Identify the impact of the covalent-bonded carbon matrix to FeN4 sites for acidic oxygen reduction

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Article

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Abstract

Atomically dispersed Fe and N co-doped carbon (Fe–N–C) catalysts exhibited superior acid oxygen reduction reaction (ORR) activities and recently been considered as the most promising alternatives to the benchmark Pt-based catalysts for proton exchange membrane fuel cells. The atomic configuration between Fe, N and C is one of the key factors to affect ORR activity. However, the traditional synthetic methods that rely on pyrolysis of the mixtures of Fe, N and C precursors often result in the plurality of local environment for the FeN\textsubscript{x} site. Unveiling the effect of covalent-bonded carbon matrix to FeN\textsubscript{4} sites towards ORR activity is important but still a great challenge due to inevitable connection of diverse N as well as random defects during the pyrolysis process. Here, we report a proof-of-concept study on the evaluation of covalent-bonded carbon environment connected to FeN\textsubscript{4} sites on their catalytic activity via pyrolysis-free approach. Basing on the closed π conjugated phthalocyanine-based intrinsic covalent organic polymers (COPs) with well-designed structures, we directly synthesized a series of atomically dispersed Fe-N-C catalysts with various pure carbon environment without any N doping directly connected to the same FeN\textsubscript{4} sites. Experiments coupled with density functional theory demonstrate that the catalytic activities appear a volcano plot with the increase of degree of delocalized π electrons from the carbon matrix. The delocalized π electrons changed anti-bonding d-state energy level of the single FeN\textsubscript{4} moieties, hence tailored the adsorption between active centers and oxygen intermediates and altered the rate-determining step of oxygen reduction reaction.

Introduction

The acutely increase in the concentration of carbon dioxide (CO\textsubscript{2}) in atmosphere has intensiefed the urgent need for clean and sustainable energy technologies to achieve carbon neutralization as soon as possible.\textsuperscript{1} Proton exchange membrane fuel cells (PEMFC) are typical clean energy conversion devices, whereas their sluggish oxygen reduction reaction (ORR) at cathode require highly efficient electrocatalysts to ensure the progress of the reaction.\textsuperscript{2,3} Iron and nitrogen co-doped carbons (Fe-N-C) electrocatalysts containing atomically dispersed FeN\textsubscript{4} moieties have been ever-increasing as the most promising alternative to commercialized platinum group metal due to maximized atom utilization and their desired activity.\textsuperscript{3–8} It has exhibited catalytic activity approaching that of platinum in acids media as well as inspiring performance in PEMFCs.\textsuperscript{9–12}

Recently, some advanced characterization techniques such as Mössbauer spectra\textsuperscript{13–15}, X-ray absorption near-edge structure (XANES)\textsuperscript{10,14,16} or annular dark-field scanning transmission electron microscope (ADF-STEM) analysis\textsuperscript{8,11,17,18} have enabled identification for Fe-N-C atomic structure as well as determination towards its correlation with catalytic properties. Meanwhile, \textit{ab initio} investigations have also deciphered the root of high instinct activity of MN\textsubscript{x}C\textsubscript{y} moieties from the perspective of electron states based on descriptor-based approach.\textsuperscript{19–21} In general, the electrocatalyst activity is restricted to the number and intrinsic activity of active sites.\textsuperscript{12,22} Studies manifest that the distinction between a high-
loading and a low-loading electrocatalyst may be less than 3 orders of magnitude, however, the
distinction in intrinsic activity between a superior electrocatalyst and an inferior electrocatalyst can
overwhelmingly exceeds 10 orders of magnitude.23 The importance of the intrinsic activity of the active
site is self-evident. Unfortunately, the nature of the active site has remained elusive and various FeN \_x C \_y
sites were proposed as active centers. In particular, the FeN\_4C\_12, FeN\_4C\_8 and FeN\_4C\_10 moiety regularly
separately function as typical active configuration,14,24–28 and thus frequently were employed as a
benchmark model for active-site identification in the Mössbauer and XANES analysis.

