Spin engineering of single-site metal catalysts

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GRAPHICAL ABSTRACT

PUBLIC SUMMARY

- Single-site FeN₄ species are designed to dangle over axial carbon micropores (d-FeN₄)
- d-FeN₄ shows much superior oxygen reduction reactivity to traditional FeN₄
- d-FeN₄ facilitates the formation of singlet-state oxygen-containing species with optimized spin states by micropore
- This work provides in-depth understanding of spin tuning for advanced catalyst design
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Single-site metal atoms (SMAs) on supports are attracting extensive interest as new catalytic systems because of maximized atom utilization and superior performance. However, rational design of configuration-optimized SMAs with high activity from the perspectives of fundamental electron spin is highly challenging. Herein, N-coordinated Fe single atoms are successfully distributed over axial carbon micropores to form dangling-FeN4 centers (d-FeN4). This unique d-FeN4 demonstrates much higher intrinsic activity toward oxygen reduction reaction (ORR) in H2O than FeN4 without micropore underneath and commercial Pt/C. Both theoretical calculation and electronic structure characterization imply that d-FeN4 endows central Fe with medium spin (t2g^6 e_g^5), which provides a channel for electron transition compared with FeN4 with low spin. This leads to the facile formation of the singlet state of oxygen-containing species from triplet oxygen during the ORR, thus showing faster kinetics than FeN4. This work provides an in-depth understanding of spin tuning on SMAs for advanced energy catalysis.

RESULTS AND DISCUSSION

Synthesis and microstructure of d-FeN4

The adsorption-thermal treatment process of d-FeN4 is illustrated in Figure 1A. Carbon materials with abundant micropores (Figure S1) were used as the carriers to capture FePc molecules on the surface of the adsorption effect. This micropore-rich substrate acts as a site-selective capture for FePc molecules, which is confirmed by the thermodynamic calculation in Figure 1B. The adsorption energy at the surface is about ~0.98 eV, indicating a favorable adsorption with 0.94 eV at the plane sites. Under pyrolysis conditions, the adsorbed FePc molecules could convert to d-FeN4 configuration in which the resulting single-site Fe atoms are freely distributed over carbon micropores. The variation trend of micropore content definitely confirms the aforementioned formation process. Because a great number of micropores are blocked with FePc-derived FeN4 species, the specific surface area (SSA) decreases remarkably. Figure 1C clearly displays the sharp change of SSA from 1,334 m^2/g MC to 523.5 m^2/g d-FeN4. In contrast, the control sample MC-700 prepared by pyrolysis of MC at 700 °C without FePc molecules possesses a comparable SSA of 1,338 m^2/g to MC (1,334 m^2/g) (Figure S2). This strongly suggests that the adsorption and conversion of FePc molecules on the micropore dominate the decrease of SSA. Meanwhile, an obvious drop can be seen at low pressure, suggesting the disappearance of a mass of micropores. It is also remarkable that pore volume less than 2 nm occurs...
obviously diving, as marked by the arrows in Figure 1D and Table S2, which is attributed to the patched FeN4 species. In detail, the cumulative volume less than 2 nm of MC is 0.533 mL/g, much larger than 0.174 mL/g of d-FeN4, showing a decreasing volume about 67.4% because of d-FeN4 covering on the micropore. On the other hand, Raman spectra also confirm the change of microstructure (Figure S3). The intensity ratio of the D band (1,350 cm\textsuperscript{-1}) to G band (1,580 cm\textsuperscript{-1}) decreases from 1.08 for MC to 0.91 for d-FeN4, as summarized in Figure 1E, which demonstrates that MC possesses more intrinsic defects than d-FeN4. With regard to the control sample, the value for MC-700 is 1.07, similar to MC. This suggests that the lower ratio for d-FeN4 originates from the adsorption and conversion of FePc above the pore.

To further analyze the single-atom d-FeN4, high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was used. The HAADF-STEM image reveals the atomic Fe in d-FeN4 sample because of the separate bright dots marked with red cycles (Figure 1F). Electron energy loss spectroscopy (EELS) at the white dotted line-marked region in Figure 1F demonstrates the co-existence of N and Fe as two peaks at 400 and 708 eV (Figure 1G). In addition, no Fe peaks can be observed in the XRD spectrum (Figure S4). This is consistent with the observation by HAADF-STEM, indicating that there is no agglomeration of Fe. The signal at g = 3.03 in the EPR spectrum is the fingerprint of the atomic FeN4 moieties (Figure S5). All above results suggest that the atomically dispersed FeN4 sites have been achieved. In addition, the same contents of C-N bonds in d-FeN4 and FeN4 illustrate that there are no edged FeN4 sites (Figure S6; Table S3).

