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# Leveraging ligand push-pull effects in Ni-based MOFs for optimized lattice oxygen activation and superior water oxidation

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# ABSTRACT

Understanding the oxygen evolution reaction (OER) mechanism is critical for the rational design of highperformance OER electrocatalysts. Theoretically, the lattice oxygen oxidation mechanism (LOM) bypassing the inherent limitations of the traditional adsorbate evolution mechanism through direct interactions between lattice oxygen and oxygen intermediates, thereby lowering the energy barrier of alkaline OER. However, effective lattice oxygen activation remains a significant challenge. Herein, a Ni-based metal-organic framework, Ni  $N_xF_{10}$ .  $x_v$  was employed as a model system to precisely regulate the local microenvironment around the Ni active site via the push-pull effect of organic ligand side groups, thus achieving an efficient LOM pathway. Experimental results demonstrated that this electronic push-pull effect induced lattice strain and morphology variations in Ni  $N_xF_{10-x0}$ , driven to generate more unsaturated metal sites. The optimized Ni  $N_3F_7/CP$  exhibited excellent OER activity, achieving a low overpotential of 213 mV at 10 mA cm<sup>-2</sup> and long-term stability in 1.0 M KOH. In-situ electrochemical impedance spectroscopy, in-situ Raman, DEMS and density functional theory calculations combined to illustrate that this ligand functionalization significantly benefited the LOM pathway and OER performance by optimizing intermediate adsorption. This work provides a new perspective for developing advanced OER catalysts.

#### 1. Introduction

Oxygen evolution reaction (OER) is a fundamental process in water splitting for hydrogen and various other electrocatalytic scenarios to sustainable fuel, pivotal to supplying clean and low carbon energy [1–3]. However, its complex and kinetically sluggish multi-electron transfer process demands a high overpotential, creating a significant bottleneck that limits the overall efficiency of these electrochemical systems [4,5]. Consequently, developing high-performance and stable electrocatalysts to accelerate the OER process is essential.

A deep understanding of the oxygen species cycling mechanism during OER is critical for the rational design of catalysts with high intrinsic activity. In general, the most widely accepted mechanism for alkaline OER is the adsorbate evolution mechanism (AEM), which involves multiple oxygen intermediates including HO\* (M-OH), O\* (M-O), and HOO\* (M-OOH) [6]. Based on the Sabatier's principle and the linear relationship between the binding energies of the oxygenated intermediates, the theoretical minimum overpotential of the catalyst obeying AEM is limited to 0.37 V [7,8]. Recently, researchers have noticed that the overpotential of oxides/(oxy)hydroxides originating from pre-catalysts under structural reconstruction can surpass, leading to the proposal of the lattice oxygen mechanism (LOM) to explain this phenomenon [9]. LOM enables direct O-O coupling to produce  $O_2$ , breaking the linear relationship of AEM and offering significant potential for more efficient OER [5,10,11].

Metal organic frameworks (MOFs), a class of coordination polymer consisting of organic ligands and metal ions, have shown great promise in electrocatalysis due to their high porosity, easy functional modifications, and tunable structure [12,13]. Despite these advantages, pristine MOFs often face challenges such as poor stability, limited electrical conductivity, and a scarcity of exposed active sites, necessitating modifications to enhance their utility [14,15]. Typically, optimizing efforts have largely focused on modulating the microenvironment of their coordination centers, and to date numerous classical and universal

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strategies have been proposed up. One is focused on constructing MOFs with unsaturated metal sites, such as defect engineering, polymetallic doping, and anionic/cationic modifications [16-18]. Additionally, the coordination environment of secondary structural units of MOFs can also be regulated by ligand modification methods, including ligand competition, ligand functionalization and partial ligand deficiency [19-22]. For instance, Yu et al. developed a core-shell amorphous OER catalyst via the ligand-competitive amorphization pathway, achieving a low overpotential of 249 mV at 10 mA cm<sup>-2</sup> [23]. Li et al. reported the design of defective MOFs by mixing ligands containing a ferrocene unit, which facilitate the structural transformation of MOFs into metal oxyexhibit excellent hydroxides and OER performance (213 mV@100 mA cm<sup>-2</sup>) [24]. Principally, organic ligand substituents impart diverse effects, such as inductive and resonance effects, endowing MOFs with unique properties [25,26]. In contrast to single-ligand systems, which are limited by low active site density, dual-ligand MOFs employ complementary ligands to address this drawback [27]. It is reasonable to assume that constructing dual-ligand MOFs through the modulation of organic ligand substituents can enhance the diversity of metal active site environments and optimize catalytic pathways. However, most current efforts in ligand engineering focus on modifying single ligands or exploring different ligand substitutions, with limited attention given to the specific influence of ligand substituents on catalytic activity.

To address these challenges, a proof-of-concept Ni MOF (named Ni N<sub>x</sub>F<sub>10-x</sub>) was developed as a surface model catalyst by modulating the side groups of organic ligands. The organic ligand design was guided by Hammett constant ( $\sigma_m$ ), which quantifies substituent effects on the electronic properties of aromatic systems:  $\sigma_m > 0$  for electron withdrawing and  $\sigma_m < 0$  for electron donating. For Ni N<sub>x</sub>F<sub>10-x</sub>, -F ( $\sigma_m = 0.34$ , BDC-F) and -NH $_2$  ( $\sigma_m=-0.16,\,\text{BDC-NH}_2)$  were chosen as the electron pulling and electron pushing groups, promoting the formation of highvalence Ni3+ species. In a 1.0 M KOH, the optimized Ni N3F7 grown on carbon paper (Ni N<sub>3</sub>F<sub>7</sub>/CP) exhibits excellent catalytic activity in OER with an overpotential of 213 mV at a current density of 10 mA cm<sup>-2</sup>, much lower than those of single-ligand MOF counterpart (Ni N/CP and Ni F/CP). Furthermore, an alkaline electrolyzer assembled with the Ni N<sub>3</sub>F<sub>7</sub>/CP as anode and Pt/C as cathode required only a low cell voltage of 1.52 V to achieve complete water splitting at a current density of 10 mA cm<sup>-2</sup>. In-situ spectroscopic, DEMS measurement and DFT results revealed that the potential-dependent electronic and structural dynamic evolutions of Ni sites, indicating that this push-pull effect facilitates the structural transformation of MOF to metal oxyhydroxides with abundant oxygen vacancies, enabling more efficient lattice oxygen triggering and accelerating OER kinetics.