Recently, Frédéric et al. have also demonstrated that their durability is inconsistent in the oxygen
reduction process: the FeN\_4C\_12 moiety with a high-spin eventually inverted into iron oxides; whereas
FeN\_4C\_10 moiety with low- or intermediate-spin remained unvaried after 50 hours operation.13 Moreover,
Wu et al.9,29 and Wang et al.30 have together demonstrated that FeN\_4C\_8 and FeN\_4C\_12 moieties are more
apt to absorb oxygen and proceed four proton-electron transfer in oxygen reduction by electrochemical
measurement coupled with density functional theory (DFT), compared to FeN\_4C\_10 moiety. These studies
implicitly indicate the carbon matrix connected to FeN\_4 sites has a nonnegligible effect on instinct
activity of active sites. Nonetheless, the significance about carbon coordination environment connected
to FeN\_4 moieties has not been enough touched,31 and further in-depth studying still exists several critical
issues: (1) The high-temperature pyrolysis of Fe, N and C precursors hardly guarantee precisely control of
pure local carbon environment due to the inevitable connection with diverse N sometime along with Fe;
(2) The effect of randomly introducing defects anchored to the carbon plane is likewise inevitable.

Most recently, our groups have developed a pyrolysis-free strategy to prepare intrinsic conductive
catalytic materials with well-designed FeN\_4 centers, depending on the platform of covalent organic
polymers (COPs)32–35. The tailorability of building blocks as well as inherent durability indwelling in
covalent bonds endows them with excellent electrocatalytic characters.36–44 Here, we report a proof-of-
concept study on the evaluation of carbon environment covalent-connected to FeN\_4 sites on their
catalytic activity via this pyrolysis-free approach. Specifically, we designed a series of fully \pi-conjugated
COPs, which contained well-defined FeN\_4 configurations whereas discrepant delocalized conjugated
carbon matrix connected to FeN\_4 sites. The electrochemical tests demonstrated that the oxygen reduction
activities of the four COPs exhibited a volcano plot with the expansion of the carbon skeletons. Further
experiments preliminarily indicated the relationship between delocalized \pi-electrons (DDE) in carbon
matrix adjacent to FeN\_4 sites and electrocatalytic activity. The detailed DFT demonstrated that \pi-
conjugated ligand configurations connected to FeN\_4 sites relocate electronic filling of antibonding states
in Fe atom and modulate their electronic configurations, hence altered the rate-determining step (RDS) in
ORR process. This study not only provides novel insights into the understanding ORR mechanism but
also inspires people to seriously consider the effects of long-range electronic configuration in the carbon
plane on active moieties.

**Results**
Synthesis of COPs with well-defined FeN$_4$ configuration and ascending DDE. Instead of a high-temperature pyrolysis process randomly riveting Fe in the carbon matrix with inevitable connection with diverse N moieties, we adopted symmetrical acid anhydride or cyan groups as reactive groups to prepare-oriented iron, nitrogen co-coordinated single-atom catalysts with well-designed configuration. Briefly, we deliberately assembled Tetracyanoethylene, Pyromellitic dianhydride, 1,4,5,8-Naphthalenetetracarboxylic dianhydride, and 3,4,9,10-Perylenetetracarboxylic dianhydride with Fe centers into extended sp$^2$ carbon networks by solid phase synthesis, denoted by COP-Ene, COP-Ppcfe, COP-Nap, and COP-Pyr, respectively (Fig. 1). The $^{13}$C solid-state nuclear magnetic resonance (NMR) spectra (Supplementary Fig. 1) confirmed that four structures have been successfully synthesized, where C = N links connecting building block were smoothly arranged in corresponding networks, which was also favored by stretch vibration peaks of C = N covalent bonds at $\sim$ 1600 cm$^{-1}$ in Fourier transform infrared spectroscopy (FT-IR spectra, Supplementary Fig. 2). More detailed characterization can be found in the supplementary materials.

Unlike conventional Fe-N-C catalysts, our pyrolysis-free strategy escapes unpredictable active-site configuration as well as accompanying diverse catalyst activities due to the pyrolysis process. The as-prepared COPs possess exclusive single Fe atom constrained in the conjugated 2D networks. Meanwhile, building blocks were orderly connected by rigid covalent bonds. As expected, Fe and N atoms kept highly homogeneous distribution in the carbon matrix for four as-synthesis samples, which was demonstrated by the high dispersion image of Fe and N atoms in high-resolution transmission electron microscopy (HRTEM, Fig. 2a, 2b and Supplementary Figs. 4–8). Furthermore, we took COP-Ppcfe sample as a typical case and performed the aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) test, which identified single Fe atoms from monodispersed bright spots images without metal clusters being observed (Fig. 2c and Supplementary Fig. 9). To verify the coordination environment and chemical states of Fe atom in as-synthesis sample, we carried out Fe K-edge analysis of X-ray absorption fine structure (XAFS). The COP-Ppcfe sample was demonstrated with high similarity to FePc benchmark, exhibiting dominated peaks corresponding to the Fe-N ($\sim$ 1.53 Å) and Fe-N-C ($\sim$ 2.7 Å) scattering paths (Fourier transform-extended XAFS spectra, Fig. 2d and Supplementary Fig. 11). Besides, a predominant intensity maximum of wavelet transform (WT) contour plots of Fe K-edge appearing at approximately 4.0 Å$^{-1}$ in $k$ space, which assigned to Fe-N(O) coordination (Fig. 2e), synergistically confirmed the existence of mononuclear Fe atoms. EXAFS quantitative least-squares fitting analysis further supported that the constructed active centers (Fig. 2f) were anastomotic with experimental EXAFS spectra of COP-Ppcfe samples, i.e., single Fe center coordinated with four N atoms and one adsorbed O atom (Fig. 2f and Supplementary Table 1).