Spin state of electrons in d-FeN4

The local structure of d-FeN4 was further unveiled by X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure. The absorption edges of d-FeN4 and FeN4 K-edge XANES load between Fe foil and Fe2O3 (Figure 2A), indicating that the valence of Fe in d-FeN4 and FeN4 is situated between 0 and +3. Higher valence of Fe in d-FeN4 originates from the shift to the higher energy direction, as shown by the enlarged spectra (Figure 2A, inset).
Figure 2. Electronic structure analyses of FeN\textsubscript{4} and d-FeN\textsubscript{4}. (A) The Fe K-edge XANES curves of Fe foil, Fe\textsubscript{2}O\textsubscript{3}, d-FeN\textsubscript{4}, and FeN\textsubscript{4}. (B) The Fe K-edge EXAFS spectra of Fe foil, Fe\textsubscript{2}O\textsubscript{3}, FeN\textsubscript{4}, and d-FeN\textsubscript{4} plotted at the R-space. (C) The Fe L-edge XANES of d-FeN\textsubscript{4} and FeN\textsubscript{4}. (D) Magnetic susceptibility of d-FeN\textsubscript{4} and FeN\textsubscript{4}. The inset shows the illustration of electrons filling in d orbitals. (E) Molecular orbital diagram of oxygen adsorbed at d-FeN\textsubscript{4} and FeN\textsubscript{4}.

FeN\textsubscript{4} demonstrates that there is only a single unpaired electron filling in the d\textsubscript{xy} orbital. Because of the symmetry conservation, the interactions between d\textsubscript{xy} and d\textsubscript{z2} orbitals of Fe and the orbitals of oxygen are negligible.\textsuperscript{26,27} As shown in Figure 2E, when oxygen with a triplet state is adsorbed at d-FeN\textsubscript{4} with a medium spin state, the unpaired electron in d-FeN\textsubscript{4} and oxygen could couple and fill in \( \sigma \) orbital and \( \pi \) orbital, leading to the formation of singlet state. However, for FeN\textsubscript{4}, the unpaired electrons in oxygen molecule couple with electron in pairs of FeN\textsubscript{4}, and the others can fill in \( \pi \) orbital and \( \sigma \) orbital.

**Electrocatalytic ORR performance**

The positive effect of medium-spin electrons in Fe during ORR was studied in 0.1 M HClO\textsubscript{4}. Linear sweep voltammetry (LSV) was first performed by using a rotating disk electrode to evaluate the electrocatalytic activity as shown in Figure 3A. The as-synthesized d-FeN\textsubscript{4} shows a high half potential of 0.83 V, which is very close to 0.85 V of commercial Pt/C and far superior to traditional FeN\textsubscript{4}. Besides, the equal onset potential (0.93 V) for both d-FeN\textsubscript{4} and Pt/C indicates a keen response at the d-FeN\textsubscript{4} sites during ORR process. The d-FeN\textsubscript{4} shows a similar Tafel slope of 73 mV dec\textsuperscript{-1} as Pt/C (64 mV dec\textsuperscript{-1}), which is far smaller than that of FeN\textsubscript{4} (135 mV dec\textsuperscript{-1}) (Figure 3B). It suggests that pore-induced spin flipping could markedly accelerate the dynamics process. After taking the loading of active sites into account, the TOF value indicates that the d-FeN\textsubscript{4} behaves the highest intrinsic activity (Figure 3C). The rotating ring-disk electrode test in Figure S12 demonstrates that d-FeN\textsubscript{4} behaves an equal excellent selectivity compared with Pt/C with an almost 4e\textsuperscript{-} process and low H\textsubscript{2}O\textsubscript{2} yields (Figure 3D). More important, the current density of d-FeN\textsubscript{4} remains 91.1% after adding methanol, much higher than 76.3% of Pt/C, displaying a superior methanol tolerance (Figure 3E). On the other hand, d-FeN\textsubscript{4} shows the long-term stability with 89% of initial current over 10,000 s, much better than 72.6% of Pt/C (Figure 3F).

**Electronic interaction between O\textsubscript{2} with FeN\textsubscript{4}**

Spin transfer of electrons is helpful for ORR, as all the intermediates (*OOH, *O, and *OH) are singlet state. To understand the electronic interaction of oxygen with FeN\textsubscript{4} and d-FeN\textsubscript{4}, the electronic structures of were first analyzed using density functional theory calculations (Figure 4). The structure models of FeN\textsubscript{4} and d-FeN\textsubscript{4} are shown in Figures 4A and 4C, respectively. Upon the structure relaxation, Fe atom in the d-FeN\textsubscript{4} model dips obviously because of the presence of vertical micropore (Table S1). This d-FeN\textsubscript{4} over micropores leads to a longer Fe-N bond than traditional FeN\textsubscript{4}, resulting in obvious electron loss from Fe (Figure S13). The more critical effects during the process of adsorbing oxygen were expounded by the electron localization functions and projected electronic densities of FeN\textsubscript{4}. As shown in Figures 4B and 4E, a stronger electron localization at the marked area with 0.17 can be observed around Fe atom in d-FeN\textsubscript{4}. In
The integral value of d-FeN₄ is nearly 3-fold that of FeN₄ (0.34 versus 0.12). This shows that d-FeN₄ could adsorb oxygen in thermodynamics more strongly than FeN₄, illustrating strong binding between d-FeN₄ and O. Thermodynamically, the rate-determining step at the d-FeN₄ site is from *OH to H₂O, requiring a driven energy of 0.26 eV, which is still lower than the RDS energy (0.42 eV) from O₂ to *OOH at FeN₄.

