Docking MOF crystals on graphene support for highly selective electrocatalytic peroxide production

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ABSTRACT
Tailoring the reaction kinetics is the central theme of designer electrocatalysts, which enables the selective conversion of abundant and inert atmospheric species into useful products. Here we show a supporting effect in tuning the electrocatalytic kinetics of oxygen reduction reaction (ORR) from four-electron to two-electron mechanism by docking metalloporphyrin-based metal–organic frameworks (MOFs) crystals on graphene support, leading to highly selective peroxide production with faradaic efficiency as high as 93.4%. A magic angle of 38.1° tilting for the co-facial alignment was uncovered by electron diffraction tomography, which is attributed to the maximization of $\pi-\pi$ interaction for mitigating the lattice and symmetry mismatch between MOF and graphene. The facilitated electron migration and oxygen chemisorption could be ascribed to the supportive effect of graphene that disperses the electron state of the active center, and ultimately regulates rate-determining step.

KEYWORDS
metal–organic frameworks, nanocomposites, support effect, oxygen reduction reaction, peroxide selectivity

1 Introduction
Hydrogen peroxide (H2O2) served as a versatile feedstock for multiple industrial purposes is mass-produced via the so-called anthraquinone oxidation process in which the organics reacts with gaseous hydrogen under demanding condition [1]. For its feasibility and on-site supply purpose, electrochemical production of H2O has long been pursued [2–6], calling for the tailored understanding and design of the electrocatalysts [7, 8]. Considerable efforts have been made to modulate the electronic structures of catalysts via strain [9], alloying [10], and doping [11]. Interfacial interactions induced from a supportive substrate represent a fruitful strategy for manipulating the electron status of nanocomposites [12–17]. Indeed, this strategy leads to materials whose performance is dictated by the axiom, “the whole is greater than the sum of its parts” [18, 19].

As emerging crystalline porous materials, metal–organic frameworks (MOFs) have shown their prospect in electrochemistry, featuring the deliberate control of reticular architectures and the ingenious manipulation of the electronic properties to optimize/interplay the resulting activity, selectivity and efficiency [20–26]. However, the bottleneck arising from the poor electronic conductivity of MOFs calls for the elaborative crystal interface between MOF and conductive supports/substrates [13]. To overcome the difficulty of significant lattice mismatch, self-assembled monolayer (SAM) has been utilized to graft MOFs on substrate through layer-by-layer method. The alkyl organic feature of SAM renders it a resistant layer in terms of electron transfer [27, 28]. Solution-phase epitaxial growth places MOFs directly on substrates, which might have explicit alignment of MOF on limited synthetic substrates such as Ag, Pd, and Cu(OH)2 [29–31]. To tailor the electrocatalytic performance, we sought to implement the solution-phase growth of MOFs on graphene materials to maximize their contacts. Specifically, we have docked a grid-layered MOFs, comprising cobaltoporphyrin linkers and paddle-wheel building units, on graphene supports (Fig. 1). With the doping and functionality of graphene optimized, the electrocatalytic performance and reaction kinetics in the oxygen reduction reactions (ORR)
were therefore optimized and steered towards two-electron pathway, showing high selectivity toward peroxide production. The mechanism of the kinetic control is attributed to the dispersed electron state of the active centers that facilitated the detachment of $\text{O}_2^-$ intermediate. Such supporting effect of graphene is originated from co-facial docking orientation of MOF and graphene that possess a twist angle of $\sim 38^\circ$ overcoming huge lattice mismatch and symmetry mismatch. This work features optimized supporting effect in the tailor-designed reaction kinetics and electron state for target-oriented electrocatalysis.