Although these as-synthesized COPs present semblable FeN$_4$ coordination structure, they have obviously discrepant linked-carbon environment adjacent to FeN$_4$ sites. As investigated by FT-IR spectra (Supplementary Fig. 2), sequential ascending C = C stretching vibrations at $\sim$ 1400 cm$^{-1}$ manifest successively incremental planar $\pi$-electron abundance in four polymers. In addition, continuously ascending deconvoluted $\pi-\pi^*$ peaks in C1s XPS spectra (Fig. 2g) consistently demonstrated that the DDE gradually increases with carbon skeleton covalent-connected FeN$_4$ sites in as-synthesized COPs. The
typical sp² carbon conjugated peak at 284.3 eV in C1s XPS spectra is closely related to the transition of \( \pi \)-band (1s \rightarrow \pi^*),\textsuperscript{49,50} therefore, full-width at half maxima value (FWHM) of conjugated C = C bond peaks can work as a criterion to quantificationally evaluate corresponding delocalization of \( \pi \) electrons in carbon matrix.\textsuperscript{51} The narrower FWHM embodies fewer topological defects, higher DDE as well as stronger electron-donating capability in the carbon plane. As expected, observed significant shrink of FWHM along with the extension of sp² carbon-conjugated frameworks doubtlessly demonstrates that the DDE indwelled in polymers obviously increases (Fig. 2h). Based on the elemental analysis results of the C element, the gradually increasing C atom contents (C wt.%, 33.18%, 47.53%, 56.65% and 66.65% for COP-Ene, COP-Ppcfe, COP-Nap and COP-Pyr, respectively) also consistently reflects structural expansion in carbon skeletons. Therefore, a series of FeN₄ sites with defined configurations yet increasingly extending surrounding carbon networks were design-oriented and systematically synthesized.

**Oxygen reduction performance and adsorption energy evaluation.** The ORR measurements for four COPs were carried out in a harsh acidic medium (0.1 M HClO₄) to evaluate their performance discrepancy (Fig. 3a). The Linear sweep voltammetry (LSV) curves revealed that the catalytic activity of the COP-Ppcfe sample was significantly ahead among the four COP samples, followed by COP-Ene; frustrating half-wave potentials mean that COP-Nap and COP-Pyr samples are difficult to undergo acidic oxygen reduction reaction. The turnover frequency (TOF) and mass activity (Ma) per mass of metal at 0.7 V versus RHE were further investigated to compare the discrepancy in the electrochemical intrinsic activity of the active sites in the four as-synthesized COPs. As observed in Fig. 3b, both TOF and Ma exhibit a volcano plot that first increases and then decreases with extension of sp² carbon skeletons connected to FeN₄ sites. In addition, the comparison in kinetic current density (\( J_k \)) of as-synthesized four COPs also embodies the volcano relationship between the electrochemical kinetics and DDE in carbon matrix connected to FeN₄ sites (Supplementary Fig. 18). Aiming at this consistent volcano relationship plot, we next try to explain it from the adsorption strength of the reactant species obtained experimentally.