CONCLUSIONS
A specific dangling FeN₄ configuration (d-FeN₄), in which single-site Fe atoms were dispersed over carbon micropores, was successfully synthesized by adsorption of FePc on micropores and subsequent pyrolysis, which shows outstanding ORR activity in acidic solution. Both DFT calculation and electronic structure characterization show that this unique d-FeN₄ endows the central Fe atom with the medium spin state (t²g⁴e₂g¹), and provides a spin channel for the electron transition, leading to the facile formation of singlet state of oxygen-containing species (e.g., *OOH, *OH, and H₂O) from triplet O₂ during the reaction.

Contrast, traditional FeN₄ displays only 0.08 at the same position, indicating that the micropore could modify the localization of electrons in d-FeN₄ and thus result in a stronger interaction between oxygen and active site. Then, the binding features between two sites and oxygen are demonstrated through pDOS as shown in Figures 4C and 4F. The energy levels of Fe β-spin d orbitals in d-FeN₄ and O β-spin 2p orbital match better than in FeN₄. Such disparity can be clearly illustrated through integrating the matched region (Figure 4G). The integral value of d-FeN₄ is nearly 3-fold that of FeN₄ (0.34 versus 0.12). This shows that d-FeN₄ could adsorb oxygen in thermodynamics more easily than FeN₄ (Figure 4G).

MATERIALS AND METHODS
Chemicals
N-methylpyrrolidone (NMP) and iron phthalocyanine (FePc) were obtained from Aladdin. HCl and KOH were obtained from Sinopharm Chemical Reagent. Acetylene black was purchased from Guangdong Canrd New Energy Technology. NaClO and Na₂CO₃ were obtained from Aldrich. Commercial 40 wt % Pt/C was obtained from Johnson Matthey. All chemicals were used as received without further purification.

Material synthesis
Synthesis of microporous carbon. Microporous carbon (MC) was synthesized according to previous literature. First, bulky coals were broken and ground into powder in a mortar with a pestle. Two grams coal powder and 8 g KOH were placed in a mortar. After grinding for 0.5 h, the mixture was placed in a crucible and placed in a metal tube furnace. The powder was heated to 750°C for 2 h in Ar atmosphere. Finally, the product was kept to commercial Pt/C in HClO₄ electrolyte, much better than traditional FeN₄ without underneath pore regulation. The theoretical calculation implied that the change of Gibbs free energy (∆G*OOH) from O₂ to *OOH intermediate is only 0.15 eV at the d-FeN₄ site, much lower than 0.42 eV at FeN₄. This further demonstrates high electrocatalytic activity and fast reaction kinetics for d-FeN₄ ascribed to optimized electron spin state induced by micropores underneath. The present strategy of catalyst design and synthesis could be also extended to other single-atom catalytic systems with great potentials in various energy conversion and storage devices.
in 1 M HCl solution for 6 h to remove residual KOH and other impurities. Then, the product was washed by deionized water three times and named MC.

**d-FeN₄ synthesis.** MC (0.1 g) was dispersed in 20 mL NMP under ultrasonication for 2 h. Then, 10 mmol FePc was added into under stirring for 4 h and then left to stand for 12 h. The powder was filtered and then pyrolyzed at 700°C for 2 h under Ar atmosphere. Finally, the black solid was washed by 1 M HCl to remove the impurities. Changing the amount (x) of FePc could prepare other d-FeN₄-x samples (x = 0.03, 0.05, 0.07, or 0.12). For comparison, MC-700 was prepared by pyrolysis of MC at 700°C for 2 h under Ar atmosphere.

**FeN₄ synthesis.** The synthesis process of FeN₄ is similar to that of d-FeN₄. However, acetylene black instead of MC was used as the support.

