Pyridine-modulated Ni/Co bimetallic metal-organic framework nanoplates for electrocatalytic oxygen evolution

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ABSTRACT Two-dimensional (2D) metal-organic frameworks (MOFs) are promising for electrocatalysis with high performance, as they possess large surface areas and high densities of exposed active sites. It attracts tremendous attention to obtain 2D nanostructures *via* simple preparation methods. Herein, a facile pyridine-modulated solvothermal synthesis of Ni/Co bimetallic MOF nanoplates (Ni_xCo_y-bpy (PyM)) is reported with well-defined 2D morphology with a thickness as thin as 20 nm and an aspect ratio larger than 50. These nanoplates possess oxygen evolution reaction activity as electrocatalysts in alkaline conditions. Specifically, Ni_{0.5}Co_{1.5}-bpy(PyM) exhibits excellent OER electrocatalytic activity with a low overpotential of 256 mV at 10 mA cm⁻² and a small Tafel slope of 81.8 mV dec⁻¹ in 1.0 mol L⁻¹ KOH with long-term electrochemical stability for 3000 cyclic voltammetry cycles. The high catalytic activity of Ni_{0.5}Co_{1.5}-bpy(PyM) can be attributed to the *in situ* formed active hydroxide and oxyhydroxide species within the inherited 2D morphology and the optimized bimetallic ratio.

Keywords: metal-organic framework, bimetallic MOF nanoplate, electrocatalysis, oxygen evolution reaction

INTRODUCTION

Metal-organic frameworks (MOFs) are a class of crystalline and porous materials of various dimensionalities built from metal cations and organic ligands [1]. MOFs possess large surface areas, high porosities, and multiple functionalities, which render them ideal candidates for catalysis, gas storage and separation, and drug delivery [2–5]. Besides the conventional three-dimensional (3D) MOFs, the conversion of traditional bulk MOFs into 2D

nanostructures with a vertical dimension of less than 100 nm has attracted tremendous attentions [6,7]. The 2D nanostructures are characterized by faster mass transport, lower diffusion barrier, and more exposed active sites, which allow the molecules or ions to directly access the active sites [8,9]. These features render them promising candidates to improve catalytic performance [10–14].

The syntheses of 2D MOF nanostructures can be realized by top-down or bottom-up methods [15]. The former refers to the exfoliation of MOFs into layered structures [16–19], while the later involves the direct synthesis from metal ions and organic ligands, such as interfacial synthesis, surfactant-assisted synthesis, and modulated synthesis [20,21]. Of the above, the modulated synthesis refers to the introduction of modulator molecules into the reaction mixture [22]. These modulator molecules possess similar functional groups in the organic linkers, and coordinate with the metal or metal clusters, thus regulating the growth kinetics of MOFs. Appropriate coordination of these molecules on certain crystal planes could inhibit the growth of MOFs, resulting in the anisotropic MOF growth. Direct modulator introduction is an effective and facile way to control the morphologies of MOFs with features of nanocubes, nanorods and nanosheets [23,24].

Electrochemical splitting of water has been considered as a promising strategy for obtaining clean and sustainable hydrogen energy source [25–27]. The oxygen evolution reaction (OER) is the critical half-cell reaction of water splitting and a rate-limiting step, which requires a high overpotential and suffers from sluggish kinetics because of the high energy barrier for the breaking-up of

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O–H bond and the formation of O–O bond [28]. Therefore, to effectively couple multiple protons and electron transfers for oxygen evolution at a low overpotential, efficient electrocatalysts are desired [29,30]. Although iridium (Ir) and ruthenium (Ru) oxides show efficient electrocatalytic activity, their scarcity and high cost hinder extensive industrial applications [31]. Recently, significant efforts have been devoted to developing OER electrocatalysts that possess fast reaction rate, small overpotential and stability [32–36].

MOFs offer a great potential as OER electrocatalysts because of their tunable surface atomic structures and coordinatively unsaturated metal sites with high catalytic activity [32]. In addition, the open channels and accessible pores could facilitate the diffusion of electrolytes and the evolution/transport of O₂. The 2D MOFs could act as effective catalysts for OER electrocatalysis, because their nanometer thicknesses facilitate rapid mass and electron transport and the 2D structure provides a high percentage of exposed catalytic active surfaces [29,37]. Zhao *et al.* [18] reported Ni/Co bimetallic MOF nanosheets (NiCo-UMOFNs) with a uniform thickness of approximately 3.1 nm through exfoliation. The NiCo-UMOFNs exhibited high OER electrocatalytic activity with an overpotential of 250 mV when loaded on glassy-carbon electrodes, and 189 mV when loaded on copper foam at 10 mA cm⁻² in alkaline conditions. Duan *et al.* [37] reported a strategy for the *in situ* growth of ultrathin nanosheet arrays of 2D MOFs on various supports *via* chemical bath deposition. In this way, a Ni/Fe MOF array was fabricated which demonstrated OER electrocatalytic activity with an overpotential of 240 mV at 10 mA cm⁻² in alkaline conditions. Many studies have been carried out on the design of 2D MOFs for OER catalysis [17,38,39].