#### 2. Experimental

#### 2.1. Materials

The reagents were supplied by the supplier without purification. 2aminobenzene-1,4-dicarboxylic acid (BDC-NH<sub>2</sub>, C<sub>8</sub>H<sub>7</sub>O<sub>4</sub>N, 98 %), 2-fluoroterephthalic acid (BDC-F, C<sub>8</sub>H<sub>5</sub>FO<sub>4</sub>, 98 %), nickel nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O, 98 %), and potassium hydroxide (KOH, > 95 % and 99.999 %) were purchased from Aladdin Chemical Reagent Co. Ltd. Absolute ethanol (EtOH, 99.7 %) and N, N-dimethylformamide (DMF, 98 %) were purchased from Xilong Chemical Reagent Co. Ltd. The carbon fiber paper (CP) was purchased from Toray Co. Ltd. and was utilized with a dimension of 2 cm × 1 cm in the experiments. Commercial Pt/C (20 wt% Pt) and Nafion solution (5 wt%) were purchased from Alfa Aesar. The RuO<sub>2</sub> was prepared by directly pyrolysis of RuCl<sub>3</sub> in air at 400 °C and RuCl<sub>3</sub>·3 H<sub>2</sub>O (37 %) were purchased from Inno-chem.

#### 2.2. Treatment of CP

The surface of CP was hydrothermally modified with 68 % HNO3 at

 $120\ ^\circ\text{C}$  for  $180\ \text{min}$  and then cleaned with deionized water and absolute ethanol.

# 2.3. Synthesis of Ni F/CP, Ni N /CP and Ni N<sub>x</sub>F<sub>10-x</sub>/CP

Ni(NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O (0.5 mmol) and BDC-F (0.5 mmol) were dissolved in 10 mL of mixed solution (V<sub>DMF</sub>:V<sub>EtOH</sub>:V<sub>DI</sub>= 7:2:1). The resulting solution was then transferred to a 25 mL Taflon-lined stainless-steel autoclave with two pieces of modified CP, sealed and maintained at 120 °C for 10 h. After natural cooling to room temperature, the samples were washed three times with absolute ethanol and dried 60 °C for 8 h. Ni N/CP was synthesized by a similar procedure to Ni F/CP except that BDC-F (0.5 mmol) was replaced by BDC-NH<sub>2</sub> (0.5 mmol). For Ni N<sub>x</sub>F<sub>10-x</sub>/CP, the synthesis method is similar to that of Ni N/CP. The only difference was that single ligand BDC-NH<sub>2</sub> was replaced by dual ligands (the total organic ligand amount of 0.5 mmol). The specific molar ratios of two ligands are denoted in the nomenclature as Ni N<sub>1</sub>F<sub>9</sub>/CP, Ni N<sub>2</sub>F<sub>8</sub>/CP, Ni N<sub>3</sub>F<sub>7</sub>/CP, Ni N<sub>4</sub>F<sub>6</sub>/CP, Ni N<sub>5</sub>F<sub>5</sub>/CP.

#### 2.4. Synthesis of RuO<sub>2</sub>/CP and Pt/C/CP

For comparison, RuO<sub>2</sub> and Pt/C on CP were also prepared. A homogeneous catalyst ink is formed by dispersing 2 mg RuO<sub>2</sub> or Pt/C in 250  $\mu$ L deionized water/isopropyl alcohol (V / V = 1:1) and 25  $\mu$ L 5 % Nafion as a binder. The mixture is then dropped on the surface of the CP (1 cm  $\times$  0.5 cm).

#### 2.5. Electrochemical Measurements

Electrochemical measurements were conducted using the Biologic VMP3 electrochemical workstation with a standard three-electrode system (The as-synthesized catalyst was acted as integrated working electrode, carbon rod and Hg/HgO were used as the counter electrode and the reference electrode, respectively) in 1.0 M KOH aqueous solution. All electrode potentials were converted to reversible hydrogen electrode (RHE) electrode potentials by the Nernst equation: E <sub>vs. RHE</sub> = E <sub>vs. Hg/HgO</sub> + 0.059 pH + 0.098 V. The oxygen evolution overpotential ( $\eta$ ) was calculated according to the following formula:  $\eta$  (V) = E <sub>vs. RHE</sub> - 1.23 V. Linear sweep voltammetry (LSV) was performed at a scan rate of 1 mV s<sup>-1</sup> from 1.2 V to 0.3 V. All LSV polarization curves were corrected using 95 % *iR* compensation.

The Tafel slope was plotted by converting the LSV curve according to the following formula:  $\eta = a + b \log j$ , where  $\eta$  was the overpotential (mV), j was the corresponding current density (mA cm<sup>-2</sup>), b was the Tafel slope (mV dec<sup>-1</sup>). Electrochemical ac impedance (EIS) was performed in the frequency range 10,000 Hz - 0.01 kHz with an amplitude of 5 mV. Chronopotentiometry (CP, no *iR* compensation) to the stability of the active electrode.

