From Metal–Organic Frameworks to Single-Atom Fe Implanted N-doped Porous Carbons: Efficient Oxygen Reduction in Both Alkaline and Acidic Media

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Abstract: It remains highly desired but a great challenge to achieve atomically dispersed metals in high loadings for efficient catalysis. Now porphyrinic metal–organic frameworks (MOFs) have been synthesized based on a novel mixed-ligand strategy to afford high-content (1.76 wt %) single-atom (SA) iron-implanted N-doped porous carbon (Fe$_{54}$-N-C) via pyrolysis. Thanks to the single-atom Fe sites, hierarchical pores, oriented mesochannels and high conductivity, the optimized Fe$_{54}$-N-C exhibits excellent oxygen reduction activity and stability, surpassing almost all non-noble-metal catalysts and state-of-the-art Pt/C, in both alkaline and more challenging acidic media. More far-reaching, this MOF-based mixed-ligand strategy opens a novel avenue to the precise fabrication of efficient single-atom catalysts.

Single-atom catalysts (SACs), a new research frontier in heterogeneous catalysis, have been intensively investigated in diverse reactions, including electrocatalysis, photocatalysis, and organic catalysis.[1–4] Given that only the coordinatively unsaturated metal atoms on the surface of solid catalysts contribute to the catalytic process, SACs would realize the utmost utilization of metal sites and thus greatly benefit the catalytic efficiency.[2] Furthermore, SACs are able to overcome the complicated multiple components in traditional supported metal catalysts and are regarded as ideal model catalysts to identify active sites and understand reaction processes at a molecular level.[2,3] Though great progress has been achieved, the rational fabrication of SACs with high metal loadings (> 1 wt %) remains a grand challenge.[4] Along with the introduction of more active metals, the optimized pore structure, large surface area, and excellent conductivity in SACs, which would facilitate mass/electron transfer, are also desirable to improve the activity.[5]

To meet these challenges, metal–organic frameworks (MOFs),[6] a class of crystalline porous materials constructed by metal ions/clusters and versatile organic linkers, are promising candidates. MOFs have been demonstrated to be great precursors/templates to produce porous carbon-based materials via pyrolysis.[7–8] More importantly, their periodic structures give rise to spatial separation of building units and thus inhibit potential agglomeration of metal sites during pyrolysis, enabling MOFs ideal precursors to create SACs. Currently, the reports on MOF-pyrolyzed materials are mostly focused on the regulation of their pore features and compositions.[7–8] The precise fabrication of active sites at the molecular level based on MOF precursors has been rarely reported. Very recently, zeolitic imidazolate frameworks (ZIFs) were reported as precursors to produce SACs based on structural tailorability, high nitrogen content, and the pore confinement effect.[46–9] Unfortunately, the microporous feature of ZIFs and their derivatives hamper mass transfer and the accessibility of the active site.[90] Therefore, it is imperative to develop SACs (providing efficient active sites) with hierarchical pores (benefitting mass transfer and active site accessibility) via the rational design of MOFs for improved catalytic performance.

With the above in mind, a porphyrinic MOF, PCN-222 (also called MOF-545 or MMPF-6)[20] featuring 1D mesochannels with a diameter of 3.2 nm (Supporting Information, Scheme S1), was chosen as a representative precursor. The ratio modulation between Fe-TCPP (TCPP = tetrakis (4-carboxyphenyl)porphyrin) and H$_2$-TCPP mixed ligands affords a series of isostructural MOFs, denoted as Fe$_x$-PCN-222 (x %: molar percentage of Fe-TCPP in both ligands) (Supporting Information, Scheme S2). The assembly of Fe-TCPP into 3D networks of Fe$_x$-PCN-222 effectively inhibits the molecular stacking, and the mixed-ligand strategy further expands the distance of adjacent Fe-TCPP ligands. Upon pyrolysis, the optimized Fe$_{54}$-PCN-222 can be converted into single-atom (SA) Fe sites implanted porous N-doped carbon, denoted as Fe$_{54}$-N-C, with the unique mesopore character (Scheme 1). By integrating single Fe atoms (highly active sites) and hierarchically porous structure with oriented mesopores (facilitating active site access and mass transfer), the optimized Fe$_{54}$-N-C exhibits superb oxygen reduction activity and ultrahigh stability, surpassing almost all reported...
non-noble-metal catalysts and the state-of-the-art Pt/C, under both alkaline and acidic conditions.