Theoretically, due to continuous multi-proton/-electron coupling reaction in the ORR process, large overpotential is ultimately stemmed from the mismatch of the adsorption energy.\textsuperscript{52} Due to the restriction of scaling relations in oxygen intermediates, a volcano relationship\textsuperscript{53} regularly emerges between ORR activity and adsorption energy, quantitatively illustrating Sabatier principle\textsuperscript{19,20,54}. Namely, the binding between catalysts and oxygen intermediates is neither too strong nor too weak. However, the direct measurement for adsorption strength in experiment is a great challenge. Promisingly, this plight was eliminated by migrations of Fe²⁺/³⁺ redox potential (\( E_{\text{redox}} \)).\textsuperscript{55} As an effective indicator, the high \( E_{\text{redox}} \) manifests weak Fe-O binding, and vice versa. As observed, a negative growth tendency in \( E_{\text{redox}} \) appears with an order of COP-Ene, COP-Ppcfe, COP-Nap, and COP-Pyr in square wave voltammetry experiment (Supplementary Fig. 19), which indicates their growing adsorption strengths along with the extension of sp² carbon skeletons connected to FeN₄ sites.
Subsequently, we theoretically preliminarily identified the reliability about above catalytic activity and adsorption strength. As observed, the theoretical $U^{on-set}$ potential by DFT calculations is consistent with experimental results (Fig. 3d). Specially, the negative $U^{on-set}$ potentials of COP-Nap and COP-Pyr samples imply that higher electrode potentials are required to overcome the grand barrier and afterward occur four-electron reaction. Meanwhile, the Tafel slopes were observed to surge from COP-Ppce to COP-Nap sample (50.42 v.s. $112.65 \text{ mV} \cdot \text{decade}^{-1}$), which mainly was ascribed to the sudden oxytropism in metal sites (Fig. 3c). As a result, the sluggish the desorption of OH* (OH* + H* + e$^-\rightarrow$H$_2$O) into RDS (vide infra, Supplementary Fig. 20), severely restricting the overall oxygen reduction kinetics. The experimental exchanged current densities ($j_{0ept}$) directly scaled with theoretic $\Delta G_{\text{max}}^{-1}$ (Fig. 3e) also indicates transformation about the RDS. Certainly, in addition to the four-electron reaction, O$_2$ also can be reduced to H$_2$O$_2$ through incomplete reduction. Therefore, the tropism of OOH* intermediates towards O*, described by $\Delta G_{O*} - \Delta G_{\text{OOH}*}$, is a criterion of the selectivity of O$_2$. A more negative value indicates that oxygen is more facilely cleaved and completely reduced to H$_2$O. Therefore, as expected, a linear relationship between $\Delta G_{O*} - \Delta G_{\text{OOH}*}$ and H$_2$O$_2$ yields (obtained by rotation ring-disk electrode) can be found (Fig. 3f and Supplementary Fig. 21). Hereto, these results manifest that the oxygen reduction activities of the four COPs exhibit a volcano plot with the expansion of the carbon skeletons regardless in experiment or theory.

The relationship between DDE and activity demonstrated by experiments. Theoretically, the electron-donating capability of electrocatalysts determines the interfacial electronic transfer with oxygen intermediates, with an extensive effect on the oxygen reduction. Generally, a catalyst with a small work function is more apt to undergo four proton-electron coupled steps, because electrons are effortless to escape from the catalyst surface. According to the Ultraviolet Photoelectron Spectroscopy (UPS) spectra (Supplementary Figs. 22–23), the obtained work function values ($\phi$) markedly decreased along with the increment of DDE in the carbon skeleton, thus FeN$_4$ sites with larger DDE are easier to react with oxygen. Moreover, since the valence orbital is involved in the binding with associate oxygen intermediates, we further evaluated the valence band energy level, which are determined to -1.37, -1.36, -1.27, and -1.02 eV relative to the Fermi level ($E_f$, Fig. 4a), respectively, for four COP-based catalysts. The obvious upshift of valence orbital reflects an inherent discrepancy of d-orbital level ($E_d$) along with DDE in the carbon matrix. Therefore, the valence band level is employed as a criterion for evaluating the transition of the d-orbital level of the monometallic Fe atom in the synthesized COPs (vide infra).

In fact, the changes in adsorption are a direct cause towards the ORR activity discrepancy. Therefore, we first associated oxygen adsorptions with DDE. As aforementioned, the DDE was obtained based on FWHM of C=C bond (284.7 eV) while oxygen adsorption was quantified by Fe$^{2+/3+}$ redox potential ($E_{\text{redox}}$). In order to be clearer and more intuitive, we then employed FWHM$^{-1}$ and $E_{\text{redox}}^{-1}$ to express intensity of DDE and adsorption strength: the larger their value, the stronger their strength. As observed from Fig. 4b, an increasing linear tendency between the $E_{\text{redox}}^{-1}$ and FWHM$^{-1}$ emerges, manifesting that
the DDE in the carbon matrix connected to the FeN₄ sites is decisive to their adsorption strength. On the other hand, since d-orbital electronic states inherently determined the catalytic activity of FeN₄ sites, thereby the relationship between the valence band level and adsorption was next regressed and fitted (Fig. 4c). As a result, lifting valence band level ultimately induces stronger interactions between active sites and oxygen intermediates, which also corresponds to the drastically reduced work function values (Fig. 4a). Therefore, we have speculated that the DDE adjusts oxygen reduction activity largely by changing the valence-band or d-orbital electrons in active centers. As a result, although configurations of FeN₄ sites are similar, their electronic states are different and thus their intrinsic activities may also be diverse. Subsequently, we constructed the relationship between TOF and FWHM⁻¹. We noted that intrinsic catalytic activities in FeN₄ catalysts presented an approximate volcano plot with the increment of DDE near FeN₄ sites (Fig. 4d). The phenomenon is likely to be ascribed to that the relationship of DDE, d-orbital level, and adsorption are unidirectionally determined in sequence (Figs. 4b-c), while electrocatalytic activity and adsorption are restricted by Sabatier principle (Fig. 4e). Hereto, we speculate that the DDE in the carbon matrix connected to the FeN₄ sites affects the d-state level in the single iron atom, and thus tailors the adsorption strength between the moieties and oxygen intermediates; eventually, catalytic activity appears a volcano plot with DDE.