The value of TOF is calculated according to the following formula:

$$TOF = \frac{jA}{4nF}$$

Here, A  $(\text{cm}^2)$  represents the geometric area of the CP. The number 4 means the four electrons transfer in OER and F is equal to the constant of 96485.3 C mol<sup>-1</sup>. n represents the number of mole metal ions in the samples.

The ECSA was assessed by  $C_{dl}$  and the corresponding curves of the catalysts were measured by cyclic voltammetry (CV) where no Faradaic process occurs (0.95–1.05 V vs. RHE) at varied scan rates of 10, 20, 30, 40, 50 and 60 mV s<sup>-1</sup>. The linear slope of the capacitive current versus scan rate was equivalent to double  $C_{dl}$ . The formula for calculating  $C_{dl}$  is:  $C_{dl} = (j_a - j_c)/(2 \times \nu)$ , where  $j_a$  and  $j_c$  correspond to the anodic and cathodic current density, respectively, and  $\nu$  represents the scanning rate. The ECSA of catalyst was calculated using the expression: A<sub>ECSA</sub> =  $C_{dl}$  / $C_s$ , where the value of  $C_s$  is generally in the range of 20–60 µF cm<sup>-2</sup>.

#### 3. Results and Discussion

#### 3.1. Theoretical studies of the catalyst design

To elucidate the impact of ligand microenvironments modulation engineering through dual doping with BDC-F and BDC-NH2 on the electronic structure, density functional theory (DFT) calculations were employed. The Ni NF catalyst model was obtained by replacing local BDC-F with BDC-NH<sub>2</sub>, where the metal unit consisted of Ni atoms in octahedral coordination geometry (Fig. 1a). The charge density difference of Ni NF revealed increased electron density concentrated from F and N toward the Ni site (Fig. 1b). This phenomenon can be attributed to local charge accumulation in the original Ni MOF induced by BDC-NH2 [21,28]. To further identity this electron push-pull effect on coordination microenvironment of the metal center, electron localization function (ELF) and Bader charge analyses were performed for Ni F and Ni NF (Fig. 1c and S1). Results showed that the degree of electron localization in Ni NF was lower than in Ni F, leading to enhanced electron conductivity and a stronger covalent character of the metal-oxygen bond, consistent with Bader charge results (Fig. S2). Previous literature reports indicate that the electronegativity of -F is stronger than that of -NH<sub>2</sub>. When BDC-F was replaced by BDC-NH<sub>2</sub>, the electrons within the MOF became confined to specific regions, resulting in observable shifts in charge density difference, ELF, and Bader charge [29]. Additionally, a detailed investigation into the projected density of states (PDOS) for Ni NF and Ni F was conducted. Analysis of the 3d orbital PDOS of the Ni site showed that Ni NF exhibited a noticeable upshift in the  $\varepsilon_d$  of the Ni atom,

moving closer to the Fermi level ( $E_f$ ) (Fig. 1d). Notably, the Ni atom in Ni NF achieved a higher  $\varepsilon_d$  value of -1.143 eV, effectively strengthening interactions between the electrocatalyst and oxygen intermediates. In the 2p orbital PDOS of the active O atom, unoccupied oxygen states (shaded region) above the Ef appeared following the incorporation of BDC-F, allowing more electrons from oxygen intermediates to enter (Fig. 1e). The upward shift of the O 2p band in Ni NF, bringing it closer to E<sub>f</sub>, indicates enhanced oxygen ion mobility, which facilitates OH<sup>-</sup> adsorption and promotes lattice oxygen activation [30]. The push-pull electronic effect was further validated through PDOS analysis of the Ni 3d, O 2p, and F 2p orbitals. Significant orbital overlap observed in the Ni NF sample (Fig. 1f) indicates strong covalent hybridization between Ni sites and the ligands. Moreover, the incorporation of BDC-NH2 introduces additional unoccupied metal-oxygen bands above the Fermi level (shaded region), suggesting enhanced Ni-O covalency (Fig. S3). This strengthened covalency facilitates electron transfer between the metal center and oxygen intermediates, promoting lattice oxygen-mediated (LOM) catalysis and thereby enhancing the OER process.

#### 3.2. Preparation and characterization of catalysts

Building on the theoretical analysis, a series of Ni  $N_xF_{10-x}$  catalysts were synthesized, with the optimized Ni  $N_3F_7$  nanosheets supported on carbon paper illustrated in Fig. 2a. Detailed experimental procedures are outlined in the experimental section. The identical -COOH groups of BDC-F and BDC-NH<sub>2</sub> ligands enable coordination with the metal center,



**Fig. 1.** (a) Schematic model of ligand microenvironments modulation engineering of Ni NF. (b) Charge density difference of Ni NF: the yellow region indicates electron accumulation, and the blue cyan region represents electron depletion. Color scheme: blue for Ni, grey for C, red for O, purple for F, green for N and white for H. (c) The two-dimension electron localization function (ELF) of Ni NF. Green to red indicates a gradual increase in charge localization. Calculated PDOS of (d) Ni 3*d* and (e) O 2*p* orbits of Ni F and Ni NF. (f) Ni 3*d*, O 2*p* and F 2*p* PDOS spectra of Ni NF with an inset of the enlarged shaded area.