A series of Fe₅₇-PCN-222, including Fe₅₇-PCN-222, Fe₂₇-PCN-222, and Fe₅₇-PCN-222, have been prepared and all present similarly high surface areas with uniform pore size distribution (Supporting Information, Figures S1, S2). Taking Fe₅₇-PCN-222 as a representative, its typical type-IV N₂ isotherms suggest a Brunauer–Emmett–Teller (BET) surface area as high as 2062 m²·g⁻¹ and two types of pores, with sizes of 1.2 nm and 3.2 nm, corresponding to the triangular micro-channels and hexagonal mesochannels, respectively. SEM and TEM images present a uniform rod-shaped morphology with a diameter of about 200 nm (Figure 1a; Supporting Information, Figure S3a). The highly oriented mesopores in Fe₅₇-PCN-222 can be finally converted into Fe₅₇-N-C without Nb elements and Fe foil. d) EXAFS fitting for Fe₅₇-N-C (Supporting Information, Figure S8a). High-resolution N 1s spectrum can be fitted into five characteristic peaks, pyridinic N (398.5 eV), Fe₅₇-N-C (399.2 eV), pyrrolic N (401.2 eV), and oxidized N (402.7 eV), in which the Fe-N peak suggests the good inheritance of Fe₅₇-N-C, units from Fe-TCPP after pyrolysis (Figure 2a). The high-resolution Fe 2p spectrum with two relatively weak peaks centered at 710.7 eV (Fe2p₁/₂) and 723.1 eV (Fe2p₃/₂) illustrates partially oxidized Fe species in Fe₅₇-N-C, further supporting the existence of Fe₅₇-N-C species (Supporting Information, Figure S8b). The existence of abundant N (4.67 wt %) and high loading of Fe (up to 1.76 wt %), strikingly consistent with XPS results, have been

any identifiable metallic particles, and the rod shape and highly oriented mesopores in Fe₅₇-PCN-222 are inherited in the resultant Fe₅₇-N-C to a large extent (Figure 1b–e). N₂ sorption for Fe₅₇-N-C suggests its high BET surface area of 532 m²·g⁻¹ and the evident hysteresis loop (P/Pe: 0.6–0.8) indicates its mesoporous structure (Supporting Information, Figure S5a), which is recognizable in the cross-section SEM and TEM images (Figure 1c–e; Supporting Information, Figure S3b). The pore size distribution analysis further manifests its hierarchical pores in 1–2 nm and about 9 nm diameters (Supporting Information, Figure S5b). It is generally believed that micropores would increase the density of active sites and mesopores are beneficial to the mass transfer, thus improving catalytic activity.

The powder X-ray diffraction (PXRD) pattern of Fe₅₇-N-C presents two broad diffraction peaks in the ranges of 20–30° and 40–45°, corresponding respectively to the (002) and (101) reflections of graphitized carbon, and no peak associated with iron-based species can be detected (Supporting Information, Figure S6). The Raman scattering spectrum for Fe₅₇-N-C gives low intensity ratio (I_d/I_g = 0.95) of D band (ca. 1345 cm⁻¹) and G band (ca. 1590 cm⁻¹), further indicating its high graphitization degree, which favors electron transfer (Supporting Information, Figure S7). X-ray photoelectron spectroscopy (XPS) results reveal that C, N, O, and Fe elements are included in Fe₅₇-N-C (Supporting Information, Figure S8a). High-resolution N 1s spectrum can be fitted into five characteristic peaks, pyridinic N (398.5 eV), Fe₅₇-N-C (399.2 eV), pyrrolic N (401.2 eV), and oxidized N (402.7 eV), in which the Fe-N peak suggests the good inheritance of Fe₅₇-N-C, units from Fe-TCPP after pyrolysis (Figure 2a). The high-resolution Fe 2p spectrum with two relatively weak peaks centered at 710.7 eV (Fe2p₁/₂) and 723.1 eV (Fe2p₃/₂) illustrates partially oxidized Fe species in Fe₅₇-N-C, further supporting the existence of Fe₅₇-N-C species (Supporting Information, Figure S8b). The existence of abundant N (4.67 wt %) and high loading of Fe (up to 1.76 wt %), strikingly consistent with XPS results, have been
quantified by elemental analysis and inductively coupled plasma atomic emission spectrometry (ICP-AES; Supporting Information, Table S1, S2). Aberration-corrected HAADF-STEM observation unambiguously identifies single Fe atoms from the bright spots in randomly selected areas, but no Fe particles are found (Figure 1f; Supporting Information, Figure S9).