In this study, we reported on a one-pot facile synthesis of Ni/Co bimetallic MOF nanoplates (Ni_xCo_y-bpy(PyM)) with a well-defined 2D morphology, which could be adopted directly as efficient OER electrocatalysts in alkaline conditions. With pyridine as the growth inhibitor in solvothermal method, the MOFs were obtained in the form of 2D rectangular nanoplates with a thickness of less than 20 nm and aspect ratio larger than 50. Among the Ni_xCo_y-bpy(PyM) MOF nanoplates, the Ni_{0.5}Co_{1.5}-bpy(PyM) displayed the best OER electrocatalytic activity with a low overpotential of 256 mV at 10 mA cm⁻² and a small Tafel slope of 81.8 mV dec⁻¹ in 1.0 mol L⁻¹ KOH solution. In addition, the Ni_{0.5}Co_{1.5}-bpy(PyM) exhibited long-term electrochemical stability for 3000 CV cycles. The *in situ* formed active species during the OER elec-

trocatalysis were also investigated in this study to explore the origin of the high OER activity. The *in situ* formed metal hydroxide and oxyhydroxide as well as its inherited 2D nanoplate morphology and optimized bimetallic ratio could provide an improved platform to deliver outstanding OER catalytic activity.

EXPERIMENTAL SECTION

Preparation of 2D MOF nanoplates

In a 50-mL Teflon-lined stainless autoclave, 4,4'-bipyridine (2 mmol, 0.31 g) and NiSO₄·6H₂O/CoSO₄·7H₂O were dissolved in 15 mL of water. After 10 min of stirring, pyridine (18.6 mmol, 1.5 g) and 8 mL of EtOH was added dropwise into the former solution under stirring. The solution was kept stirring for another 10 min. The autoclave was then sealed and heated at 100°C for 24 h. After natural cooling to the room temperature, solid products were collected by centrifugation. Then the products were washed with ethanol (10 mL×3) and water (10 mL×3) and dried at room temperature under vacuum.

Similarly, for the syntheses of other groups of nanoplates, the mixtures were heated at 100°C for 12/36 h, or at 80/120°C for 24 h. The detailed molar quantities of each reactants are shown in Supplementary information.

Fabrication of working electrodes

To fabricate the working electrodes, the as-synthesized MOFs (3 mg), and Nafion solution (5 wt%, 25 μL) were mixed with 250 μL of water and 250 μL of ethanol, followed by ultrasonication for 1 h. The dispersion (5 μL) was deposited on the surface of a glassy carbon electrode (GCE) with a loading density of 0.40 mg cm⁻² and dried at room temperature.

Electrochemical measurement

The electrochemical water oxidation was carried out on an electrochemical working station (CHI 760E, Shanghai Chenhua). A conventional three-electrode system was implemented for all the electrochemical measurements by utilizing a GCE (diameter: 3.0 mm) as the working electrode, a graphite rod as the counter electrode, and a Hg/HgO electrode as the reference electrode in nitrogen-bubbled 1.0 mol L⁻¹ KOH electrolyte. According to the Nernst equation ($E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059\text{pH} + 0.098$), the current density was normalized to the geometrical surface area and the measured potential *vs.* Hg/HgO was converted to a reversible hydrogen electrode (RHE). Cyclic voltammograms (CVs) were obtained at a scan rate of 50 mV s⁻¹ and CV data were collected until stabilization

after several times of scanning. The linear sweep voltammograms (LSVs) were obtained with a scan rate of 5 mV s^{-1} . The working electrodes were scanned several times until the signals were stabilized and then LSV data were collected. The electrochemical impedance spectroscopy (EIS) measurements were conducted in the frequency range of 100 kHz to 0.01 Hz at 1.53 V.

