BDC, (b) Fe\textsubscript{3}O\textsubscript{4} and (c) Fe\textsubscript{3}O\textsubscript{4}/Ni-BDC-4. TEM images of Ni-BDC (d) and Fe\textsubscript{3}O\textsubscript{4} (e). Inset of (e) is the particle size distribution. (f) High-resolution TEM image of Fe\textsubscript{3}O\textsubscript{4}. (g and h) TEM image of Fe\textsubscript{3}O\textsubscript{4}/Ni-BDC-4. (i) High-resolution TEM image of Fe\textsubscript{3}O\textsubscript{4}/Ni-
BDC-4. HAADF STEM image (j) and corresponded STEM-EDS mapping of elemental Ni (k), Fe (l), O (m) and C (n) for Fe$_3$O$_4$/Ni-BDC-4, respectively.

**3.3 Electrochemical behaviour and OER performance**

OER performance of the proposed electrocatalysts was investigated in a conventional three-electrode cell containing O$_2$-saturated 1.0 M KOH solution by LSV at a scan rate of 5 mV s$^{-1}$. As controls, the OER activities of pristine Ni-BDC, Fe$_3$O$_4$ and commercial RuO$_2$ with the same mass loading on GCE are examined. Catalytic performance of Fe$_3$O$_4$/Ni-BDC-4 is tested for screening the optimal Fe ratio (Fig. 3a and Fig. S11). The best OER performance is obtained with the Fe$_3$O$_4$/Ni-BDC-4 (Ni 24.7 %, Fe 75.3 %), exhibiting the lowest $\eta$ of 295 mV at a current density of 10 mA cm$^{-2}$. In comparison, large $\eta$ of 369, 465 and 339 mV (Fig. 3b) is registered for pristine Ni-BDC, Fe$_3$O$_4$ and commercial RuO$_2$, respectively. It is noteworthy that introducing Fe$_3$O$_4$ nanoparticles, although themselves being poor OER catalysts, radically improves the overall water oxidation ability of Ni-BDC, decreasing $\eta$ with as much as 170 mV. The enhanced OER performance of Fe$_3$O$_4$/Ni-BDC-4 is attributed to the optimal electronic structure of transition metals and hierarchical-layer structure, which are confirmed by XPS and TEM results (Fig. 1c and d, Fig. 2g-i). To illustrate the role of electronic structure change upon OER performance, the $\eta$ of 337 mV at 10 mA cm$^{-2}$ of physical mixture of Fe$_3$O$_4$ and Ni-BDC (Fig. S12a) is significantly larger than that of Fe$_3$O$_4$/Ni-BDC-4. High-resolution Ni 2p and Fe 2p spectra (Fig. S12b and c) of physical mixed samples shows no shifts from the individual samples. In situ growth of Ni-BDC in the presence of Fe$_3$O$_4$ nanoparticles causes the binding energy changes of Ni 2p and Fe 2p in the composites (Table S1), optimizing the integral electronic structure of Fe$_3$O$_4$/Ni-BDC-4 composite for high OER performance. Tafel curves of Fe$_3$O$_4$/Ni-BDC-4, Ni-BDC, Fe$_3$O$_4$ and commercial RuO$_2$ are shown in Fig. 3c. Tafel slope of
Fe₃O₄/Ni-BDC-4 (47.8 mV dec⁻¹) is considerably smaller than those of Ni-BDC (60.5 mV dec⁻¹), Fe₃O₄ (148.1 mV dec⁻¹) and commercial RuO₂ (83.5 mV dec⁻¹), revealing the significantly improved catalytic reaction kinetics on Fe₃O₄/Ni-BDC-4 [66]. The change of Tafel slope is related to the potential-determining step (PDS) of the electrochemical reaction, indicating the PDS of Fe₃O₄/Ni-BDC-4 is the second step for electron transfer (formation of O*) [40,67]. In addition, stability is also a critical parameter to evaluate the catalyst. The chronopotentiometric curve of Fe₃O₄/Ni-BDC-4 is shown in Fig. 3d. Compared with previously reported Fe₃O₄ or Ni-BDC based catalysts (Table S3), Fe₃O₄/Ni-BDC-4 demonstrates a superior durability over 40 h with a stable OER activity at a constant current density of 10 mA cm⁻². As a control, the OER catalytic stability of pure Fe₃O₄ (Fig. S13a) shows a sharp decay after 8 h, and the pristine Ni-BDC (Fig. S13b) exhibits a weak catalytic stability with a lifetime of less than 5 h. The good catalytic stability of Fe₃O₄/Ni-BDC-4 implies that the active sites continuously interact with the reaction intermediates for OER during operation. It’s apparent that stability is achieved with the intermixing of Fe₃O₄ nanoparticles with Ni-BDC. The coupling effects between Fe₃O₄ nanoparticles and Ni-BDC layers could support the structural stability during OER process by efficiently preventing the aggregation of Ni-BDC. Furthermore, the hierarchical structure of the composite could offer abundant defects and edges.
Fig. 3. (a) LSV polarization curves of OER for Ni-BDC, Fe$_3$O$_4$, Fe$_3$O$_4$/Ni-BDC-4 and RuO$_2$ in O$_2$-saturated 1.0 M KOH solution with a scan rate of 5 mV s$^{-1}$, respectively. (b) $\eta$ for Ni-BDC, Fe$_3$O$_4$, Fe$_3$O$_4$/Ni-BDC-4 and RuO$_2$ at a current density of 10 mA cm$^{-2}$, respectively. (c) The corresponding Tafel plots from LSV curves (a). (d) Chronopotentiometric response of Fe$_3$O$_4$/Ni-BDC-4 at 10 mA cm$^{-2}$.