In addition to the localized microstructural information above, X-ray absorption spectroscopy (XAS) was further used to unveil the electronic and structural information of Fe-involved species in Fe\textsubscript{54\texttextsuperscript{54}}-N-C. From the Fe K-edge XANES spectra, the energy absorption threshold of Fe\textsubscript{54\texttextsuperscript{54}}-N-C locates between Fe foil and Fe\textsubscript{2}O\textsubscript{3} and is closer to that of FeTTPPCl and FePc, implying the positively charged Fe\textsuperscript{4+} stabilized by N atoms in Fe\textsubscript{54\texttextsuperscript{54}}-N-C (Figure 2b). Furthermore, the absence of the edge peak at about 7171.1 eV, which is the fingerprint of \(D_{4h}\) symmetry, suggests the lower symmetry of Fe-N TA\textsubscript{KOH} (inset: K-L plots and electron transfer number). d) Stability and dynamical behaviour can be detected, manifesting that the evolution of Fe\textsubscript{54\texttextsuperscript{54}}-N-C can be successfully obtained (Supporting Information, Scheme S3c). First, the mixed ligands of H\textsubscript{2}TCPP and Fe-TCPP (Fe\textsuperscript{2}N\texttextsuperscript{2} coordinated by Na\textsubscript{2} atoms) are employed to construct PCN-222, its 3D skeleton composed of metal nodes and organic ligands creates the average distance (d) of adjacent Fe-TCPP ligands by simply changing the ratio (denoted as Fe\textsubscript{2-2}PCN-222, Scheme S3). Conversely, when more Fe-TCPP is loaded and Fe\textsuperscript{2}Fe distance is shortened, Fe aggregation would be inevitable during the MOF pyrolysis (Supporting Information, Scheme S3b). When the distance reaches to a critical value (for example, in Fe\textsubscript{2-2}PCN-222), the formation of Fe NPs is effectively inhibited in pyrolysis process. Upon the ZrO\textsubscript{2} removal, single Fe atoms anchored N-doped carbon can be successfully obtained (Supporting Information, Scheme S3b). In addition to the localized microstructural information above, X-ray absorption spectroscopy (XAS) was further used to unveil the electronic and structural information of Fe-involved species in Fe\textsubscript{54\texttextsuperscript{54}}-N-C. 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In view of the intrinsic activity of Fe-N\textsubscript{4} sites for efficient oxygen reduction reaction (ORR),\textsuperscript{[13, 55-57] the performance of Fe\textsubscript{54\texttextsuperscript{54}}-N-C was first investigated in 0.1 m KOH. The CV curve of Fe\textsubscript{2}N-C sample (obtained from Fe\textsubscript{2}Pc-PCN-222) without Fe doping displays a much lower oxygen reduction peak than that of Fe\textsubscript{54\texttextsuperscript{54}}-N-C and FeNP\textsubscript{2}N-C, reflecting an indispensable role of Fe-N sites on boosting ORR activity (Supporting Information, Figure S12). Linear sweep voltammetry (LSV) curves indicate the best performance of Fe\textsubscript{54\texttextsuperscript{54}}-N-C among all related catalysts, featuring a higher half-wave potential (\(E_{1/2} = 0.891\) V) than Fe\textsubscript{2}Pc-N-C (0.795 V), Fe\textsubscript{2}Pc-N-C (0.889 V), and the commercial Pt/C (0.848 V) (Figure 3a,b). Furthermore, the superb activity of Fe\textsubscript{54\texttextsuperscript{54}}-N-C is supported by the much higher kinetic current density (J\textsubscript{k}) at 0.85 V (23.27 mA cm\textsuperscript{-2}) than that of Fe\textsubscript{2}Pc-N-C (0.98 mA cm\textsuperscript{-2}), Fe\textsubscript{2}Pc-N-C (18.43 mA cm\textsuperscript{-2}) and Pt/C (5.61 mA cm\textsuperscript{-2}), signifying its much more favorable kinetics (Figure 3b). The LSV curve of Fe\textsubscript{54\texttextsuperscript{54}}-N-C/ZrO\textsubscript{2} was also obtained and its inferior performance to Fe\textsubscript{54\texttextsuperscript{54}}-N-C illustrates the importance of HF etching (Supporting Information, Figure S13). Furthermore, Fe\textsubscript{54\texttextsuperscript{54}}-N-C also shows better activity than mix-Fe-N-C, which is derived from the physical mixture of Fe-TCPP and H\textsubscript{2}TCPP, further demonstrating the superiority of MOFs as precursors (Supporting Information, Figure S13). All of the above results suggest that Fe\textsubscript{54\texttextsuperscript{54}}-N-C possesses the optimal activity.