**Structure characterization.**

X-ray diffraction (XRD) was performed to determine the crystallographic structure with a Cu Kα (λ = 0.15405 nm) radiation source. Raman spectrometry was tested with a laser wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250 X-ray photoelectron spectrometer with the Al Kα (hν = 1486.6 eV) radiation source. The morphology and microstructure of the samples were observed using scanning electron microscopy (SEM; JEOL JSM-5610) and transmission electron microscopy (TEM; JEM-2100 F). Electron paramagnetic resonance (EPR) was performed using Bruker EMX spectrometer. Calculation of the spin number was based on a reference powder of Cu(II) TPP with 1 spin per molecule. The zero-field cooling (ZFC) temperature-dependent magnetic susceptibility was obtained using a vibrating sample magnetometer (VSM) with MPMS XL-7. The specific surface areas were obtained using the multipoint Brunauer-Emmett-Teller method. Pore size distribution curves, pore volume, and pore diameter were calculated by the desorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) method. X-ray absorption fine structure (XAFS) spectra at the Fe K-edge were obtained at the Advanced Photon Source (APS), beamline BM9. The samples were measured in X-ray fluorescence mode. The data were processed using the ATHENA program for background subtraction, normalization, and energy calibration. The extended XAFS (EXAFS) was analyzed using the IFEFFIT package, and EXAFS fitting was performed with FEFF6L. A k range of

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**Figure 4. Theoretical calculation on electronic structures and oxygen-adsorption ability for FeN₄ and d-FeN₄.** (A–F) Structure models, electron localization functions, and projected electronic densities of states (pDOS) of (A–C) FeN₄ and (D–F) d-FeN₄. (G) The integral of matched region in Fe β-spin d orbitals and oxygen adsorption energy at FeN₄ and d-FeN₄. (H) The spin densities of Fe in FeN₄ and d-FeN₄.
The data were normalized to the incident photon flux. The thickness of the vacuum layer is 20 Å. The atomic positions were fully optimized with:

\[ R = 1.28 \text{Å}, \] \[ R = 1.48 \text{Å}. \]

3.0–12.5 Å\(^{-1}\) was selected for the conversion to Fourier transform (FT)-EXAFS, which was the range subsequently used for EXAFS fitting. The Fe L\(_{33}\)-edge XANES was obtained at beamline 20A1 at the Taiwan Light Source, operated by the National Synchrotron Radiation Research Center (NSRRC). The spectra were obtained using the mode of total electron yield. The Fe L\(_{33}\)-edge XANES was obtained at beamline 20A1 at the Taiwan Light Source, operated by the National Synchrotron Radiation Research Center (NSRRC). The spectra were obtained using the mode of total electron yield. 

**Electrochemical measurements**

Electrochemical measurements including cyclic voltammetry (CV), rotating disk electrode (RDE), rotating ring-disc electrode (RRDE), and chronoamperometric (CA) measurements were carried on an electrochemical workstation (AFM/LSRCE; Pine Research Instrumentation). All measurements were performed in the electrolyte of 0.1 M HClO\(_4\) solution using a three-electrode system. A graphite rod and saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. A rotating disk electrode (RDE), rotating ring-disk electrode (RRDE), and chronoamperometric (CA) measurements were conducted following the method used by Kulkarni et al.\(^{38}\)

Before collecting the data, the electrode was activated using the CV measurement for 100 cycles with a scan rate of 100 mV s\(^{-1}\). RRDE measurements were taken to evaluate the electron transfer number (n) and peroxide yields during ORR catalytic process. The equations are as follows:

\[ n = \frac{4 \times i_d}{i_d + i_r/n}. \] (Equation 2)

Where * stands for an active site on the catalytic surface.

The free energy \( \Delta G \) of each step is obtained using the following equation:

\[ \Delta G = \Delta E + \Delta E_{ZPE} - T \Delta S + \Delta G_U + \Delta G_H. \] (Equation 9)

Where \( \Delta E \), \( \Delta E_{ZPE} \), and \( \Delta S \) represent the different intermediate energy, zero-point energy changes, and entropy of the reaction, respectively. \( \Delta E \) was obtained from DFT calculations, and \( \Delta E_{ZPE} \) is the zero-point energy of each adsorbate or free molecules calculated by the vibrational frequency, \( T \) is the temperature, and \( \Delta S \) is the entropy change. And the energy of \( \text{H}^\circ \) is considered as 1/2 \( E_{\text{OH}} \).

The bias effect on the free energy of each initial, intermediate, and final state involving electrons transfer in the electrode is also taken into account by shifting the energy of the state by:

\[ \Delta G_U = - neU. \] (Equation 10)

where \( U \) is the electrode applied potential, \( e \) is the transferred charge, and \( n \) is the number of proton-electron transferred pairs.
where $k_B$ is the Boltzmann constant.

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AUTHOR CONTRIBUTIONS

R.M. and J.W. conceived the idea. Z.L. and R.M. synthesized the samples and carried out the electrochemical experiments and DFT calculations. L.L. performed the XAFS measurements. Q.J., Q.L., Y.Z., and M.Y. analyzed the data and contributed to the scientific interpretation. Z.L., R.M., and J.W. wrote the manuscript. All authors commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

SUPPLEMENTAL INFORMATION

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