2 Results and discussion

2.1 Oxygen reduction behavior of graphene supported MOF

Observed by scanning electron microscopy (SEM), as-synthesized layered cobalt-porphyrin MOFs was ca. 20–30 μm in size and tetragonal prismatic shaped crystals in appearance through solvothermal reaction, as shown in Fig. S1 in the Electronic Supplementary Materials (ESM). The MOF adopts a square-grid layered structure (sq1 net) by stitching the CoTCPP linkers with the Co$_2$(COO)$_4$ paddle-wheel clusters (Figs. S2 and S3, and Table S1 in the ESM). Perfectly-defined tetragonal electron diffraction pattern rendered its good crystallinity, which is also in line with the simulated pattern (Figs. S3(d) and S3(e) in the ESM). Reconstruction of the hk0 plane indicates its finely-ordered in-plane structure (Figs. S3(c) and S3(f) in the ESM). However, the observed diffusive reconstructed pattern and reciprocal rod along the c direction (Figs. S3(g) and S3(h) in the ESM) implied its irregular stacking of single MOF layer onto one another. Nevertheless, a family of such MOF structures are of ease in controlled synthesis and have been widely used in constructing nanocomposites [32–34]. In such solvothermal reaction, addition of certain types of graphene supports, namely EG (electrochemically exfoliated graphene), NG (nitrogen-doped graphene), and NG' (high-power sonicated nitrogen-doped graphene) yield MOF-graphene nanocomposites with well-retained MOF structure verified from the powder X-ray diffraction patterns (PXRD) shown in Fig. S4 in the ESM.

Investigated through cyclic voltammetry (CV), the ORR behaviors of graphene supported MOF displayed intense reduction peaks in $\text{O}_2$-purged 0.5 M H$_2$SO$_4$ electrolyte than that of pristine MOF (Fig. 2(a); Fig. S5 in the ESM), implying the supportive contribution from graphene. Hydrodynamic voltammograms at various rotation speeds were recorded to elucidate the role of graphene supports in ORR electrochemical kinetics (Fig. 2(b); Fig. S6 in the ESM). At 1,600 rpm, mass-transfer-corrected Tafel slopes in Fig. 2(c) were tilted from > 120 mV·dec$^{-1}$ (all MOF-graphene nanocomposites except MOF@NG'), around 90 mV·dec$^{-1}$ (MOF) and ultimately to 58 mV·dec$^{-1}$ (MOF@NG'). The corresponding kinetics were gradually changing from a single electron transfer-controlled step to a $\text{O}_2$ chemisorption-controlled step [34].

The gradual tuning of the electrode kinetics indicates a change in the underlying ORR performance. In the absence of graphene supports, pristine MOF transferred 3.61 electrons to $\text{O}_2$, which corresponds to a H$_2$O$_2$ selectivity of only 19.7% (Fig. 2(b)). The ability for four-electron reduction behavior is likely arising from the stepwise 2-electron process judging from their reduction behavior in H$_2$O$_2$ (Fig. S7 in the ESM). The peroxide yield on MOF@EG and MOF@NG was moderately improved to 56%–59% suggesting the ratio for the two-electron pathway starts to increase. Specifically on MOF@NG', it exhibited the number of electrons transferred per $\text{O}_2$ reached 2.24, which corresponding to a peroxide yield of 88.2% based on rotating ring-disk voltammetry results (Fig. 2(e)), uncovering its dominant two-electron pathway. When it was further subject to constant potential electrolysis of $\text{O}_2$ at 0.4 V vs. reversible hydrogen electrode (RHE), the concentration of H$_2$O$_2$ showed a steady increment over 6 h, giving the highest Faradaic efficiency of 93.4% for MOF@NG' (Fig. 2(d); Fig. S8 in the ESM). Such peroxide selectivity is higher than those of the oxidized carbon nanotube and defect contained carbon [35], nitrogen-doped graphene [36], boron nitride [37], and other reported electrocatalysts (Table 1), and is comparable to mildly oxidized