To gain more insight into the electron-transfer mechanism of Fe\textsubscript{54\texttextsuperscript{54}}-N-C, LSV curves at different rotating rates of rotating disk electrode (RDE) were recorded (Figure 3c). The K-L plots obtained from the LSV curves exhibit excellent linearity, presenting the first-order reaction kinetics for ORR with a potential-independent electron transfer rate (Figure 3c, inset). Based on the K-L equation, the electron transfer number is determined to be about 4.0, manifesting an ideal 4 e\textsuperscript{-} ORR mechanism. Rotating ring disk electrode (RRDE)
measurement for Fe₅ₓ-N-C was further performed to show the very low (\(<5.5\%\)) H₂O₂ yields with an electron transfer number larger than 3.9 (Supporting Information, Figure S14), similar to the results from the K-L plots. Furthermore, the negligible decay of activity after stability tests and the methanol addition experiments for Fe₅ₓ-N-C demonstrate its excellent durability and strong tolerance against methanol-crossover effect, in stark contrast to the significant decline of Pt/C (Figure 3d; Supporting Information, Figure S15). The results suggest that Fe₅ₓ-N-C possesses the best ORR performance among all non-noble metal catalysts ever reported under alkaline condition (Figure 3a–d; Supporting Information, Table S4).

The excellent ORR performance of Fe₅ₓ-N-C in alkaline media prompted our further exploration under the more challenging acidic condition. Strikingly, superior ORR activity with a $E_{1/2}$ of 0.776 V in 0.1M HClO₄ can be achieved for Fe₅ₓ-N-C, which is much higher than that of Fe₅₋N-C, Fe₃₋N-C, Fe₃₋N-C/ZrO₂, mix-Fe-N-C and even comparable to (5 mV lower) that of benchmark Pt/C (Figure 3e; Supporting Information, Figures S16, S17). The high kinetic current density (9.60 mA cm⁻²) at 0.75 V manifests the favorable kinetics of Fe₅ₓ-N-C (Supporting Information, Figure S16b). Further RRDE test suggests a H₂O₂ yield lower than 1.0% with an ideal 4 e⁻ transfer process, in consistence with the result from K-L plots (Supporting Information, Figure S18). Moreover, Fe₅ₓ-N-C exhibits excellent durability with only 6 mV decay after 5000 cycles and 4% drop after the i-t test, which is much better than for Pt/C, which is possibly due to the strong affinity between atomic Fe sites and coordination N within carbon (Supporting Information, Figure S19a,c,e). Additionally, Fe₅ₓ-N-C demonstrates a superior tolerance to the crossover effect of methanol compared with Pt/C, making it a promising candidate for direct application in methanol fuel cells (Supporting Information, Figure S19b,d,f). Furthermore, a preliminary constant-current test for Fe₅ₓ-N-C was conducted in real fuel cell device (Supporting Information, Figure S20). It is noteworthy that, although much endeavor has been devoted, a very limited number of catalysts were reported simultaneously possessing comparable performance with Pt/C in both alkaline and acidic media, further highlighting the conspicuous advantage of the single Fe atom-involved Fe₅ₓ-N-C over other reported catalysts (Supporting Information, Table S5).