Determination of double-layer capacitance (C_{dl})

The C_{dl} was determined by measuring CVs with multiple scan rates in non-Faradaic potential region. In this potential region, all measured currents were assumed to be associated with the double-layer charging. The potential range typically centered at the non-Faradaic region with a potential window of 0.1 V. In this study, CVs were measured in a potential range of 1.02–1.22 V vs. RHE at different scan rates.

RESULTS AND DISCUSSION

Preparation and characterization of MOF nanoplates

The 2D MOF nanoplates were synthesized *via* one-pot solvothermal reaction as shown in Scheme 1. Firstly, 4,4'-bipyridine, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (with Ni/Co molar ratio 1:3) were mixed and dissolved in water. Next,

pyridine and EtOH were added dropwise into the solution. Then, the mixture was heated at 100°C for 24 h to obtain the target nanoplate $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$. The synthesis procedure and molar concentrations are explained in detail in the Experimental Section.

The scanning electron microscopy (SEM) images reveal the $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ with a well-defined nanoplate morphology, relatively uniform scale and smooth surface (Fig. 1a). The lateral dimension of the rectangles ranges from hundreds of nanometers to approximately $1 \mu\text{m}$. Transmission electron microscopy (TEM) image also demonstrates the nanoplate feature (Fig. 1b). The thickness of the $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ nanoplates was measured to be about 20 nm by an atomic force microscope (AFM) (Fig. 1c), indicating an aspect ratio as large as 50. Pyridine was utilized for inhibiting the growth in the vertical direction to obtain the 2D morphology. As depicted in Scheme 1, 4,4'-bipyridine is a rod-like bidentate ligand that can link metals and help the growth of MOF in all dimensions. Pyridine is just half of the 4,4'-bipyridine and a monodentate ligand. Thus, it coordinates with metal atoms and plays the role of an inhibitor for layer stacking. $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ nanoplates grow faster in the lateral direction, which results in a lamellar morphology. In this study, to demonstrate the modulation effect of pyridine,

Scheme 1 Schematic illustration of the Ni/Co MOF nanoplates $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ and cuboid MOF bulks $\text{Ni}_x\text{Co}_y\text{-bpy}$ for the oxygen evolution reaction.

Figure 1 Morphological and structural characterizations of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$. (a) SEM and (b) TEM images of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$. (c) AFM image of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$, inset: measured thickness of individual nanoplate. (d) HRTEM image of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$. (e) High-angle annular dark-field scanning transmission electron microscopy image of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ and corresponding EDX elemental mapping images of (f) Ni, (g) Co, (h) C, (i) N, (j) O and (k) S in $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$.

Ni/Co MOFs were synthesized without the addition of pyridine as well, to produce micron-scale cuboid MOF bulks Ni-bpy and Co-bpy. The Ni-bpy bulks had lengths ranging from 20 to 60 μm , whereas the Co-bpy bulks had lengths ranging from 50 to 500 μm as investigated by SEM (Fig. S1). The clear difference between the nanoplates and the micron-scale cuboid bulks demonstrates the successful modification in the morphology and scale *via* a simple procedure.

To illustrate the inner structure of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$, high-resolution TEM (HRTEM, Fig. 1d) characterization and energy dispersive X-ray (EDX) spectroscopy analyses were carried out. The lattice fringes of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ could not be observed in the HRTEM image as the MOF structures tended to be destroyed by the high-energy electron beam irradiation [40]. The EDX spectra demonstrate the presence of Ni, Co, C, N, S and O in the $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ MOF (Fig. S2a). The S and O may originate from the counter sulfate ion. The EDX elemental mapping further proves the existence and

homogeneous distribution of these elements (Fig. 1e–k). According to the N_2 adsorption-desorption isotherms, the $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ exhibits a high Brunauer-Emmett-Teller (BET) surface area of $851.5 \text{ m}^2 \text{ g}^{-1}$ which could be ascribed to the unique 2D structure (Fig. S2b, c).