Electronic structure analysis and mechanism study. To comprehensively study the in-depth effect of the adjacent carbon environment on the ORR performance, we accomplished detailed DFT calculations. In addition to the four COPs discussed above, we further in silico designed two more types of asymmetric carbon matrix structures connected to FeN₄ sites that are difficult to synthesize experimentally, named as COP-Nap1 and COP-Nap2, to study mechanism of DDE towards FeN₄ electronic structures (Fig. 5a). The climbing total electron numbers observed from the total density of states (TDOS, Supplementary Fig. 25) and electronic localization functions (ELF) diagrams (Supplementary Fig. 26) theoretically demonstrated the DDE in carbon matrix is gradually increasing with the expansion of the carbon skeleton connected to FeN₄ sites, which also inosculates with the FWHM of conjugated C=C bond peaks experimentally (Fig. 2g-h). The Bader charge population analysis manifests that these carbon matrix functions as a ‘motor’, gradually donating more electrons from themselves into FeN₄ sites thereby altering the net charge of the single Fe atom (Fig. 5b), strengthening iron oxophilicity and binding with adsorbates. Generally, for most Fe-N-C catalysts, protonation of O₂* (O₂* + H⁺ + e⁻ → OOH*) or desorption of OH* (OH* + H⁺ + e⁻ → H₂O) is RDS in oxygen reduction. The protonation of O₂* is the initial step and directly affects the next electron transfer. Therefore, we initially focused on the changes in the electron states of oxygen adsorption to unveil the effect of the DDE on oxygen reduction. Among six systems, COP-Ene, COP-Ppcfe, COP-Nap1 and COP-Nap2 display an end-on adsorption models, whereas COP-Nap and COP-Pyr exhibit side-on adsorption models (Fig. 5c). For FeN₄ sites with abundant DDE, such as COP-Nap and COP-Pyr samples, the Fe atom occupied orbitals transfer more electrons into anti-bonding orbitals of O₂ via two O atoms, thereby adsorbed dioxygen adopts side-on configuration on Fe atom (transferred electrons ~ 0.65 |e| in side-on configuration v.s. 0.3–0.4 |e| in end-on configuration). Partial density of
state analysis (Fig. 5d) indicates that electrons mainly transfer from 3dxz and 3dyz orbitals in Fe atom to 1π* orbitals in dioxygen through π-back bonding. In contrast, for other COPs, superoxide species form when O2 molecules are absorbed on Fe atom by end-on interaction, where electrons mainly transfer from the Fe 3dz^2 orbitals to the oxygen 1π* orbitals and form σ bonds. These completely antithetical manners imply that even if active sites possess semiable geometric structure, their electronic transfer paths and bonding patterns may be completely different (Fig. 5d and Supplementary Figs. 27–28).  

Distinguish from the interaction between Fe atoms and O2*, the 1π valence orbital in lone pair O 2px, 2py electrons, and 3σ orbital in H 1s - O 2p_x of OH* intermediate occurred renormalizing when OH* reacted on 3d orbitals of Fe atom (Fig. 5e and Supplementary Fig. 29). This coupling makes their energy level split into bonding states under the Fermi level and antibonding states above the Fermi level (Fig. 5f). The higher the energy of Ed relative to Ef means the less electronic occupancy in the antibonding states and corresponding stronger adsorption. This precise tailor pointing at Ed energy level was also validated by a series of increasing absolute value of integrated crystal orbital Hamilton population value (ICOHP, Fig. 5e). Thus, it can be concluded that although the d-orbitals electron in FeN4 sites determines the progress of ORR by affecting oxygen intermediates, π-conjugated ligand configurations connected to FeN4 sites can relocate electronic filling of antibonding states in Fe atom and modulate electronic configurations of FeN4 sites.