**Fig. 2.** (a) Schematic illustration of the synthesis of Ni N<sub>3</sub>F<sub>7</sub>/CP. (b) XRD patterns of simulated Ni MOF, Ni F/CP, Ni N/CP and Ni N<sub>3</sub>F<sub>7</sub>/CP. (c) FT-IR spectra of Ni F/CP, Ni N/CP and Ni N<sub>3</sub>F<sub>7</sub>/CP. (d) N<sub>2</sub> adsorption–desorption isothermal curves (the inset is the corresponding pore-size distribution plot) of Ni N<sub>3</sub>F<sub>7</sub>/CP.

while the unique electronic properties of the electron-withdrawing and electron-donating groups induce a synergistic effect. This interaction influences the local electronic structure of the secondary structural units, leading to lattice strain in the dual-ligand MOFs [31]. X-ray diffraction (XRD) analysis confirmed the structural integrity of the samples (Fig. 2b and S4). The single Ni F/CP and Ni N/CP were isostructural to previously reported Ni-based MOFs [32,33]. Introducing BDC-NH<sub>2</sub> at lower concentrations caused no significant changes to the crystalline structure of Ni F/CP, though the characteristic peak at approximately 9.2° shifted to a lower angle. This shift, attributed to spatial site resistance alterations, suggests lattice stress stretching and a corresponding movement of the d-band center, which could enhance catalytic performance [34]. As the BDC-NH2 content increased, a mixed phase of Ni F and Ni N emerged, demonstrating a controllable transition from a dual-ligand single-phase MOF to a multi-phase mixed MOF (Table S1).

Fourier Transform Infrared (FT-IR) spectroscopy further verified the molecular structure of the dual-ligand MOF (Fig. 2c). A broad band around 3420 cm<sup>-1</sup> was observed, attributed to surface-absorbed water and hydroxyl groups. Peaks at 791, 1370, and 1590 cm<sup>-1</sup> corresponded to C-H bending and the symmetric (V<sub>s</sub>) and asymmetric (V<sub>as</sub>) stretching modes of -COO<sup>-</sup> groups, respectively [35,36]. Besides, the Ni N/CP show peaks at 1500–1700 and 3300–3500 cm<sup>-1</sup>, regarding the free and uncoordinated NH<sub>2</sub> groups [37]. For Ni N<sub>3</sub>F<sub>7</sub>/CP, the C-F stretching band and the C-N stretching vibration were observed at 1227 cm<sup>-1</sup> and 1278 cm<sup>-1</sup>, respectively [38,39]. The weaker C-F peak intensity in Ni N<sub>3</sub>F<sub>7</sub>/CP, compared to Ni F/CP, indicates occupied coordination sites in the Ni<sub>6</sub> cluster by BDC-NH<sub>2</sub> [40]. Furthermore, the characteristic carboxylate (-COO<sup>-</sup>) stretching vibration in Ni N<sub>3</sub>F<sub>7</sub>/CP exhibited a blue shift from 1584 cm<sup>-1</sup> to 1592 cm<sup>-1</sup> compared to Ni F/CP, reflecting strengthened metal-carboxylate bonds due to BDC-NH<sub>2</sub> incorporation.

Raman spectroscopy confirmed the characteristic peaks of both organic ligands, substantiating the successful integration of BDC-NH<sub>2</sub> into Ni F (Fig. S5). The characteristic peaks of the two organic ligands were also visible in the corresponding Raman spectra, further demonstrating the successful integration of BDC-NH<sub>2</sub> into Ni F. The Braeuer-Emmett-Teller (BET) specific surface area and pore size distributions of Ni N<sub>3</sub>F<sub>7</sub>/CP were investigated by N<sub>2</sub> adsorption-desorption isotherms. Indeed, the Ni N<sub>3</sub>F<sub>7</sub> (85.8 m<sup>2</sup> g<sup>-1</sup>) had a larger BET surface area than single Ni F (4.1 m<sup>2</sup> g<sup>-1</sup>) and Ni N (11.5 m<sup>2</sup> g<sup>-1</sup>), the increased BET surface area is favorable for promoting its potential catalytic performances (Fig. 2d and S6).

The morphology of Ni N<sub>x</sub>F<sub>10-x</sub>/CP was identified with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As illustrated in Fig. 3a, the Ni F/CP exhibits a stacked nanosheet shape with smooth, well-defined edges. With the introduction of BDC-NH<sub>2</sub>, the catalyst achieved a series of transformations, evolving from crosslinked nanosheets (Ni N1F9/CP), petal-shaped nanosheets (Ni N<sub>2</sub>F<sub>8</sub>/CP), coral-like nanosheets (Ni N<sub>3</sub>F<sub>7</sub>/CP) to nanoflowers composed of nanosheets (Ni N<sub>4</sub>F<sub>6</sub>/CP). Interestingly, at higher BDC-NH<sub>2</sub> content, distinct morphologies—curled nanosheets and two nanoflowers-coexist in Ni N<sub>5</sub>F<sub>5</sub>/CP. This suggests that a small amount of BDC-NH<sub>2</sub> acts as a ligand regulator, influencing product size and morphology, whereas excessive amounts lead to ligand competition, resulting in mixed MOF morphologies, consistent with XRD findings (Fig. 3b-c and S7). The TEM image in Fig. 3d further corroborates the ultra-nanosheet morphology of Ni N<sub>3</sub>F<sub>7</sub>/CP observed via SEM. The HR-TEM image shows a fringe lattice space of 1.02 nm in the Ni F/CP, corresponding to the (100) plane (Fig. 3e). When part of BDC-F is replaced by BDC-NH<sub>2</sub>, the interlayer spacing of (100) plane is resized from 1.02 to 0.95 nm, further confirmed the successful introduction of lattice strain (Fig. 3f). EDS mapping in Fig. 3g supports the uniform



**Fig. 3.** (a) SEM image of Ni F/CP. (b) Low-, and (c) high-magnification SEM images of Ni N<sub>3</sub>F<sub>7</sub>/CP. (d) TEM image of Ni N<sub>3</sub>F<sub>7</sub>/CP. HR-TEM images of (e) Ni F/CP and (f)Ni N<sub>3</sub>F<sub>7</sub>/CP. (g) Corresponding EDS mapping of Ni N<sub>3</sub>F<sub>7</sub>/CP.

distribution of O, Ni, F and N elements in Ni  $N_3F_7$ /CP. Additionally, inductively coupled plasma mass spectrometry (ICP-MS) quantification verified the real Ni content in the dual-ligand MOFs, indicating an increased presence of Ni species (Table S2). This suggests that more metal ions are available to coordinate with ligands during the reaction.