To investigate the electrocatalytic activity of the $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ nanoplates, as well as the function of the bi-metallic ions, the stoichiometric ratio of nickel and cobalt was varied to obtain other four groups of $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ (Fig. S3). The total dosages of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ were fixed as 2.0 mmol with Ni:Co molar ratios of 1:0, 3:1, 1:1, and 0:1. The reaction conditions remained the same as that of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ and the products were denoted as Ni-bpy(PyM), $\text{Ni}_{1.5}\text{Co}_{0.5}\text{-bpy(PyM)}$, $\text{Ni}_1\text{Co}_1\text{-bpy(PyM)}$, Co-bpy(PyM), respectively. Similar to $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$, the four products also reveal nanoplate morphologies as shown in SEM and TEM images (Figs 2a1–d1, a2–d2). When nickel was predominant in the MOF (i.e., in Ni-bpy(PyM)), the corners of the nanoplates became sharper. The rectan-

Figure 2 Morphological characterizations of $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$. (a1–d1) SEM, (a2–d2) TEM and (a3–d3) AFM images of (a) Ni-bpy(PyM), (b) $\text{Ni}_{1.5}\text{Co}_{0.5}\text{-bpy(PyM)}$, (c) $\text{Ni}_1\text{Co}_1\text{-bpy(PyM)}$, and (d) Co-bpy(PyM) nanoplates. The measured thicknesses of the nanoplates are marked in (a3–d3).

gular surfaces of the nanoplates became arc-shaped on the two opposite sides as the proportion of cobalt ions increased in the MOFs. The thicknesses of the MOF nanoplates were also calculated to be ranging from 28.5 to 43.4 nm *via* AFM (Fig. 2a3–d3). The UV-vis absorption spectra of $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ were converted from optical diffuse reflectance spectra by using the Kubelka–Munk function (Fig. S4a). With the Co(II) content increasing, the absorption band in the red region decreased, while the absorption band in the blue-green region increased. As a result, the color of the MOF powder changed from light green to brown (Fig. S3 upper row). Tauc plots were drawn from the absorption spectra and the optical band gaps were determined. The band gap of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ was estimated to be 2.73 eV, which was narrower than those of the other four nanoplates, as well as those of several semi-conductor materials (Fig. S4b) [41]. The narrow band gap could improve its catalytic performance significantly. The $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ nanoplates remained well-dispersed in ethanol solution and exhibited Tyndall effect due to the scattering of light of the nanoplates in the colloidal suspensions (Fig. S3 bottom row) [42].

The solvothermal reaction conditions of the Ni/Co bi-

metallic MOFs were optimized by tuning the reaction temperature and time. With variations of solvothermal temperature (80 and 120°C), the as-synthesized nanoplates showed nonuniform distribution in the lateral direction unlike the ones synthesized under 100°C (Fig. S5). In the other group, the samples were synthesized under 100°C with different reaction times. An insufficient time (12 h) resulted in irregular shaped products with similar thicknesses. The nanoplates were of uniform size with sufficient heating (36 h); however, the thickness of the samples could not be controlled (Fig. S6). Therefore, $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ showed the most uniform lateral size and thickness with the solvothermal synthesis carried out under 100°C for 24 h.

The X-ray diffraction (XRD) patterns of the $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ nanoplates and the Ni-bpy and Co-bpy bulks were analyzed (Fig. 3a). The XRD patterns of Ni-bpy and Co-bpy displayed very good crystallinity and were in close agreement with previously reported Co MOFs ($[\text{Co}_3(4,4'\text{-bpy})_2(\text{SO}_4)_3(\text{H}_2\text{O})_{11}]_n$, No. 826371, space group of *P*-1, Cambridge Crystallographic Data Centre) [43]. The MOF structure contained three crystallographically unique M (II) centers which were all in six-coordinated environ-

Figure 3 The XRD patterns and crystal structures of the MOFs. (a) Powder XRD patterns of the Ni/Co MOFs. (b, c) Structural schematic graphs of Co-bpy $[\text{Co}_3(4,4'\text{-bpy})_2(\text{SO}_4)_3(\text{H}_2\text{O})_{11}]_n$. (b) Crystal stacking along a axis. The coordination of cobalt: octahedrally coordinated in three patterns. (c) Crystal stacking along c axis.

ments (Fig. 3b). One M(II) center was coordinated with two 4,4'-bipyridine (4,4'-bpy) ligands, one sulfate ion and three H_2O molecules (blue octahedron). The second M(II) center was coordinated with two 4,4'-bpy ligands and four O atoms from two monodentate sulfate ions and two H_2O ligands (red octahedron). The third M(II) center formed a hexaqua metal (II) ion (green octahedron). There were two different 1D chains (marked red and blue in Fig. 3b) which were arranged in a cross-like pattern around the mid-point of the 4,4'-bpy ligands. The O-H...O hydrogen-bond between the H_2O molecules and the sulfate anions resulted in a 3D supramolecular network (Fig. 3c) [43]. The fraction peaks (at 6.7° , 9.7° , and 13.3°) of Ni-bpy(PyM) and Co-bpy(PyM) were distinctly different from that of the samples without pyridine. In those two cases, the addition of pyridine inhibited the growth of the framework and induced the formation of a new phase and coordination structure. For the pyridine-participated bimetallic MOF samples, the diffraction peaks at 16.6° (020), 16.8° (002), 17.7° (112), 18.2° (102), 23.6° (102), and 25.5° (200) agreed well with those of the Ni-bpy and Co-bpy MOFs, while the diffraction peaks at 6.7° , 9.7° , and 13.3° agreed with those obtained with the single metallic Ni-bpy(PyM) and Co-bpy(PyM) MOF nanoplates (Fig. 3a). These results reveal that the bimetallic MOF is a mixture of the MOF structures both with and without the addition of pyridine.