The key parameter involved the number of transferred electrons during OER is further investigated by a RRDE. A much lower current density (Fig. S14) on the ring electrode at 1.50 V compared with that on the disk electrode during OER process was recorded. It indicates a desirable four-electron reaction path ($4OH^- \rightarrow O_2 + 2H_2O + 4e^-$) occurs on Fe$_3$O$_4$/Ni-BDC-4 with negligible generation of hydrogen peroxide during OER [52,68]. This further confirms the observed disk current density results from water oxidation rather than other side reactions (Fig. S14). The above results validate that Fe$_3$O$_4$/Ni-BDC-4 is an efficient OER catalyst.
**Fig. 4.** (a) CV curves of Ni-BDC and Fe$_3$O$_4$/Ni-BDC-$n$ ($n$: 1, 2, 3, 4 and 5) in O$_2$-saturated 1.0 M KOH; scan rate: 50 mV s$^{-1}$. Inset is oxidation peak area ratio normalized on the basis of Ni-BDC. (b) Anodic peak potential ($E_{pa}$) and onset potential ($E_{onset}$) of Ni-BDC and Fe$_3$O$_4$/Ni-BDC-$n$ ($n$: 1, 2, 3, 4 and 5) corresponded to the CV curves (a). (c) Current density as a function of the scan rate to derive $C_{dl}$ for Ni-BDC, Fe$_3$O$_4$ and Fe$_3$O$_4$/Ni-BDC-4. (d) Nyquist plots of Ni-BDC, Fe$_3$O$_4$ and Fe$_3$O$_4$/Ni-BDC-4 measured at 1.525 V vs. RHE.