![Figure 2](image-url)  
**Figure 2** Electrochemical ORR activities and local structures of MOF-graphene composites. (a) CVs of MOF and MOF-graphene nanocomposites in N$_2$(dash line)/O$_2$(solid line) purged 0.5 M H$_2$SO$_4$ solution with a scan rate of 10 mV·s$^{-1}$. (b) Rotating ring-disk voltamograms of MOF-graphene nanocomposites in $\text{O}_2$ purged 0.5 M H$_2$SO$_4$ solution with a scan rate of 5 mV·s$^{-1}$ at 1,600 rpm. (c) Tafel slopes of the MOF-graphene nanocomposites. (d) Faradaic efficiencies of peroxide formation on MOF-graphene nanocomposite. (e) High resolution XPS of Co 2p core level. (f) $k^2$-space EXAFS of MOF and MOF-graphene nanocomposites.
graphene [52], hetero-atom doped mesoporous carbon [51, 64–66], graphitized carbon nanohorns [67], and carbon dots [68]. Since sole NG in constant potential electrolysis do not produce H2O2 (Fig. S8 in the ESM), the promotion of H2O2 selectivity in MOF@NG' probably correlated with the nanocomposite interface.

Additionally, the electrocatalytic turnover of oxygen to H2O2 can be further optimized by the graphene substrate. As NG showed the least Rn (Table S2 in the ESM), it enabled MOF@NG to have the highest electron conductivity (see Fig. S9 and Table S3 in the ESM) along with a higher amount of O2 chemisorption (Fig. S10 in the ESM). They could be further optimized by means of increasing the electrochemically active surface area (Fig. S10 in the ESM) implying the distortion of ligand field of Co(II) in the ESM) and downshifts of certain typical bands of the MOF in the Raman spectroscopy of the MOF-graphene nanocomposites (Fig. S13 in the ESM).

### 2.2 Electron state modulated by supported graphene

As neither NG nor NG’ exhibited selective oxygen reduction to H2O2, local electronic states at the Co(II) active center of MOF-graphene composite interface were characterized by a combined X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and X-ray absorption spectroscopy (XAS) study to probe the MOF-graphene interaction. In the Co 2p high-resolution spectra (Fig. 2(e)), the Co 2p3/2 peak can be deconvoluted into two peaks in the binding energy (B.E.) region between 780–782 eV, indicating the co-existence of Co-N4 and Co-N3 paddlewheel units (Fig. S10 in the ESM). Notably, the Co 2p3/2 moiety peaks in MOF@NG and MOF@NG’ shifted to the higher B.E. region, and the Co-N interatomic distance was increased compared to CoTCPP and MOF according to the first peak from the Fourier transformed 3-space extended X-ray absorption fine structure (EXAFS) spectra (Fig. 2(f)). Such finding was further supported by the downshift of the Raman spectroscopy of the MOF-graphene nanocomposites (Fig. S13 in the ESM) and downshifts of certain typical bands of the MOF in the Raman spectroscopy of the MOF-graphene nanocomposites (Fig. S14 and Table S6 in the ESM). Also, the more intense peak at 7,679 eV in the pre-edge region of the Co K-edge (Fig. S15 in the ESM) implies the distortion of ligand field of Co(II) in MOF@NG’ [80] also supports our hypothesis. Several works