The surface chemical composition and valence state of Ni F/CP, Ni N/CP and Ni N<sub>3</sub>F<sub>7</sub>/CP were probed by X-ray photoelectron spectroscopy (XPS). The full survey spectrum of Ni N<sub>3</sub>F<sub>7</sub>/CP demonstrates the coexistence of O, Ni, F and N, validating the successful incorporation of the dual ligand system (Fig. 4a). In the Ni 2p XPS spectrum, the peaks located at around 586 and 857 eV corresponding to the Ni<sup>2+</sup> and Ni<sup>3+</sup>, respectively (Fig. 4b) [39]. While Ni3 + signals were detected by surface-sensitive XPS, no distinct changes were observed in FT-IR and Raman spectra, likely due to their bulk sensitivity and limited ability to resolve subtle Ni<sup>2+</sup>/Ni<sup>3+</sup> differences. The ratio of Ni<sup>3+</sup>/Ni<sup>2+</sup> in Ni  $N_3F_7$ /CP (0.95) is larger than that in Ni F/CP (0.84) and Ni N/CP (0.77), indicating that ligand engineering has modified the coordination environment of Ni active centers, increasing the presence of Ni<sup>3+</sup> species. This result is consistent with the charge density difference analysis. In the N 1 s spectrum (Fig. 4c), two fitted peaks at 399.1 and 401.5 eV are attributed to C-N and -NH2, respectively. Compared to Ni N/CP, the N 1 s peak intensity of Ni N<sub>3</sub>F<sub>7</sub>/CP shows moderately weaker, which is attributed to the partial substitution of -NH<sub>2</sub> by -F [41]. Similarly, in the F 1 s XPS spectrum, the C-F of Ni N<sub>3</sub>F<sub>7</sub>/CP shows a positive shift, and this can be explained by the electron push-pull effect formed via dual

ligands (Fig. 4d). XPS valence band spectra (Fig. S8) show that the valence band maximum energy of Ni N<sub>3</sub>F<sub>7</sub>/CP shifts closer to the Fermi level compared to Ni F/CP and Ni N/CP, indicating improved conductivity [41]. The electronic properties were further analyzed using the ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectrum (Fig. 4e). Ni  $N_3F_7$ /CP exhibited higher absorbance in the 200 – 600 nm wavelength range compared to Ni F/CP, suggesting that the introduction of BDC-NH<sub>2</sub> influences the electronic state [42]. Additionally, the zeta potential of Ni F/CP, Ni N/CP, and Ni N<sub>3</sub>F<sub>7</sub>/CP were measured in 1.0 M KOH dispersions to evaluate surface charge (Fig. 4f). The zeta potential of Ni N<sub>3</sub>F<sub>7</sub>/CP (-22.2 mV) was higher than that of Ni F/CP (-16.9 mV) and Ni N/CP (-10.7 mV), indicating enhanced  $\mathrm{OH}^{\text{-}}$  adsorption on the electrode surface. This improvement in hydrophilicity facilitates better OER kinetics [43,44]. Moreover, the magnetic properties of all samples were characterized by vibrating sample magnetometry (VSM). Linear magnetization curves without hysteresis loops were observed, consistent with paramagnetic behavior (Fig. 4g). It was also observed that Ni  $N_3F_7/CP$  has the highest intrinsic magnetic strength, attributed to the fact that increasing the Ni<sup>3 +</sup> ratio produces more unpaired electrons. According to the previous results, the Ni atoms in the classical Ni MOF display an octahedral coordination structure consisting of six O atoms. As for the Ni-MOF nanosheets proposed in this research, a mixed coordination state of MO<sub>6</sub> and MO<sub>5</sub> is formed due to the limitation of edge growth, which in turn generates more unsaturated metal sites [45]. Further combining the magnetic measurements with molecular orbital



**Fig. 4.** (a) XPS survey spectra and (b) Ni 2*p* spectra of Ni F/CP, Ni N/CP and Ni  $N_3F_7$ /CP. (c) N 1 *s* spectra of Ni N/CP and Ni  $N_3F_7$ /CP. (d) F 1 *s* spectra of Ni F/CP and Ni  $N_3F_7$ /CP. (e) UV-Vis-NIR absorption spectrum of Ni F/CP and Ni  $N_3F_7$ /CP. (f) Zeta-potential and (g) vibrating sample magnetometer (VSM) curves of Ni F/CP, Ni N/CP and Ni  $N_3F_7$ /CP. (h) The illustration of the electronic coupling in Ni  $N_3F_7$  (Ni<sub>1</sub> and Ni<sub>2</sub> represent the MO<sub>6</sub> and MO<sub>5</sub> coordination patterns, respectively).

theory analysis shows that the precise introduction of BDC-NH<sub>2</sub> reduces the local ligand symmetry of MOF, which promotes the conversion of Ni<sup>2+</sup> to Ni<sup>3+</sup> and generates more unpaired electrons (Fig. 4**h**). These experimental and computational findings collectively confirm that the electron push-pull effect mediated by dual organic ligands alters the microenvironment of the MOF's secondary structural units, thereby enhancing catalytic activity.