Electrochemical behaviour of the samples was characterized by CV in O$_2$-saturated 1.0 M KOH solution in a potential window of 1.123-1.573 V vs. RHE, a region without OER and pre-oxidation peaks are generally observed. Such pre-oxidation peaks are usually related to the oxidation of transition metals (from $2^+$ to $3^+$), which are involved in OER process [25,52]. Ni-BDC (Fig. 4a) and Fe$_3$O$_4$ (Fig. S15) show anodic peaks potential ($E_{pa}$) at 1.406 and 1.460 V vs. RHE, respectively [69,70]. The oxidation peak area ratio of Fe$_3$O$_4$/Ni-BDC-4 (Fig. 4a)
normalized on the basis of Ni-BDC in CV curves is larger than that of others synthetic samples, and such an increased oxidation peak area is believed to be significant for enhanced OER catalytic ability [71,72], in good agreement with above measured η data. As summarized in Table S4 and Fig. 4b, $E_{pa}$ of Fe$_3$O$_4$/Ni-BDC-$n$ has a slight positive shift trend with increasing $n$ ($n=1, 2, 3, 4$), but the trend reverses when $n=5$, revealing that the amount of Fe$_3$O$_4$ nanoparticles could affect $E_{pa}$. As a control, the main $E_{pa}$ (1.411 V vs. RHE) in the CV of physical mixture of Fe$_3$O$_4$ and Ni-BDC (Fig. S16) show a negligible change compared with the $E_{pa}$ of pristine Ni-BDC, furtherly revealing that directly prepared Fe$_3$O$_4$/Ni-BDC composites modify the integral electronic structure for higher oxidation-state situations. With the increasing amount of Fe$_3$O$_4$ nanoparticles in the Fe$_3$O$_4$/Ni-BDC-$n$ ($n=1, 2, 3, 4$ and 5), more positive $E_{pa}$ is observed than that of pristine Ni-BDC (Fig. 4a). The strong interaction between Fe$_3$O$_4$ and Ni-BDC suggests that the corresponded $E_{pa}$ peaks from the synergistic effects of oxidation of Ni and Fe species, which shifts positively. The more positive $E_{pa}$ peaks indicate the higher oxidation state of active sites accounts for good OER catalytic performance [25]. Most importantly, there is likely a link between $E_{pa}$ and onset potential of OER ($E_{onset}$). The optimal Fe$_3$O$_4$/Ni-BDC-4 composite demonstrates the highest $E_{pa}$ (1.431 V vs. RHE) and the lowest $E_{onset}$ (i.e. smallest η) among Fe$_3$O$_4$/Ni-BDC-$n$. Previous reports [25,73] indicate this could be due to higher-oxidation-state metal originating from the coupling effects of Ni and Fe in the composite is responsible for an enhanced OER performance. Overall, we successfully demonstrate that the modulation of the oxidation state of elemental Ni and Fe of 2D Ni-BDC by incorporating with Fe$_3$O$_4$, which is revealed by XPS, leads to a high $E_{pa}$ and a small η.

ECSA is another crucial parameter, which is correlated to the number of active sites and has been determined via $C_{dl}$ measurement (Fig. S17) [32,41,74]. As displayed in Fig. 4c, the $C_{dl}$ of Fe$_3$O$_4$/Ni-BDC-4 is 478 μF cm$^{-2}$, much higher than those of Fe$_3$O$_4$ (277 μF cm$^{-2}$) and Ni-BDC
(283 μF cm⁻²). Meanwhile, Fe₃O₄/Ni-BDC-ₙ (ₙ=1, 2, 3, 5) exhibit C_dl values of 249, 299, 360 and 407 μF cm⁻², respectively (Fig. S18). Fe₃O₄/Ni-BDC-4 shows the highest C_dl value, mainly attributed to assumption that the introduction of Fe₃O₄ nanoparticles on the surface of Ni-BDC layers can lead to the formation of hierarchical structure, offering abundant defects and edges. Besides, the coupling effects between Fe₃O₄ and Ni-BDC could effectively optimize the electronic structure modulation. These effects are favorable for the improvement of active sites, which is likely to be related to ECSA. Although ECSA can assess the number of active sites, it is hard to ensure all active sites measured by ECSA are catalytically active [41], we adopted ECSA value for normalizing the current density of LSV in Fig. 3a. Fe₃O₄/Ni-BDC-4 (Fig. S19) demonstrating the lower η than those of pristine Ni-BDC and Fe₃O₄ after normalization. The normalized current density of Fe₃O₄/Ni-BDC-4 is considerably large, for example, reaching 2.6 mA cm⁻² at 1.55 V vs. RHE, in comparison to 0.19 and 0.05 mA cm⁻² for pristine Ni-BDC and Fe₃O₄, respectively. This result strongly indicates that the incorporation of Ni-BDC and Fe₃O₄ effectively promotes the catalytic activity. Further, EIS helps to understand charge transfer kinetics at the electrolyte/electrode interface. Nyquist plots of Fe₃O₄/Ni-BDC-4, Ni-BDC and Fe₃O₄ are shown in Fig. 4d. Diameter of the semicircles in high-middle frequency region corresponds to the charge-transfer resistance (R_ct) [75]. R_ct (10 Ω) of Fe₃O₄/Ni-BDC-4 during OER is significantly lower than those of pristine Ni-BDC (82 Ω) and Fe₃O₄ (746 Ω), implying a rapid charge transfer process on Fe₃O₄/Ni-BDC-4.