| Catalyst | j_{\text{lim}} (mA cm^{-2}) | E_{\text{onset}} (V vs. RHE) | n | H2O2 FE (%) | Ref. |
|----------|-----------------|-----------------|----|-------------|-----|
| MOF@NG' | 0.816           | 0.50            | 2.2| 93.4        | This work |
| MOF@NG  | 1.812           | 0.57            | 2.8| 72.2        |       |
| Mesoporous nitrogen-doped carbon | – 3.5 | – 0.73 | 2.52–2.72 | 65–73 | [38] |
| Polypyrole/anthraquinones composite film | (-) | – 0.19 | 2.02 | (-) | [39] |
| TiN nanoparticle (12 nm) | – 0.4 | 0.7 | (-) | –70 | [40] |
| Ju-NG | – 1.8 | – 0.57 | 1.9–2.1 | (-) | [41] |
| NC900 | – 4 | 0.8 | 2.1 | (-) | [42] |
| C(Pt)/C | –1.8 | 0.57 | 3.2–3.3 | 41 | [43] |
| Mesoporous nitrogen-doped carbon | – 2.6 | 0.4 | 2 | 93–95 | [44] |
| Nitrogen doped graphene | – 0.8 | 0.67 | 2.5 | (-) | [45] |
| MOF(Fe/Co)+SP | – 4 | – 0.67 | 2–3 | (-) | [46] |
| GOQDs | – 2.7 | – 0.66 | 2.21–2.24 | (-) | [47] |
| RGO/Au | – 0.5 | 0.8 | 2 | (-) | [48] |
| Fe(meso-tetraphenylporphyrin) | – 0.15 | 0.3 | 2.4 | – 60 | [50] |
| Fe/pyrroled polyimide | – 1.3 | 0.7 | 2.4 | – 60 | [50] |
| Mesoporous Nitrogen-Doped Carbon | – 3 | – 0.4 | 2 | 65.15 | [51] |
| Co-POC-O | (-) | 0.84 | (-) | 87.7 | [52] |
| Co-N(C)G | – 3 | – 0.75 | (-) | – 82 | [53] |
| Co-N-C | 2.9 | – 0.75 | 2.5 | 80 | [54] |
| MOF NSs-300 | 3 | 0.75 | 2.5 | 99 | [55] |
| Mn-O/N@NCs-50 | – 1.3 | – 0.3 | 2.4 | 74 | [56] |
| NCMK3IL50_800T | – 1.8 | 0.55 | 2.1 | 95–98 | [57] |
| PEI50CMK3_800T | – 1.5 | 0.49 | 2.05 | 95.2–98.5 | [58] |
| 5-Ni3(HITP)2 | – 1.7 | – 0.7 | 2.5 | 80 | [59] |
| N-mFLG-8 | – 3 | – 0.72 | < 2.1 | 95 | [60] |
| Pt/Ag/C | (-) | – 0.55 | 2.1 | > 90 | [61] |
| G/CDs | 0.4 | 0.85 | 2.3 | 82 | [62] |
| Exfoliated 2H-MoTe2 | 1.9 | 0.56 | (-) | 93 | [63] |
reported that oxygen moieties like epoxy groups are responsible for the high peroxide selectivity for Co-N₄ electrocatalysts [81]. We cannot rule out such possibility, since oxygen contents existed in the EG, NG, and NG’ substrates (Fig. S16 in the ESM). Judging from the neglectable peroxide TON for NG’ in the constant potential electrolysis, we conjecture that the oxygen contents do not play significant role in enhancing the peroxide selectivity in our case. We anticipate surface-sensitive operando techniques like surface-enhanced Raman spectroscopy [82] would uncover the in-depth understanding of the peroxide production mechanism on MOF@NG’.

The interfacial structure for the nanocomposites were further characterized to rationalize electron density dispersion. SEM images of MOF-graphene displayed diversified MOF morphologies among the nanocomposite samples (Fig. 3(a); Fig. S17 in the ESM). In both of their NG and EG nanocomposites, MOF sheets with thickness at ~1 μm in relatively larger size (5-10 μm) were found (Figs. S17(a) and S17(b) in the ESM), where random docking orientations were generally observed. Contrasted, co-facially aligned orientation of MOF sheets was observed on the NG’ support with decent uniformity (Fig. 3(a); Figs. S18 and S19 in the ESM). Selected area electron diffraction (SAED) were also performed to verify this orientation. We were able to obtain both sets of diffraction spots belonging to MOF (tetragonal) and graphene (hexagonal) lattices, respectively (Fig. 3(b)). Magnification of this diffraction further showed a set tetragonal spots around the spot of NG’, as it was shown in Fig. 3(c). This secondary diffraction phenomenon confirmed that MOF sheets were actually co-facially docked onto rather than randomly anchored to nitrogen-doped graphene support. Additional results from scanning transmission electron microscopic (STEM) images displayed clear tetragonal fringes of MOF docked on NG’ (Fig. 3(d); Fig. S20(a) in the ESM). Fast Fourier transformation (FFT) of the whole region led to a similar emergence of both patterns further supports the proposed co-facial aligned regime. Surprisingly, we also observe an intersection angle of ~38.1° between two sets of diffraction (Fig. 3(e); Fig. S20(b) in the ESM), which may be related to the twist angle compensating their mismatch in lattice and symmetry (tetragonal vs. hexagonal). Based on these evidences, a unit cell matching for the alignment between MOF and graphene is thus proposed and illustrated in Fig. 3(f). Compared with the reported FDM-23 or Ni-CAT-1 on single layer graphene system [83-85], the current CoTCP MOF-nitrogen doped graphene system have overcome the unmatched crystal symmetry and lattice constant.