The structures of the as-synthesized $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ nanoplates were further studied by Fourier transform infrared (FT-IR) spectroscopy (Fig. S7). Similar absorption bands could be found in the IR spectra of the seven samples. The results demonstrated that the $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ nanoplates retained the same functional groups after addition of pyridine. The strong absorbed peaks at 1610, 1537, 1490 and 1413 cm^{-1} demonstrated that there was a pyridine skeleton vibration in the MOF (Fig. S7 red

area). The absorption peaks at 1110 and 632 cm^{-1} confirmed the presence of the coordinated SO_4^{2-} ions (Fig. S7 blue area).

X-ray photoelectron spectra (XPS) were utilized to investigate the composition and chemical structure of the $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ samples (Fig. 4a and Fig. S8). Taking $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ as an example, the survey spectrum of this sample demonstrated the presence of Co, Ni, C, N, S and O (Fig. S8d). The characteristic peaks of Co 2p at 797.4 and 781.5 eV in the high-resolution XPS spectrum corresponded to the Co^{2+} $2p_{1/2}$ and $2p_{3/2}$ energy levels, respectively (Fig. 4a). Furthermore, in the high-resolution Ni 2p spectra of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$, two peaks located at 856.1 and 873.7 eV could be assigned to Ni^{2+} $2p_{3/2}$ and $2p_{1/2}$, respectively (Fig. 4b) [20,44]. The N 1s spectrum could be deconvoluted into two peaks centered at 399.7 and 401.3 eV, which could be assigned to pyrrolic N and pyridinic N, respectively (Fig. 4c) [17]. In the high-resolution XPS spectrum of C 1s, the peaks at 285.2 and 286.0 eV corresponded to C-N and C-C from the pyridine or 4,4'-bipyridine ligands (Fig. 4d) [45]. Ni 2p and Co 2p XPS spectra revealed the Ni/Co ratios on the surface of the nanoplates, which were 2.16 for $\text{Ni}_{1.5}\text{Co}_{0.5}\text{-bpy(PyM)}$, 0.94 for $\text{Ni}_1\text{Co}_1\text{-bpy(PyM)}$, and 0.37 for $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ (Fig. S9). Meanwhile, the Ni/Co atomic ratios in the bimetallic MOFs were determined to be 2.32, 1.01 and 0.40 individually, according to the inductively coupled plasma optical emission spectrometry (ICP-OES) analysis. The results were close to the dosage ratios of Ni^{2+} and Co^{2+} utilized in the synthesis, which demonstrated the efficient regulation and modification of the solvothermal synthesis.

Electrocatalytic performance of MOF nanoplates

The electrochemical performances of the $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ samples were measured with a typical three-elec-

Figure 4 XPS of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$. High-resolution (a) Co 2p, (b) Ni 2p, (c) N 1s, and (d) C 1s spectra.

trode system in a 1.0 mol L^{-1} KOH solution. LSV was utilized to obtain the polarization curves (Fig. 5a). Among the $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ MOFs, $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ displayed the highest current density at the same potential. To obtain a current density of 10 mA cm^{-2} , the $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ nanoplates needed an overpotential of 256 mV, which was the lowest among all the overpotentials for the $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ MOFs. The results established that $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ had the best OER performances with a pristine MOF as a catalyst (Table S2). The OER polarization curves of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ after iR correction revealed negligible changes compared with those before iR correction (Fig. S10). The OER electrocatalytic kinetics of all the $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ MOFs were obtained from the corresponding Tafel plots (Fig. 5b). The lower Tafel slope represented a faster enhancement of the OER catalysis with the potential increasing [46]. The Tafel slope of Co-bpy(PyM) (69.1 mV dec^{-1}) was the smallest among those of the $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ MOFs, while the Tafel slope of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ was the smallest among those of the three bimetallic-bpy(PyM) MOF samples (81.8 mV dec^{-1}). Thus, both types of nanoplates displayed favorable electrocatalytic kinetics for OER.