The morphology and crystalline change of Fe₃O₄/Ni-BDC-4 after duration test have been evaluated. XRD pattern of Fe₃O₄/Ni-BDC-4 (Fig. S20a) after LSV shows the disappearance of Fe₃O₄ peaks, indicating the possible amorphous transformation of Fe₃O₄. This observation may be attributed to the oxidation of ultra-small Fe₃O₄ nanoparticles (6 ± 2 nm) during OER, leading to the formation of oxy-hydroxides. Besides, TEM images (Fig. S20b and c) show iron
oxides nanoparticles are still tightly anchored on the surface of Ni-BDC layers. While it is hard to obtain the clear crystalline interplanar of Fe$_3$O$_4$ nanoparticles in the high-resolution TEM image (Fig. S20d), further suggesting the amorphous transformation of Fe$_3$O$_4$ during OER process. STEM-EDS mapping (Fig. S20e-i) demonstrates the uniform distribution of elemental Ni, Fe, O and C. Meanwhile, XPS results of Fe$_3$O$_4$/Ni-BDC-4 (Fig. S21) after long-term test indicate the partial transformation of metal units in Fe$_3$O$_4$/Ni-BDC-4 to high-oxidation state (Ni$^{3+}$, Fe$^{3+}$) due to the partial oxidation during OER process. In comparison to the pristine Fe$_3$O$_4$/Ni-BDC-4, larger satellite peaks in the XPS spectra (Fig. S21) after long-term test are observed, correlating with the oxidation of metal units in Fe$_3$O$_4$/Ni-BDC-4 during OER [27,76].