To understand the origin of the excellent ORR performance of Fe₅ₓ-N-C, more investigations were carried out. The SCN⁻ (0.01mol), with strong affinity to Fe ion, was employed as a probe to poison Fe-N₄ sites.⁹⁸ As a result, the half-wave potential of Fe₅ₓ-N-C for ORR in 0.1M HClO₄ decreased significantly by 50 mV (Figure 3f). The SCN⁻-poisoned electrode was subsequently rinsed with pure water and re-measured in 0.1M KOH. The $E_{1/2}$ of the first LSV curve negatively shifts by 10 mV as compared to the original catalyst. With increasing cycle numbers, the LSV curves gradually overlap with the original one obtained before SCN⁻ treatment, which should be ascribed to the desorption of SCN⁻ from Fe site in 0.1M KOH (Supporting Information, Figure S21). The activity recovery accompanied by the release of SCN⁻ from blocked Fe-N₄ sites clearly reflects that single Fe atoms are responsible for the high ORR activity of Fe₅ₓ-N-C.

Furthermore, the hierarchically porous structure in Fe₅ₓ-N-C is generally believed to affect the accessibility of active sites and mass transfer in catalytic process. Small-angle X-ray scattering (SAXS) for Fe₅ₓ-N-C gives a broad hump between 0.28 to 0.84 nm⁻¹, hinting the ordering of pore structure with size distribution from 7 to 22 nm (Figure 3g), in good agreement with the above microstructure observation and N₂ sorption data (Figure 1d,e; Supporting Information, Figure S5). It should be pointed out that although reported MOF-derived carbon materials exhibit high surface areas, their pore structures are usually disordered and non-interconnected after uncontrollable pyrolysis, which is not favorable to mass transfer in catalysis.⁹⁷ Therefore, the development of porous carbon with oriented channels, which remains to be a long-term target yet a great challenge to date, has been achieved for the first time. The hierarchically porous Fe₅ₓ-N-C, possessing abundant micropores (accommodating high-density Fe-N₄ active sites) and open mesoporous channels with particular orientation (facilitating the high-flux mass transfer), would greatly accelerate the ORR process (Supporting Information, Figure S22). This is in sharp contrast to sluggish mass transfer in traditional MOF-derived carbons with non-interconnected pores. Taking jointly the above Fe-N₄ active sites and pore structure merits, we may come to the conclusion that single-atom Fe sites accessible by hierarchial pores in Fe₅ₓ-N-C mainly contribute to the superb ORR performance.

In summary, we have developed a novel mixed-ligand strategy in MOF system to fabricate SACs. The ratio optimization of the mixed porphyrin ligands with and without Fe⁺⁺ centers gives rise to long spatial distance of Fe⁺⁺ ions in the MOF skeleton, favoring the formation of single Fe atoms upon pyrolysis. Benefiting from periodic and tailorable MOF structures, the spatial distance control of Fe⁺⁺ in porphyrinic MOFs effectively suppresses the Fe aggregation during pyrolysis, leading to atomic dispersion of Fe with a high loading (1.76 wt %) in porous carbon. Thanks to the single-atom Fe sites (superior activity), hierarchically porous structure (accessible active sites) with oriented mesopores (fast diffusion of O₂ and electrolyte), and high conductivity (fast electron transfer), Fe₅₋N-C demonstrates excellent ORR performance in both alkaline and acidic media, surpassing any other reported non-noble-metal catalysts and even the Pt/C. In light of the tremendous diversity and tailorability of MOFs, this work opens up an avenue to the rational synthesis of efficient SACs via multiscale control.

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Conflict of interest

The authors declare no conflict of interest.

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