EIS was performed at a potential of 1.53 V to further explain the catalytic kinetics of $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ nano-

plates (Fig. S11). The Nyquist plots revealed that the single metallic-bpy(PyM) MOFs, namely Ni-bpy(PyM) and Co-bpy(PyM) had the largest and the smallest semicircular diameters, respectively in the high frequency region among the $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ nanoplates. The charge transfer resistance (R_{ct}) was calculated to be 57.13 and 8.47Ω for Ni-bpy(PyM) and Co-bpy(PyM), respectively. $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ displayed the smallest R_{ct} at 12.95Ω among the bimetallic-bpy(PyM) MOFs, suggesting the fastest charge transfer process between the electrolyte and the catalyst [47]. Meanwhile, $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ displayed a larger slope than the other bimetallic MOF nanoplates in the low frequency region, indicating a favorable diffusion rate for the ions and O_2 [33]. The electrochemical active surface area (ECSA) of the catalyst plays a vital role in the OER catalysis and the C_{dl} is proportional to the ECSA [46]. The C_{dl} of $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ nanoplates was measured by CV with various scan rates under the non-Faradaic potential 1.02–1.22 V (vs. RHE) without the redox processes. Similar to the results of the Tafel slope, the Co-bpy(PyM) MOFs showed a higher C_{dl} (10.63 mF cm^{-2}) as depicted in Fig. 5c (calculated from the corresponding CVs in Fig. S12). $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ possessed the largest C_{dl} (6.69 mF cm^{-2}) among the bimetallic-bpy(PyM) MOFs,

Figure 5 OER performance of $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$. (a) OER polarization curves of $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ in 1.0 mol L⁻¹ KOH at scan rate of 5 mV s⁻¹. (b) OER Tafel plots obtained from the OER polarization curves in (a). (c) Plots of the capacitive currents as a function of scan rate of $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$. (d) OER polarization curves of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ before and after 3000 CV cycles.

indicating the greatest roughness of the electrode and the most active sites. The results suggest that the contribution of Co in the MOFs to the active surface area is crucial in promoting the OER catalytic performance.

The OER electrocatalytic performance of the cuboid MOF bulks Ni-bpy and Co-bpy were also investigated (Figs S13–S16) and summarized (Table S3). The comparison of Co-bpy(PyM) and Co-bpy revealed the significant positive effect of pyridine addition on the OER electrocatalysis. The Co-bpy(PyM) nanoplates possessed lower overpotential (136 mV), better kinetics (22.3 mV dec⁻¹ lower in Tafel slope), better conductivity (9.37 less in R_{ct}) as well as larger ECSA (3.29 mF cm⁻² larger in C_{dl}). It could be attributed to the pyridine modulation on the morphology, structure and phase. It was noteworthy that the contrast between OER performances of Ni-bpy(PyM) and Ni-bpy was not accordant with the Co MOFs. The Ni-bpy nanoplates displayed lower overpotential and smaller Tafel slope than Ni-bpy(PyM) , suggesting the greater contribution of structure and phase than morphology on the electrocatalysis in this case. The single metallic Co MOFs (both Co-bpy(PyM)

and Co-bpy) in this study were confirmed with better OER catalytic activity than the corresponding Ni MOFs. Meanwhile, Co-bpy(PyM) showed the best kinetics and conductivity (favorable for oxidation reaction), and the highest surface roughness (active for catalytic reaction), even though its overpotential was still higher than that of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$. The phenomenon could be attributed to the contribution from the bimetal Ni/Co ions in the MOFs. 1) The bimetallic MOF $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ show mixed structures with the single metallic MOF Ni-bpy(PyM) and Co-bpy(PyM) and a 3D supramolecular network according to the XRD pattern (Fig. 3a). The unique structure might greatly contribute to the ion flux and conductivity. 2) The high specific surface area (851.5 m² g⁻¹), low thickness (favorable for electron transport) and narrow band gap of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ also contributed significantly to the electrocatalytic reaction. 3) It was reported previously that Ni was more beneficial than Co for the desorption of OH⁻ in alkaline solutions and that Co had a higher activity for the Tafel steps than Ni [34,48]. Therefore, for the $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$, the Ni sites could accelerate water dissociation

efficiently and the Co sites would be beneficial for gas generation and release [49]. By controlling the Ni/Co ratio in the MOFs, stronger synergistic interaction between the bimetallic centers could be achieved for promoting OER performance. This synergistic effect of Ni and Co in $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ results in the best catalyst performance among the $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ nanoplates.