3.4 Density functional theory (DFT) calculations of OER on Ni-BDC(200) and Fe$_3$O$_4$(311)/Ni-BDC(200) surfaces

DFT calculations have been performed to uncover the nature of Ni-BDC and Fe$_3$O$_4$/Ni-BDC catalyst and reveal their different performances on the oxygen evolution electrocatalytic process. The (200) surface of Ni-BDC was studied according to the XRD data (Fig. 1a), which is exposed with five-coordinated Ni atoms (Ni$_{5c}$) and two-coordinated O atoms (O$_{2c}$) (Fig. S26). The Bader charge analysis shows that the average charge of surface Ni in the Ni-BDC(200) system is +1.345 |e| (Fig. 5e). After incorporation with Fe$_3$O$_4$, the XRD results (Fig. 1a and Fig. S1) show the gradual disappearance of the (200) main peak of Ni-BDC and emergence of (311) main peak of Fe$_3$O$_4$ in the Fe$_3$O$_4$ /Ni-BDC composites. The Fe$_3$O$_4$(311) surface, therefore, has been considered as the possible active surface to investigate in the Fe$_3$O$_4$(311)/Ni-BDC(200) system (Fig. 5b and Fig. S26b). There are five-coordinated Fe atoms (Fe$_{5c}$), two-coordinated O atoms (O$_{2c}$) and three-coordinated O atoms (O$_{3c}$) exposed on the Fe$_3$O$_4$(311) surface (Fig.
Interestingly, the average charge of surface Ni in Fe$_3$O$_4$(311)/Ni-BDC(200) is slightly reduced to +1.341 $|e|$ |e|e. The average charge of surface Fe is +1.867 $|e|$ in Fe$_3$O$_4$(311)/Ni-BDC(200), higher than that in pristine Fe$_3$O$_4$(311) for +1.522 $|e|$ (Fig. 5e). The valence states of surface Ni sites are reduced while the surface Fe sites become oxidized on the Fe$_3$O$_4$(311)/Ni-BDC(200) surface. Those agree well with our XPS characterizations that the Ni 2p peak shifts to negative and Fe 2p peak shifts to positive (Fig. 1c and d, Fig. S3 and Table S1). It is safe to conclude that the valence states change of surface Ni and Fe sites are correlated to the improved OER performance. Furthermore, relative to the density of state (DOS) of the pristine Fe$_3$O$_4$ system [77], the density of states of Fe$_3$O$_4$(311)/Ni-BDC(200) system in Fig. 5d shows the Fermi level slightly left-shifting, indicating the electron donator role of the Fe$_3$O$_4$ in the composite system. The electrostatic potential analysis (Fig. S25) illustrates that the electrostatic potential of surface Ni layer is lower than that of Fe$_3$O$_4$ slab, indicating the partial electrons transferring from Fe$_3$O$_4$ to Ni-BDC in Fe$_3$O$_4$(311)/Ni-BDC(200) system, thereby leading a higher oxidation state of surface Fe sites and a reduced oxidation state of surface Ni sites. Therefore, the interaction mechanism of Fe$_3$O$_4$ and Ni-BDC from Fe$_3$O$_4$/Ni-BDC could be proposed. The local electronic environment of Ni nodes in the Ni-BDC is changed after coupling with Fe$_3$O$_4$, partial Ni nodes may be interacted or replaced by Fe$_3$O$_4$ nanoparticles. As BDC ligands are good electron acceptors [30], it suggests that Fe sites in the Fe$_3$O$_4$/Ni-BDC composites provide more electrons with a higher oxidation state in comparison to that of the pure Fe$_3$O$_4$, ensuring the successful formation of composites. Meanwhile, Ni sites in the Fe$_3$O$_4$/Ni-BDC composites will share the extra electrons from the Fe$_3$O$_4$, thus maintaining a reduced oxidation state in comparison to that of pristine Ni-BDC. The optimal electronic structure of Ni and Fe in the Fe$_3$O$_4$/Ni-BDC composites benefits the OER catalytic performance.
Fig. 5. (a and b) The free energy profiles of OER on the pristine Ni-BDC surface and Fe\textsubscript{3}O\textsubscript{4}/Ni-BDC surface, respectively. The potential at 0 and 1.5 V were considered. The inserted graphs are the corresponding geometrical structures. The while, grey, pink, blue and red balls represent H, C, Ni, Fe and O atoms, respectively. (c and d) The projected density of states (DOSs) for Ni-BDC and Fe\textsubscript{3}O\textsubscript{4}/Ni-BDC systems. (e) The Bader charges of Fe and Ni sites in different systems. (f) The energy barriers of the OH dissociation step on the Ni-BDC surface and Fe\textsubscript{3}O\textsubscript{4}/Ni-BDC surfaces.

To further understand the difference in OER electrocatalytic activity of Fe\textsubscript{3}O\textsubscript{4}/Ni-BDC and pristine Ni-BDC systems, we adopt the electrochemistry model developed by Nøskov et al. and investigated the thermodynamics of four-electron reactive paths for OER from the free energy landscape (T=298.15 K) \cite{78,79}. the elementary steps are shown as follows, with * denoted as the catalytic active sites or adsorbed species:

\begin{align}
\ast + \text{H}_2\text{O}(l) & \rightarrow \text{OH}^\ast + \text{H}^+ + \text{e}^- \quad (3.1) \\
\text{OH}^\ast & \rightarrow \text{O}^\ast + \text{H}^+ + \text{e}^- \quad (3.2) \\
\text{O}^\ast + \text{H}_2\text{O}(l) & \rightarrow \text{OOH}^\ast + \text{H}^+ + \text{e}^- \quad (3.3)
\end{align}
Fig. 5a and b show the free energy diagrams of OER on both Ni-BDC(200) and Fe$_3$O$_4$(311)/Ni-BDC(200) surfaces. The free energy diagrams show the step (3.2) referring to the formation of adsorbed O* species is the PDS for both two systems (blue line at 0 V in Fig. 5a and b).

Specifically, the free energy change of step (3.2) is 1.39 eV at the surface F$_{5c}$ site of the Ni-BDC(200) surface. The overpotential ($\eta$) is 0.16 V. In contrast, the free energy change for that step becomes 1.22 eV on the Fe$_3$O$_4$(311)/Ni-BDC(200) surface, 0.17 eV lower than that on the Ni-BDC(200) surface. This implies that the adsorbed O* species are more stabilized at the Fe$_3$O$_4$(311)/Ni-BDC(200) surface, thus enhancing the OER performance. The energy barriers for OH dissociation were also calculated in the two systems. The dissociation barrier of adsorbed OH to generate the adsorbed O is as low as 0.13 eV on the Fe$_3$O$_4$(311)/Ni-BDC(200) surface, lower than that (0.21 eV) on the Ni-BDC(200) surface (see Fig. 5f). OH dissociation is more favourable on the Fe$_3$O$_4$(311)/Ni-BDC(200) surface, consistent with the free energy diagrams in this study. There are also four-coordinated Fe$_{4c}$ sites exposed on the Fe$_3$O$_4$(311)/Ni-BDC(200) surface and was also investigated to compare with Fe$_{5c}$ site. The step (3.1) was found to be the PDS (Fig. S27) with reaction energy of 1.67 eV. It is much higher than that at Fe$_{5c}$ site (0.96 eV) with an overpotential of 1.44 V. Thus the surface Fe$_{5c}$ site is more active towards OER on the Fe$_3$O$_4$(311)/Ni-BDC(200) surface. The Bader charge analysis shows that the adsorbed O* species on the surface Fe$_{5c}$ site possesses a charge of -0.60 |e|, while the charge of adsorbed oxygen at the surface Ni site on the pristine Ni-BDC(200) surface is -0.48 |e|. This indicates the stronger electronic interaction of Fe-O relative to that of Ni-O, stabilizing oxygen adsorption and lowering the free energy for step (3.2) in Fe$_3$O$_4$(311)/Ni-BDC(200) system. By applying a potential of 1.5 V (red lines of Fig. 5a and Fig. 5b), the free energy diagrams for both systems go down, showing the favourable thermodynamics for OER.
The step 3.2 still has a lower free energy change in the Fe$_3$O$_4$(311)/Ni-BDC(200) system than the Ni-BDC(200) system (Fig. 5b), consistent with the better OER performance observed in the experiments. These theoretical findings propose the possible structure of Fe$_3$O$_4$/Ni-BDC system and reveal the Fe$_3$O$_4$/Ni-BDC catalyst favours the step of OH dissociation into adsorbed O species that boosts the OER performance. The introduction of balanced amount of Fe$_3$O$_4$ nanoparticles in the composite effectively modulates the electronic structure that lowers the potential required for PDS, enhancing OER catalytic activity [25,73]. Besides, the 2D hierarchical-layer structure created by ultrafine Fe$_3$O$_4$ nanoparticles immobilized on 2D Ni-BDC layers provides a large surface area and promotes fast mass transport of the electrolyte to the reactive sites and the liberation of the generated oxygen gas. Meanwhile, the hierarchical composite structure could efficiently prevent the aggregation present in pure Ni-BDC layers that have poor stability (Fig. S13), maintaining the structural integrity during OER for a superior catalytic stability. The detailed XPS binding energy results (Table S1) differ from those in pristine Ni-BDC and Fe$_3$O$_4$, i.e. binding energy level of Ni 2p$_{3/2}$ decreases, while the binding energy of Fe 2p$_{3/2}$ increases slightly with the amount of Fe$_3$O$_4$ nanoparticles. This indicates that the Ni atoms in the composites possess higher electron densities than that of pristine Ni-BDC with the increasing amount of Fe$_3$O$_4$ nanoparticles. While Fe atoms in the composites have lower electron densities comparing with that of pure Fe$_3$O$_4$ and then trend to the stable electron densities. Initially, when the mass ratios of Fe$_3$O$_4$ in the composites are relatively low (Fe$_3$O$_4$/Ni-BDC-1, 2 and 3). The electronic densities of Fe and Ni atoms in the composites are tuned, offering improved OER performance. Further, Fe$_3$O$_4$/Ni-BDC-4 possesses the optimal electronic structure of Fe and Ni atoms, showing the best OER catalytic activity among five composites. When the Fe$_3$O$_4$ nanoparticles are further added to form Fe$_3$O$_4$/Ni-BDC-5, the electronic densities of Fe and Ni atoms in the composite is hardly
changed in comparison to that of Fe$_3$O$_4$/Ni-BDC-4. Reversely, the further addition of Fe$_3$O$_4$ limits the OER performance with a reduced catalytic activity. All above results ensure that Fe$_3$O$_4$/Ni-BDC-4 could be a promising and stable OER electrocatalyst.