#### 3.3. OER electrocatalytic performance

The OER performance of as-prepared catalysts and RuO<sub>2</sub>/CP was evaluated in a three-electrode system using a 1.0 M KOH. The BDC-NH<sub>2</sub>: BDC-F ratio significantly influenced OER activity, with Ni N<sub>3</sub>F<sub>7</sub>/CP demonstrating better OER performance (Fig. S9). From the LSV curves shown in Fig. **5a**, the N<sub>3</sub>F<sub>7</sub>/CP exhibits the lowest overpotential of 213 mV at the current density of 10 mA cm<sup>-2</sup>, far beyond than that of Ni F/CP (250 mV), Ni N/CP (307 mV), RuO<sub>2</sub>/CP (298 mV) and most of the recently reported MOF-based OER catalysts (Fig. **5c**, Table S4). Furthermore, the Tafel plot of Ni N<sub>3</sub>F<sub>7</sub>/CP is 73.1 mV dec<sup>-1</sup>, lower than that of Ni F/CP (88.4 mV dec<sup>-1</sup>), Ni N/CP (99.8 mV dec<sup>-1</sup>) and RuO<sub>2</sub>/CP (207.1 mV dec<sup>-1</sup>), indicating faster reaction kinetics (Fig. **5b**).

Electrochemical double-layer capacitance  $(C_{dl})$ , measured via cyclic voltammetry in the non-Faradaic region, provided an estimate of the electrochemical surface area (ECSA) (Fig. S10). The calculated  $C_{dl}$  value of Ni N<sub>3</sub>F<sub>7</sub>/CP is 2.1 mF cm<sup>-2</sup>, higher than that of Ni F/CP (1.1 mF cm<sup>-2</sup>) and Ni N/CP (1.4 mF cm $^{-2}$ ), s indicating better exposure of active sites, consistent with BET results (Fig. 5d). Turnover frequency (TOF) and ECSA-normalized current density measurements were used to assess the intrinsic electrocatalytic activity of the catalysts. Ni N<sub>3</sub>F<sub>7</sub>/CP demonstrated the highest normalized current density and TOF values at all applied potentials, highlighting the electron push-pull effect's role in enhancing intrinsic activity (Fig. 5e). Additionally, EIS plots at different applied potentials (vs. RHE) were performed to further survey the kinetics of charge transfer during OER process and the associated equivalent circuit model was shown in Fig. 5f. Compared to Ni F/CP and Ni N/ CP, Ni N<sub>3</sub>F<sub>7</sub>/CP has the smallest radius in the Nyquist plots from EIS, indicating that faster electron transfer occurs at the electrolyte-catalyst interface in OER, also agreed with the Tafel slope results (Fig. S11) [46]. In the corresponding frequency response plots of phase angle, the peak of Ni N<sub>3</sub>F<sub>7</sub>/CP is the lowest among the prepared catalysts, suggesting that more electrons are involved in the water splitting (Fig. 5g) [47,48]. OER electrocatalyst stability is of great relevance for practical



**Fig. 5.** (a) Linear sweep voltammetry (LSV) curves of Ni F/CP, Ni N/CP, Ni N<sub>3</sub>F<sub>7</sub>/CP and RuO<sub>2</sub>/CP in 1.0 M KOH. (b) Corresponding Tafel slope derived from the LSV curves. (c) Comparison the overpotential at 10 mA cm<sup>-2</sup> and Tafel slope with previously reported MOF-based catalysts. (d) Corresponding  $C_{dl}$  values and (e) turnover frequencies (TOF) value (left) and LSV curves normalized by ECSA (right) of Ni F/CP, Ni N/CP and Ni N<sub>3</sub>F<sub>7</sub>/CP. (f) Operando EIS spectra, (g) corresponding bode plot acquired through EIS spectra and (h) chronopotentiometry curve of Ni N<sub>3</sub>F<sub>7</sub>/CP and Ni F/CP at 100 mA cm<sup>-2</sup>.

applications, whereby chronopotentiometry is used to evaluate O<sub>2</sub> evolution stability of Ni N<sub>3</sub>F<sub>7</sub>/CP. As shown in Fig. 5h, the Ni N<sub>3</sub>F<sub>7</sub>/CP displays remarkable stability at 100 mA cm<sup>-2</sup> over 100 h with barely any loss in performance. These results demonstrate that the introduction of BDC-NH<sub>2</sub> and the formation of coral-like nanosheets enhanced the intrinsic activity and electrocatalytic kinetics of Ni N<sub>3</sub>F<sub>7</sub>/CP, resulting in its outstanding OER performance.

Considering that even a trace amounts of Fe ions in the electrolyte can significantly impact the OER performance of Ni-based catalysts, extensive experiments were conducted to prove that the results presented here are attributable to the Ni-based catalyst alone rather than iron impurities that may come from the electrolyte. Firstly, according to Boettcher's report, the Fe doping was detected by XPS [49]. By comparing the full XPS spectra before and after the catalyst stabilization, a Ni LM5 Auger peak around 712 eV was found to have weakened but still existed after a long stabilization test (Fig. S17b). No obvious characteristic Fe peaks were detected, indicating the absence of Fe in the catalyst. To provide a more precise quantification of this influence, we conducted catalyst tests using high-purity (Fe-free) KOH (Fig. S12). It is worth noting that the two cases (1.0 KOH and Fe-free 1.0 M KOH) show similar current densities and Tafel slopes. Based on this, we infer that iron in the electrolyte does not contribute to the activity of Ni N<sub>3</sub>F<sub>7</sub>/CP