The long-term durability of the $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ catalyst was also explored. Continuous CV scanning in the range of 1.13–1.73 V (vs. RHE) was conducted with a scan rate of 100 mV s^{-1} . LSV curves were compared at a scan rate of 5 mV s^{-1} to assess the durability before and after the continuous scan. The current density remained almost identical after 3000 CV cycles ignoring minor variations, confirming its fine cycling stability (Fig. S5d). In addition, the current-time (*i-t*) curve of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ showed slight current oscillations after 8 h of testing, which also indicated its excellent stability (Fig. S17). Over all, the excellent OER performance of the $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ electrode displayed more potential applications compared with other MOF catalysts (Table S2).

Investigation on the origination of high OER activity

The morphological, structural and chemical variations were then investigated through the post-CV $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$

bpy(PyM) to understand the origins of the OER activity. The $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ MOF nanoplates deposited on a GCE were characterized by SEM before and after 1000 CV cycles (Fig. S18). The electrode samples were also collected and observed under TEM after 1000 CV cycles (Fig. 6a). The morphology of the MOFs was maintained, with smaller lateral sizes and thicknesses. These changes resulted in larger surface areas and more active sites. The *ex-situ* Raman spectra could further provide evidence of the structural variations (Fig. S19). The typical vibrational peaks of the organic ligands in the $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ nanoplate at 1028, 1293, 1614 cm^{-1} , and other minor peaks disappeared after the OER catalysis. It was accompanied with the appearance of two broad and weak bands located at approximately 495 and 625 cm^{-1} respectively, which could be attributed to the formation of CoO(OH) [50]. To further study the chemical state and composition of the $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ after the CV cycles, HRTEM and XPS spectra of the $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ were conducted. The HRTEM image revealed clear lattice fringes with interplanar distances of about 2.47, 1.64, 1.24 and 2.77 Å, corresponding to (100), (104), (200) planes of CoO(OH) phase (JCPDS No. 26-1107) and (100) planes of Co(OH)_2 (JCPDS No. 45-0031) (Fig. 6b). The selective area electron diffraction (SAED) pattern displayed several bright rings with discrete spots.

Figure 6 Post-CV structural characterization of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$. (a) TEM, (b) HRTEM images and (c) SAED pattern of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ after 1000 CV cycles. (d–f) High-resolution XPS spectra of (d) Ni 2p, (e) Co 2p and (f) O 1s of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ before (bottom) and after (upper) 1000 CV cycles.

They could be indexed to the (001)/(100)/(110) planes of $\text{Co}(\text{OH})_2$, (100)/(200) planes of $\text{CoO}(\text{OH})$, and (101) plane of $\text{NiO}(\text{OH})$ (JCPDS No. 27-0956) (Fig. 6c). The EDX spectra and the elemental mapping results confirmed the uniform distribution and considerable existence of Ni, Co and O, suggestive of their retention, in spite of the structural variation during the OER test (Figs S20, S21). Moreover, the XPS spectra of the $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ were investigated to analyze the changes of the chemical states. The survey spectrum agreed with the elemental mapping result which revealed the existence of Ni, Co and O elements (Fig. S22). The electronic structures of Ni and Co were investigated through high-resolution spectra. The Ni 2p spectra reflected that the peaks shifted to a lower binding energy (BE) after 1000 cycles compared with those of the pristine $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ nanoplate (Ni^{2+} 2p_{3/2} from 856.1 to 854.8 eV; Ni^{2+} 2p_{1/2} from 873.7 to 872.4 eV) (Fig. 6d). This can be ascribed to the destruction of the Ni–N coordination bond and the direct connection between the Ni and O atoms. This phenomenon increased the local electron density and resulted in a lower BE of Ni 2p in $\text{Ni}(\text{OH})_2$ [51]. In addition, two new peaks at 874.6 and 855.8 eV were observed after 1000 CV cycles, which were derived from Ni^{3+} in the electrochemically formed $\text{NiO}(\text{OH})$. Similarly in the Co 2p high-resolution spectra, the down-shifted Co^{2+} 2p peaks (Co^{2+} 2p_{1/2} from 797.2 to 794.7 eV; Co^{2+} 2p_{3/2} from 781.4 to 779.3 eV) and the emergence of two new Co^{3+} peaks (796.5 and 780.9 eV) demonstrated the possible structural variation from the pristine $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ to $\text{Co}(\text{OH})_2$ and $\text{CoO}(\text{OH})$ (Fig. 6e) [52]. The high-resolution O 1s spectra revealed that the dominant peaks originated from H_2O (532.7 eV) and M–O (531.6 eV) distinctly shifted to 534.2, 532.8, and 531.0 eV from O–H, H_2O , and M–O–M groups, respectively, thus confirming the formation of oxyhydroxide during the electrocatalysis [35].