Structure of graphene support in terms of morphology and functionality is a crucial factor for realizing such varied docking orientation. Although EG, NG, and NG’ all possessed 2-4 layers of graphene (Figs. S21-S23 in the ESM), NG’ was cleaved into much smaller sizes of ~1 μm via high-power ultrasonication compared to an average of 5-10 μm for NG (Fig. S24 in the ESM). Additionally, the functionality densities increased in the order of EG, NG, and NG’ judging from their Raman spectra (Fig. S25 in the ESM). Oxygen content in the graphene poses deleterious effect for the orientation, as MOF aligned randomly in MOF@EG and exhibited much more inferior crystallinity and morphology in MOF@GO (Fig. S6(c) in the ESM). The type of nitrogen dopant, however, plays a critical role in aligning MOF onto graphene. With nearly the same nitrogen occupancy (3.95% for NG vs. 4.05% for NG’), pyrrolic and graphitic-type nitrogen are found dominant in NG’ from XPS investigation (Figs. S13 and S16 in the ESM) [86, 87]. They may serve as orientation modulator for the formation of co-facial aligned MOF-graphene nanocomposite, thus maximizing their interface for the modulation to the active site.

![Figure 3](image-url)  
**Figure 3**  Alignment of MOF on NG’ substrate. (a) SEM image of MOF@NG’, in which MOF sheets and graphene sheets are illustrated by purple and yellow, respectively. (b) SAED of MOF@NG’, the intersected angle between MOF (guided by orange line) and NG’ (guided by green line) is ~38.5°. (c) Magnified diffraction pattern of the cyan squared region showing tetragonal secondary diffraction points of MOF around one spot belongs to NG’. (d) High-resolution TEM image of MOF@NG’ displaying tetragonal lattice fringes of MOF. (e) FFT of the whole region also showing both sets of diffraction patterns of MOF and NG; the intersection angle is 38.1°. (f) Proposed unit cell matching for the alignment between MOF and graphene. Grey, blue, red, purple spheres represent carbon, nitrogen, oxygen, and cobalt atoms, respectively. Green hexagonal frames represent graphene.
3 Conclusion
In summary, through tailoring the structure of graphene substrate in terms of their sizes and nitrogen functionality, docking alignment of MOF can be therefore controlled, and their ORR performance can be ultimately tuned in terms of their reaction kinetics, catalytic pathway, peroxide production selectivity and catalytic turnover. The interfacial alignment has overcome the ultra large lattice mismatch and symmetry mismatch, leading to a promoted dispersity of electronic states of the active centers, which preferentially ferry 2.24 electrons to O_2 and results in a high peroxide selectivity up to 93.4%. The new dimension of tuneability in both meso-scale structures and ORR performances, as well as the high peroxide selectivity comparable to the concurrent widely used anthraquinone oxidation (AO) method, rendering the MOF-graphene nanocomposites a new class of promising electrocatalyst for mild H_2O_2 production and other industrial on-site applications.

4 Experimental

4.1 Synthesis of MOF@NG
Few-layer graphene is synthesized through electrochemical exfoliation in two-electrode configuration with slight modification to previous reports [88]. The exfoliated graphene sheets were then ultrasonicated by a high-power ultrasonic probe (20 kHz, 120 W, Fisher Scientific) until a fully dispersed solution at a concentration of 2 mg mL$^{-1}$ is obtained. Then, TCPP (23.7 mg, 0.03 mmol) was dissolved in the graphene-DMF solution. The mixture was heated under refluxing condition for 20 h under N_2 protection, and then was cooled down to room temperature. Co(NO$_3$)$_2$$\cdot$6H$_2$O (23.7 mg, 0.03 mmol) was further added into the solution and sonicated for another 15 min. The resulting mixture was transferred to a 10 mL Teflon-lined stainless-steel autoclave and kept at 80 °C for 72 h. After cooling down to room temperature at a ramping rate of 0.05 °C·min$^{-1}$, the precipitates in the autoclave were collected and washed by ethanol for three times. The product was dried under vacuum and denoted as MOF@NG. Detailed synthesis protocol of MOF-graphene composites as control samples were described in the ESM.