# [50].

## 3.4. OER mechanism

The structural evolution of Ni N<sub>3</sub>F<sub>7</sub>/CP after stability tests (named post-Ni N<sub>3</sub>F<sub>7</sub>/CP) was first investigated by ex-situ SEM, TEM and XRD. Following prolonged stability testing, post-Ni N<sub>3</sub>F<sub>7</sub>/CP transformed into a cross-linked nanosheet structure with a rough, bumpy surface. This morphology enhances the contact area between the catalyst and electrolyte, outperforming the stacked nanosheets of post-Ni F/CP and the irregular blocks of post-Ni N/CP (Figs. S13-S14). XRD patterns of post-Ni N<sub>3</sub>F<sub>7</sub>/CP revealed new diffraction patterns distinct from the original MOF, indicating reconstruction and transformation into NiOOH during electrochemical processes (Fig. S15). HR-TEM imaging confirmed distinct lattice fringes and corresponding diffraction rings, while EDX spectra showed a uniform distribution of C, O, Ni, F, and N elements (Fig. S16). The chemical state of post-Ni N<sub>3</sub>F<sub>7</sub>/CP was further examined via XPS. The  $\rm Ni^{3*}/\rm Ni^{2*}$  ratio increased to 1.18, reflecting the formation of NiOOH (Fig. 6a) [48]. Notably, while the presence of F and N is evident in the elemental mapping, their signals are barely detectable in the XPS survey spectra. This may be attributed to the dissociation of organic ligands during the electrochemical process-leaving the metal active sites



**Fig. 6.** (a) Ni 2*p* XPS spectra of post-Ni N<sub>3</sub>F<sub>7</sub>/CP. Electrochemical in situ Raman spectra of (b) Ni N<sub>3</sub>F<sub>7</sub>/CP and (c) Ni F/CP. (d) LSV curves of Ni N<sub>3</sub>F<sub>7</sub>/CP under different pH conditions (KOH electrolyte). (e) Current density at 1.55 V (vs. RHE) as a function of pH value of the Ni N<sub>3</sub>F<sub>7</sub>/CP and Ni F/CP in KOH electrolytes. (f) LSV profiles of Ni N<sub>3</sub>F<sub>7</sub>/CP and Ni F/CP in 1.0 M KOH and 1.0 M TMAOH. (g) DEMS signals of <sup>18</sup>O<sup>16</sup>O (<sup>34</sup>O<sub>2</sub>) over time for Ni N<sub>3</sub>F<sub>7</sub>/CP and Ni F/CP. (h) Gibbs free energy diagrams and (i) schematic illustration of the LOM pathway on the β-NiOOH.

intact, as evidenced by the sustained catalytic activity-thereby resulting in only trace amounts of N and F remaining on the catalyst surface (Fig. S17a and Table S3). Based on previous reports, such dissociation could have possibly led to oxygen defects [48,51]. EPR spectra visualizes the presence of abundant oxygen defects in post-Ni  $N_3F_7$ /CP (Fig. S18). In-situ Raman spectroscopy was employed to study the dynamic surface reconstruction of Ni F/CP, Ni N/CP, and Ni N<sub>3</sub>F<sub>7</sub>/CP during the OER process across applied potentials of 1.1–1.6 V (vs. RHE). For Ni N<sub>3</sub>F<sub>7</sub>/CP, as the potential increased, characteristic peaks of the MOF gradually disappeared, and new peaks appeared at  $\sim$ 477 cm<sup>-1</sup> and  $\sim$ 559 cm<sup>-1</sup>, corresponding to the Eg bending vibration and A<sub>1g</sub> stretching vibration modes of Ni-O in NiOOH, respectively [52]. It is noteworthy that despite Ni<sup>2+</sup> signals observed in ex situ XPS, in situ Raman confirms NiOOH as the active phase during OER. This discrepancy arises from spectral overlap, partial reduction during handling, and incomplete oxidation. Enhanced Ni<sup>3 +</sup> signals post-OER, supported by complementary techniques, affirm NiOOH formation as the active species [53-55]. And NiOOH generation occurred at a lower potential in Ni N<sub>3</sub>F<sub>7</sub>/CP compared to Ni F/CP and Ni N/CP, indicating that the introduction of BDC-NH<sub>2</sub> accelerates NiOOH formation (Fig. 6b-c and S19). The A<sub>1g</sub>/E<sub>g</sub> intensity ratio for Ni  $N_3F_7/CP$  (1.18) was higher than in other samples, suggesting a greater proportion of the active  $\beta$ -NiOOH phase, correlating with enhanced catalytic activity and stability [56,57]. At potentials exceeding 1.4 V, a broad Raman band (~800-1200 cm<sup>-1</sup>) was observed for Ni N<sub>3</sub>F<sub>7</sub>/CP, corresponding to superoxide species (-OO-), further

indicating that the OER mechanism likely follows the lattice oxygen mechanism (LOM) [53,58]. To understand the OER mechanism, the pH dependence of OER activity was investigated to probe proton-electron transfer kinetics. Ni N<sub>3</sub>F<sub>7</sub>/CP exhibited pronounced pH-dependent kinetics, indicative of significant lattice oxygen involvement in OER, unlike Ni F/CP, which showed weaker dependence (Fig. 6d and S20) [59]. Besides, the pH dependence is closely related to the proton reaction order ( $\rho$ ), with LOM occurring preferentially at values of  $\rho$  close to 1 [60]. As shown in Fig. 6e, the calculated  $\rho$  value of Ni N<sub>3</sub>F<sub>7</sub>/CP (0.95) is larger than that of Ni F/CP (0.67), confirming that introducing BDC-NH<sub>2</sub> may propel LOM pathway. Tetramethylammonium hydroxide (TMAOH) can be adopted as a chemical probe to detect the presence of superoxide species (-OO-) due to its strong electrostatic interaction with -OO- [61]. In 1.0 M TMAOH solution, the OER activity of Ni N<sub>3</sub>F<sub>7</sub>/CP is more significantly reduced than that of Ni F/CP, indicating that the LOM process of Ni  $N_3F_7/CP$  is strongly inhibited with TMA<sup>+</sup> (Fig. 6f). To further support this hypothesis, we performed DEMS measurements using <sup>18</sup>O isotope labeling to track the oxygen evolution during the OER [62]. According to the LOM mechanism, oxygen is produced from both the electrolyte and the catalyst lattice. Thus, if the reaction proceeds via LOM,  ${}^{18}\text{O}{}^{16}\text{O}$  (*m*/*z* = 34) should be observed during OER on  ${}^{18}\text{O}{}^{-1}\text{abeled}$ Ni N<sub>3</sub>F<sub>7</sub> and Ni F in an  $H_2^{16}O$  environment. As shown in Fig. 6g, a more intense <sup>34</sup>O<sub>2</sub> signal was detected for Ni N<sub>3</sub>F<sub>7</sub> compared to Ni F, indicating greater involvement of lattice oxygen in the reaction. These results are consistent with the findings from the TMA<sup>+</sup> probe experiments.