Finally, we studied ORR pathways and catalytic activities of the six well-defined catalytic models in oxygen reduction process. Although four-electron/ proton coupling reaction theoretically includes the associative mechanism and the dissociative mechanism, the grand barriers of directly breaking the O = O bond means that the dissociative mechanism for uniform and continuous single-atom catalysts is insurmountable (Supplementary Fig. 20). Nevertheless, the delocalized π electrons in the carbon matrix can change the RDS of the four-electron oxygen reduction reaction (Fig. 6a-b, Supplementary Fig. 30). As we all known, the intrinsic activity of the electrocatalysts can be determined by the limiting reaction barrier in the RDS. For COP-Ene, COP-Ppcfe, COP-Nap1, the RDS is oxygen protonation to OOH* with limiting barriers of 0.64, 0.58 and 0.56 eV, respectively (Fig. 6c). However, when the degree of delocalization in carbon matrix continues increasing, the RDE of oxygen reduction reaction were transformed from protonation of O2* into desorption of OH*, with limiting barrier of 0.78 eV for COP-Nap2, even as large as 1.24 and 1.37 eV for COP-Nap and COP-Pyr. In addition, the free energy of the six COP models is more negative, successively suggesting that the DDE in carbon matrix induce a stronger chemical adsorption with oxygen intermediates, which is also the direct reason for the transition of RDS. By correlating the onset potential and Gibbs free energy of OHH* intermediates, a typical volcano plot was constructed. Notedly, the ‘JUST’ DDE in carbon matrix connected to FeN4 sites makes COP-Ppcfe, and COP-Nap1 have the optimum d-state level, thereby exhibit ‘RIGHT’ adsorption, and lie at the apex of volcano plot (Fig. 6d). Therefore, our calculation results manifest that the carbon matrix connected to FeN4 sites remarkably contributes much to the catalytic activity of electrocatalysts and the RDS in oxygen reduction processes.
Discussion

In summary, we have constructed a series of fully π-conjugated COPs with analogous FeN₄ configurations to study-orient the effect of carbon environment covalent-connected to FeN₄ sites on their catalytic activity. Significantly, the FWHM, valence-band spectra, Fe²⁺/³⁺ redox potential, as well as electrochemical measurements together reveal that the relationship of DDE, d-orbital level and adsorption is unidirectionally determined in sequence, while electrocatalytic activity and adsorption are restricted by Sabatier principle, exhibiting a volcano plot. The DFT calculations further analyses that superior intrinsic active moieties are stemmed from the moderate electron filling of the d-state antibonding orbitals of Fe center in the FeN₄ sites, which is directly related to the π-conjugated electrons in the connected carbon matrix. This study not only clarified the origin of intrinsic-activity diversity of FeN₄ catalysts, but also provided a strategy for regulating the oxygen reduction performance of the active site by changing electronic configuration of the carbon atom covalent-connected to the FeN₄ sites.

Methods

Pyrolysis-free approach to synthesize electrocatalytic materials. In brief, for the synthesis of metal COP-Ppcfe sample, pyromellitic dianhydride (PMDA, 0.525 g), urea (2.4 g), NH₄Cl (0.2675 g), (NH₄)₆Mo₇O₂₄·4H₂O (0.155 g) and FeCl₃ (0.225 g) were mixed and ground adequately; the mixture was then transferred into crucible, and heated in a muffle furnace at 220°C for 3 h. After cooling to room temperature, the product was washed repeatedly with 1M HCl, 0.5 M NaOH, and ethanol. The precipitates were dried under vacuum at 60°C overnight to obtain COP-Ppcfe. The preparation methods of COP-Ene, COP-Nap and COP-Pyr samples are similar to that of COP-Ppcfe sample. In particular, we choose tetracyanoethylene, 1,4,5,8-Naphthalenetetracarboxylic dianhydride, and 3,4,9,10-Perylenetetracarboxylic dianhydride as the corresponding monomers to replace PMDA in the preparation process of COP-Ppcfe sample. More detailed characterization can be found in the supplementary materials.