Therefore, the enhanced catalytic activity of $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ could be attributed to the formation of active hydroxide and oxyhydroxide species evolved from the pristine MOF. Firstly, the inherited 2D nanoplate morphology with short transport paths, more specific surface area, and exposed potential active sites contribute significantly to the ion and molecular flux. In addition, the metal hydroxide and oxyhydroxide possess better electrical conductivity than the pristine $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$, thus, accelerating the electron transport. Moreover, the Ni/Co bimetallic synergistic interplay with an appropriate molar ratio optimizes the electronic structure and promotes the electrocatalytic process. As a result of these

advantages, the bimetallic MOF nanoplates $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ show advanced OER catalytic activity.

CONCLUSIONS

In conclusion, the Ni/Co bimetallic MOF nanoplates $\text{Ni}_x\text{Co}_y\text{-bpy(PyM)}$ with well-defined 2D morphology were obtained through a one-pot facile solvothermal synthesis and can be adopted directly as efficient electrocatalysts. With pyridine as the growth modulator, all the MOFs were obtained as rectangular 2D nanoplates. Among the MOF nanoplates, $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ exhibited the best OER electrocatalytic activity with a low overpotential of 256 mV at 10 mA cm^{-2} and a small Tafel slope of 81.8 mV dec^{-1} under alkaline conditions. The electrocatalyst also exhibited long-term electrochemical stability for 3000 CV cycles. Moreover, the combined results indicated that the *in situ* formed active hydroxide and oxyhydroxide species from the pristine $\text{Ni}_{0.5}\text{Co}_{1.5}\text{-bpy(PyM)}$ nanoplates with inherited 2D nanoplate morphology and optimized bimetallic ratio could provide an improved platform to deliver outstanding OER catalytic activity. It is expected that this work would contribute to the further exploration of unique MOF nanostructures to achieve advanced electrocatalysis performance.

Received 15 February 2020; accepted 9 April 2020;

published online 5 June 2020

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Acknowledgements This work was supported by the National Natural Science Foundation of China (U1904215, 21671170 and 21875207), the Top-notch Academic Programs Project of Jiangsu Higher Education Institutions (TAPP), the Program for New Century Excellent Talents of the University in China (NCET-13-0645), the Six Talent Plan (2015-XCL-030) and Qinglan Project. We also acknowledge the Priority Academic Program Development of Jiangsu Higher Education Institutions and the technical support we received from the Testing Center of Yangzhou University. We also acknowledge the support from the postdoctoral fund of Yangzhou University.

Author contributions Pang H designed this study and supervised the experimental work. Bai Y performed the synthesis and characterizations. Zhang G, Zheng S and Li Q performed the characterizations; Bai Y wrote the paper with support from Pang H and Xu Q. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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吡啶调节2D双金属有机框架及其电催化析氧性能研究

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摘要 二维金属有机骨架(2D MOF)具有较大的比表面积和较高的活性位点密度, 是改善电催化性能的理想载体. 通过简单的制备方法获得2D纳米结构受到了广泛的关注. 本文提出了一种吡啶调节溶剂热合成方法, 用于合成镍/钴双金属MOF纳米片. 得到的MOF材料具有矩形2D形貌, 厚度约20纳米. 这些纳米片作为电催化剂在碱性条件下表现出析氧反应(OER)活性. 其中, Ni_{0.5}Co_{1.5}-bpy(PyM)在1.0 mol L⁻¹ KOH溶液中、电流密度10 mA cm⁻²时过电位低至256 mV, Tafel斜率为81.8 mV dec⁻¹, 且具有良好的电化学稳定性. 对催化反应后的电极材料研究表明, Ni_{0.5}Co_{1.5}-bpy(PyM)的高催化活性来源于原位形成的活性氢氧化物和羟基氧化物. 该研究为2D MOF材料的可控合成及其与电催化性能构效关系的研究提供了理论基础.