Theoretical calculations were also carried out to gain a deeper insight into the OER mechanism, modeled on active species participating in the reaction (Fig. S21). The calculated Gibbs free energies of  $\beta$ -NiOOH are shown in Fig. 6h, along with the corresponding geometries of the various intermediates at the Ni site (Fig. S22). It can be observed that the transformation of \*O to \*OOH was the rate-determine step (RDS) with the overpotential of 0.52 eV, much smaller than that of NiOOH (0.71 eV) (Fig. S23). According to previous reports, one possible LOM reaction pathway is schematically presented in Fig. 6i [63,64]. In detail, the (oxy)hydroxides first undergo deprotonation to form oxyhydroxide (step 1). Then, the exposed lattice oxygen receives OH via nucleophilic attack to form \*OOH (step 2). Following the deprotonation of \*OOH (Step 3), gaseous O2 is released from the lattice, creating an oxygen vacancy at the surface (Step 4). At last, the generated oxygen vacancies are refilled by OH<sup>-</sup> and the surface is recovered (step 5). These results collectively demonstrate that introducing BDC-NH2 into Ni F enhances structural reorganization, facilitates β-NiOOH formation with oxygen defects, and strengthens the LOM pathway, contributing to the outstanding OER performance of Ni N<sub>3</sub>F<sub>7</sub>/CP.

## 3.5. Overall water splitting

To evaluate the catalytic activity of Ni  $N_3F_7$ /CP for overall water splitting, a double-electrode electrolyzer was assembled using Ni  $N_3F_7$ /CP as the anode and Pt/C/CP as the cathode. The electrolyzer

demonstrated excellent catalytic performance, achieving a current density of 10 mA cm<sup>-2</sup> at a cell voltage of 1.52 V and 100 mA cm<sup>-2</sup> at 1.63 V. These values are slightly lower than those of the commercial RuO<sub>2</sub>/CP<sup>(+)</sup>||Pt/C/CP<sup>(-)</sup> system and compare favorably with other previously reported catalysts (Fig. 7**a-c**, Table S5). The stability of Ni N<sub>3</sub>F<sub>7</sub>/CP was further confirmed through chronopotentiometry, where the system maintained a stable current density of 100 mA cm<sup>-2</sup> for over 80 h without significant performance degradation (Fig. 7**d**). This sustained electrocatalytic activity and stability under prolonged operation underscore the robustness of Ni N<sub>3</sub>F<sub>7</sub>/CP. These findings highlight the potential of Ni N<sub>3</sub>F<sub>7</sub>/CP for practical applications in renewable energy generation, offering a highly active and stable electrocatalyst for overall water splitting.

# 4. Conclusion

The introduction of dual ligands, BDC-NH<sub>2</sub> and BDC-F, into the MOF framework induced a synergistic electron push-pull effect, enhancing the electronic structure, catalytic activity, and structural stability of the catalyst. The comprehensive experimental results confirm that the cobinding of -F and -NH<sub>2</sub> significantly promotes the reconstruction of Ni MOF into high-activated and oxygen-defective  $\beta$ -NiOOH, thereby enabling the active LOM pathway. Further DFT calculations revealed that the introduced BDC-NH<sub>2</sub> can regulate the Ni  $\varepsilon_d$  and the O 2*p* band simultaneously, thereby leading stronger metal-oxygen covalency and



**Fig. 7.** (a) Schematic diagram of the overall water splitting electrolyzer. (b) Comparison of the polarization curves of Ni  $N_3F_7/CP^{(+)}||Pt/C/CP^{(-)}|$  and the RuO<sub>2</sub>/ $CP^{(+)}||Pt/C/CP^{(-)}|$  in 1.0 M KOH. (c) Comparing cell voltages with the recently reported electrolyzers at 10 mA cm<sup>-2</sup> in 1.0 M KOH. (d) Long-term stability test of Ni  $N_3F_7/CP^{(+)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}||Pt/C/CP^{(-)}$ 

lower OER reaction energy barrier. As a consequence, the optimized Ni N<sub>3</sub>F<sub>7</sub>/CP possess enhanced OER activity compared to single Ni N/CP and Ni F/CP, having low overpotentials of 213 mV at 10 mA cm<sup>-2</sup> with fast kinetics (73.1 mV dec<sup>-1</sup>) in OER and a small bias of 1.52 V at 10 mA cm<sup>-2</sup> for overall water splitting (Ni N<sub>3</sub>F<sub>7</sub>/CP<sup>(+)</sup>||Pt/C/CP<sup>(-)</sup>). These fundings demonstrate a promising strategy in the precise synthesis of MOF-based catalysis that can also be extended to other electrocatalysis.

#### Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2025.XXXXX.

#### CRediT authorship contribution statement

**Haoran Yin:** Conceptualization, Writing – original draft. **Ziyan Lin:** Methodology. **Lixia Wang:** Investigation. **Yong Huang:** Writing – review & editing. **Tayirjan Taylor Isimjan:** Writing – review & editing. **Xiulin Yang:** Writing – review & editing, Supervision, Funding acquisition.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Conflict of Interest

The authors declare no conflict of interest.

### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2025.125610.

# Data availability

Data will be made available on request.

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