Characterizations. Field-emission scanning electron microscopy (FE-SEM, JSM-6701/JEOL) was used to observe the morphologic and structural characteristics of the samples. Monodisperse morphology and further single atom character of the sample were obtained by high resolution transmission electron microscopy (HRTEM, JEM 2200FS) and the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, JEM-ARM300F). The Fourier Transform Infrared (FT-IR) analysis was performed on a Nicolet 8700/Continuum XL with wavenumber from 2200 to 500 cm⁻¹. Solid-state nuclear magnetic resonance (NMR) spectra were measured on a Burker 400M spectrometer operating at 10 kHz for ¹³C. Chemical compositions and elemental oxidation states of the samples were investigated by X-ray photoelectron spectroscopy (XPS, ThermoFischer, ESCALAB). The elemental spectra were all corrected concerning C1s peaks at 284.8 eV. Ultraviolet photoelectron spectroscopy (UPS, PHI5000 VersaProbe III, Scanning ESCA Microprobe with SCA Spherical Analyzer) was collected using He I (21.2 eV) radiation. The content of metallic iron in the four samples was gained by inductive ely coupled plasma Optical Emission Spectrometer (ICP-OES, Agilent 7700X & Agilent 7800). The X-ray absorption
spectra (XAS) including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) of the samples at Fe K-edge (6974–8110 eV) were collected at Beijing Synchrotron Radiation Facility (BSRF), where a pair of channel-cut Si (111) crystals was used in the monochromator. The Fe K-edge XANES data were recorded in a transmission mode. Fe foil, Fe$_2$O$_3$ and FePc were used as references. The storage ring was working at the energy of 2.5 GeV with an average electron current of below 200 mA. The acquired EXAFS data were extracted and processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software packages. The obtained XAFS data was processed in Athena (version 0.9.26) for background, pre-edge line and post-edge line calibrations. Then Fourier transformed fitting was carried out in Artemis (version 0.9.26). The k$^3$ weighting, k-range of 3–12 Å$^{-1}$ and R range of 1 - ~3 Å were used for the fitting. The four parameters, coordination number, bond length, Debye-Waller factor and E$_0$ shift (CN, R, $\sigma^2$, $\Delta E_0$) were fitted without anyone was fixed, constrained, or correlated. For Wavelet Transform analysis, the $\chi(k)$ exported from Athena was imported into the Hama Fortran code. The parameters were listed as follow: R range, 1–4 Å, k range, 0–13 Å$^{-1}$; k weight, 2; and Morlet function with $\kappa = 10$, $\sigma = 1$ was used as the mother wavelet to provide the overall distribution.

**Computational methods.** We employed the spin-polarized DFT method for all calculations, as implemented in the Vienna ab initio Simulation Package (VASP) code. The projector-augmented-wave (PAW) basis set was adopted to describe ion-electron interaction with cut-off energy of 500 eV. Perdew-Burke-Ernzerhof (PBE) of the generalized gradient approximation (GGA) functional was used to treat exchange-correlation interaction. The $\Gamma$ center 4*4*1 k-points grids was chosen for optimization of COP-Ene, and 3*3*1 k-points grids were chosen for optimization of COP-Ppcfe, COP-Nap1, COP-Nap2, COP-Nap and COP-Pyr. The denser $\Gamma$ center 9*9*1 k-points grids were chosen for electronic structure calculations. The convergence tolerance of energy and force was $10^{-5}$ eV and 0.01 eV/Å. A 15 Å thickness vacuum was inserted to eliminate the interaction induced by a periodic boundary condition. The Gibbs free energy ($\Delta G$) diagram of the oxygen reduction reaction (ORR) was calculated using the computational hydrogen electrode (CHE) model proposed by Nørskov et al, where the free energy of ($\text{H}^+ + e^-$) under standard conditions is equal to the value of 1/2 H$_2$. Free energy is calculated by the formula $\Delta G = \Delta E + \Delta ZPE - \Delta TS + \Delta G_U + \Delta G_{PH}$, where E is the total energy of the system, ZPE is the zero-point energy, and S is the entropy. ZPE corrections were calculated as $ZPE = 1/2h\nu_i$, where $h$ is Planck's constant and $\nu_i$ is the frequency of the vibrational mode of binding molecules. Since DFT cannot accurately obtain the Gibbs free energy of oxygen molecules, this value can be obtained indirectly through water and hydrogen ($G_{O_2} = 2G_{H_{2}O} - 2G_{H_{2}} + 4.92 \text{ eV}$). The free energy of liquid water is equal to the free energy of gaseous water at 0.035 atm and 298.15 K. The oxygen-containing intermediates O* and OH* are stabilized by the solvation effect of ~0.3 eV$^{19}$. In acidic media, the pH is assumed to be 0. The electrode potential adopts the reversible hydrogen electrode potential (RHE).

**Declarations**
Acknowledgments

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Author Contributions

X. L. performed the synthesis, structural characterizations, electrochemical tests and the DFT calculations. X. L. and Z. X. wrote this paper. Z. X. supervised and led this project. All authors provided critical feedback and helped shape the research and manuscript. All authors commented on the manuscript.