4. Conclusion

Ultrafine Fe$_3$O$_4$ nanoparticles homogeneously immobilized on 2D Ni based MOFs (Fe$_3$O$_4$/Ni-BDC) were synthesized. The functionalized Fe$_3$O$_4$ nanoparticles (Ø 6 ± 2 nm) with abundant surface hydroxide groups are produced by a hydrothermal method, and then mixed into 2D Ni-BDC layers during synthesis (thickness: 4 ± 1 nm) creating strong interactions not achieved by physically mixing the two components. Introduction of Fe$_3$O$_4$ modifies the integral electronic structure for reduced overpotential and prevents the aggregation of 2D Ni-BDC layers for enhanced OER catalytic stability. Different atom ratios of (Ni/Fe) in Fe$_3$O$_4$/Ni-BDC are tested for OER. Fe$_3$O$_4$/Ni-BDC-4 demonstrates the optimized OER performance with a $\eta$ of 295 mV at 10 mA cm$^{-2}$, a Tafel slope of 47.8 mV dec$^{-1}$ and superior catalytic durability (40 h). DFT calculations further identify the active sites for Fe$_3$O$_4$/Ni-BDC as mainly contributed by Fe species with a higher oxidation state, and the PDS is the formation of the adsorbed O* species, which are facilitated in the Fe rich composite. The persistent stability during cycling (Fig. 3d) and the TEM images show that agglomeration is not occurring, indicating that this typically performance reducing effect can be handled. Such structure design methodologies for electronic structure and adsorbate modulation will inspire further development of promising catalysts for OER.

Supporting information
The supporting figures including XPS patterns, TEM images, EDS spectra and mapping images, electrochemical data with those reported in literatures.

Notes
The authors declare no competing financial interest.

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Graphic abstract

Ultrafine Fe$_3$O$_4$ nanoparticles are homogeneously immobilized on 2D Ni based MOFs for enhanced oxygen evolution reaction. DFT calculations confirm the potential-determining step (PDS) is the formation of the adsorbed O* species.

Highlights

- Ultrafine Fe$_3$O$_4$ nanoparticles are homogeneously immobilized on Ni based MOFs layers.
- Electronic structure modulation and morphology changes in the composite are examined.
- The optimized composite achieves an overpotential of 295 mV at 10 mA cm$^{-2}$ for OER.
- Valance state of metal species in the composite affects OER performance.
- DFT calculations help to understand the working mechanism of the OER catalyst.