4.2 Structural characterizations
The morphology of as-synthesized material is characterized by SEM (Phenom Pro and JEOL 7800F Prime) at various acceleration voltages. The crystallinity information was characterized by PXRD (Bruker D8 advance) using Cu Ka at $\lambda$ = 0.15406 nm. Selected area electron diffraction and 3-D electron diffraction was characterized by TEM (JEOL 2100 Plus) using amorphous carbon grid. Spherical aberration transmission electron microscopy and electron energy loss spectroscopy (EELS) inspection was performed by using a cold FEG JEOL Grand-ARM 300F, which was operated at 300 and 80 kV. XPS (Kratos Analytical) is adopted to characterize the chemical states of C, O, N, Co elements of the as-synthesized materials. Inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Fisher iCAP 7000) is used to quantitatively determine the amount of Co in each sample. All samples are firstly digested by concentrated nitric acid (guaranteed reagent). After that, sample solutions are prepared by diluting with 1% nitric acid and stored at 4 °C. Atomic force microscopy (AFM, Bruker Fastscaan/ICON) is used to investigate the thickness of EG, NG. Samples are firstly dispersed in DMF. The as-formed dispersion is drop casted onto Si substrate and dried under N$_2$ flow. Raman spectroscopy (Renishaw, Invia) is used to investigate vibrational state in the material with the laser power setting at 5%. N$_2$ adsorption/desorption isotherm of MOF-graphene nanocomposites are characterized using Quadrasorb under 77 K.

4.3 Electrochemical measurements
CV, electrochemical impedance spectroscopy (EIS), and chronocoulometry are conducted on an electrochemical workstation (CH Instrument, CHI660E) with a three-electrode configuration. Polarization curves and hydro-dynamic voltammetry are conducted on a bipotentiostat (CH Instrument, CH1760D) and analytical rotator (PINE instrument) with a three-electrode configuration. Catalysts modified glassy carbon (GC, 0.0707 cm$^2$) electrode is used as the working electrode. Ag/AgCl filled with saturated KCl solution is used as reference electrode, and Pt wire is the counter electrode, respectively. Detailed electrode preparation protocol for electrochemical characterization are provided in the ESM.

4.4 Constant potential production of H$_2$O$_2$
Constant potential electrolysis of O$_2$ is conducted in a homemade H-type electrochemical cell. The cathodic and anodic compartment is separated by Nafion-117 membrane (Dupont). Both chambers were filled with 0.5 M H$_2$SO$_4$ as the electrolyte solution. GC plate with an area of 1.0 cm × 1.0 cm is used as working electrode to support the catalysts. Ag/AgCl filled with saturated KCl solution is used as the reference electrode while Pt foil with an area of 2 cm$^2$ is used as the counter electrode. Prior to electrolysis, the GC plate is polished sequentially by 1.0, 0.3, and 0.05 μm alumina powder. For modification, 30 μL dispersed catalyst ink is drop-cast onto the glassy carbon plate and was dried under gentle N$_2$ flow. The modified GC plate is connected to a copper wire and sealed with silicone glue to prevent it from exposure in the electrolyte. High purity O$_2$ (99.99%) is purged into the electrolyte for at least 20 min to completely expel impurity gases. During electrolysis, potentials are kept at 0.4 V (vs. RHE) for 6 h. At certain time interval, 100 μL of the sample aliquots is taken from the cathode chamber and diluted by another 900 μL 0.1 M sodium acetate solution. The concentration hydrogen peroxide is then determined using Merck peroxide test kit.

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