Competing interests

The authors declare that they have no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/.

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**Figures**

![Figure 1](image_url)

**Figure 1**

Synthesis routes of four full p-conjugated covalent organic polymers (COPs). a-d, Scheme of formation towards COP-Ene, COP-Ppcfe, COP-Nap and COP-Pyr samples by tailoring monomers constructed corresponding building blocks.
Figure 2

Morphology and structure characterization. a, The HRTEM images of COP-Ppcfe sample. b, STEM image and the corresponding EELS elemental mapping of C (green), N (blue) and Fe (yellow) in COP-Ppcfe sample. c, The HAADF STEM images of COP-Ppcfe sample. d, The k3-weighted Fourier transform of the EXAFS spectra for COP-Ppcfe sample. e, The Wavelet transform of COP-Ppcfe sample. f, Fourier-transformed experimental EXAFS spectrum and fitting spectrum based on the predicted polyphthalocyanine structure with oxygen adsorption for COP-Ppcfe sample. g, The C1s XPS spectra of the four as-synthesized COP samples. h, The full-width at half maxima value (FWHM) of C=C bond in C 1s of the four as-synthesized COP samples.
Figure 3

Electrochemical characterization. a, LSV curves of COP-En, COP-Ppcfe, COP-Nap, and COP-Pyr samples in O2-saturated 0.1 HClO4 solution at a scan of 5 mV s-1 and a rotation speed of 1600 rpm. b, The turnover frequency (TOF) at 0.7 V versus RHE and mass activity (Ma) per mass of metal at 0.7 V versus RHE. c, Tafel plots. d, Comparison of experimental and theoretical Uon-set potential. e, Linear relationship of theoretical reaction free energy of DRS (ΔGmax) versus the logarithm of exchange current density in the experiment (j0exp). f, Linear relationship of experimental yields of H2O2 versus theoretically thermodynamic propensity for O-O bind preservation (ΔGO*-ΔGOOH*).

Figure 4
The relationship between DDE and catalytic activity. a, The schematic diagram of the valence band spectra and work function spectra (Ø) for COP-Ene, COP-Ppcfe, COP-Nap, and COP-Pyr samples (Ef is the Fermi level). b, The linear relationship of the E_{redox-1} versus FWHM-1. c, The linear relationship of the E_{redox-1} versus the valence band level. d, Volcano plot between catalytic activity (quantified by TOF) and DDE (quantified by FWHM-1). e, Schematic diagram of the mechanism of DDE affecting catalytic activity.

Figure 5

The ORR mechanism revealed in depth through DFT. a, Six models of COPs architectures: COP-Ene, COP-Ppcfe, COP-Nap1, COP-Nap2, COP-Nap, COP-Pyr. (In addition to the four COPs synthesized experimentally, we have also constructed Nap1 and Nap2 models to enrich the DDE in carbon matrix. The red, dark blue, white, and black colors represent Fe, N, H, and C atom, respectively. To distinguish their structure discrepancy, the carbon skeleton connecting the two FeN4 sites is displayed in different colors on purpose). b, Taking FeN4 as a whole, the numbers of electrons are transferred from the surrounding C skeleton to the FeN4 moieties (Constructed COP-Nap1 and COP-Nap2 models are marked by the star symbol). c, The most stable configurations for oxygen adsorption and charge density differences of O2 chemisorbed on different Fe-N-C moieties (Cyan and yellow represent positive and negative charges, respectively). d, Projected density of states (pDOS) plots of 2p orbitals (2px, 2py, 2pz) for O2 and 3d orbitals (3dxy, 3dyz, 3dz2, 3dxz, 3dx2-y2) for corresponding COPs. e, Crystal orbital Hamilton population (COHP) analysis and corresponding Integrated crystal orbital Hamilton population (ICOHP) value of OH*
absorbed on corresponding COP surfaces. f, Schematic diagram of orbital hybridization of the adsorbates bonding orbitals and 3d orbitals of COPs with the increment of DDE.

Figure 6

Schematic diagram of rate-determining step transition. a-b, Proposed ORR reaction scheme with the intermediates towards COP-Ene (a) and COP-Nap (b). RDS is rate-determining step. The blue, grey, red, pink and golden spheres represent N, C, O, H and Fe, respectively. c, The Free energy diagram of COP-Ene, COP-Ppcfe, COP-Nap1, COP-Nap2, COP-Nap and COP-Pyr at equilibrium electrode potential. d, The volcano plot of onset potential versus adsorption energy of OH*.

Supplementary Files

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