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Chemical design and synthesis of superior single-atom electrocatalysts *via in situ* polymerization†Haomin Xu,^{ab} Shibo Xi,^c Jing Li,^b Shikai Liu,^d Pin Lyu,^a Wei Yu,^a Tao Sun,^a Dong-Chen Qi,^e Qian He,^d Hai Xiao,^f Ming Lin,^g Jishan Wu,^{*a} Jia Zhang^{*h} and Jiong Lu^{ab}

Molecule-like electrocatalysts with FeN₄ motifs have been demonstrated to be excellent candidates for various renewable energy conversions. The ability to further tune the electronic properties of molecular FeN₄ motifs and integrate them onto conductive supports represents a key step towards the synthesis of highly robust and efficient single-atom catalysts (SACs) for practical applications. Here, we developed a new route for the synthesis of a well-defined single-atom FeN₄ electrocatalyst *via in situ* polymerization of four amino groups functionalized iron phthalocyanine (NH₂-FePc) molecules on conductive carbon nanotubes. The intermolecular oxidative dimerization between the amino groups of NH₂-FePc creates the desired electron-withdrawing pyrazine linker between FeN₄ motifs, which can significantly optimize their electrocatalytic performances. As a result, the FeN₄-SAC exhibits both outstanding ORR activity (a half-wave potential of 0.88 V vs. RHE) and excellent performance in Zn–oxygen batteries, outperforming the commercial Pt/C and pristine iron phthalocyanine (FePc) catalysts. Our theoretical calculations reveal that the presence of electron-withdrawing linkers shifts the occupied antibonding states towards lower energies and thus weakens the Fe–O bond, which is primarily responsible for the enhancement of ORR activity.

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Introduction

Electrocatalysis plays a vital role in a diversity of efficient and renewable energy conversions. The oxygen reduction reaction (ORR) represents one of the key electrochemical conversions for a variety of applications including fuel cells and metal–air batteries.¹ Unfortunately, both the chemical stability of the O=O bond and the sluggish kinetics of the ORR make it very difficult to proceed without efficient electrocatalysts.² To date, Pt and its alloys have been demonstrated to be the most effective electrocatalysts for the ORR. However, their practical application on a large scale is limited by the high cost and

insufficient reserves of Pt.³ Because of this, intensive research efforts have been devoted to exploring a variety of noble-metal-free materials as alternative catalysts including transition metal oxides,⁴ transition metal nitrides,⁵ polymer-derived materials,⁶ carbon materials,⁷ nitrogen-doped carbon,⁸ and metal–organic frameworks.⁹

Among all these noble-metal-free catalysts, iron-based molecules and materials with the FeN_x motif containing an iron atom coordinated by several pyrrolic nitrogen atoms have attracted great attention since Brodd reported that iron phthalocyanine (FePc) molecular catalysts show a remarkable ORR performance in alkaline media.¹⁰ Despite encouraging progress in recent decades, the electrocatalytic activity and stability of these FeN_x-based catalysts still need to be improved for practical applications. For example, it has been reported that macrocyclic FeN₄ complexes suffer from chemical instability in fuel cell environments due to the demetallation and/or degradation of FePc by ORR intermediates.¹¹ A common strategy involving a high-temperature pyrolysis process has been utilized to synthesize FeN_x-based catalysts with enhanced activity and stability.^{12,13} Unfortunately, high-temperature pyrolysis often generates multiple FeN_x species with different coordination environments.^{14–16} Therefore, it still remains a grand challenge to design and synthesize highly efficient and stable FeN_x-based electrocatalysts with a well-defined atomic structure of the FeN_x active center.

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In contrast to high-temperature pyrolysis, low-temperature polymerization could offer a promising way to design atomically well-defined FeN_x -based catalysts with enhanced activity and stability. For example, the polymerization of macrocyclic FeN_4 molecules produces highly dense FeN_4 active sites with a retained chemical structure of FeN_4 motifs.¹⁷ To date, the majority of polymerized FePc catalysts are prepared using 1,2,4,5-tetracyanobenzene or its derivative-pyromellitic dianhydride.^{18–21} Indeed, the structural fusion of these monomers produces FeN_4 -based catalysts with improved stability, but their intrinsic activity remains approximately unchanged because the linker between the polymerized building blocks shows a negligible effect on the electronic properties of the fused FeN_4 active site. The electronic and catalytic properties of the FeN_4 center are expected to be modulated by local atomic structures including the first and second nearest neighboring atoms or functional groups.^{22,23} Therefore, a rational integration of atomically precise FeN_4 motifs into a polymerized matrix towards a superior electrocatalytic ORR with optimized activity and stability is highly desired.

To this end, we report a novel *in situ* polymerization approach for the synthesis of FeN_4 -based SACs on conductive carbon nanotubes (CNTs). Previous studies suggest that the FeN_4 site in an unsubstituted FePc molecule delivers strong adsorption of oxygen species and thus limits its ORR activity.²³ Here, we designed four amino groups functionalized iron phthalocyanine (NH_2 -FePc), whereby the electron-withdrawing pyrazine linker can be formed in the polymerized iron phthalocyanine (p-FePc), leading to further depletion of the electron density of the FeN_4 active center. Therefore, the interaction between oxygen species and FeN_4 active sites will be weakened in the p-FePc for an improved ORR activity. In addition, p-FePc with extended π conjugation is enveloped on conductive CNTs substrates, whereby the active sites can be accessible to reactants and thus result in a dramatically enhanced electron transport. Due to these merits, an Fe_1 -SAC containing p-FePc/CNTs shows a half-wave potential of 0.88 V vs. RHE in alkaline solution, superior to that of the Pt/C catalyst under the same conditions. Moreover, a p-FePc/CNTs-decorated gas diffusion electrode applied to a Zn–oxygen battery also demonstrates outstanding performance and stability, outperforming the Pt/C catalyst.

Results and discussion

Fig. 1a illustrates the *in situ* polymerization approach developed in this work. A monomer (NH_2 -FePc) is used to synthesize the p-FePc *via* an oxidative polymerization mechanism.²⁴ The amino groups at the periphery of two NH_2 -FePc molecules can be oxidized to couple with adjacent phthalocyanine molecules forming a layered polymer in the presence of the oxidant 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and trifluoroacetic acid (TFA). The layered structure of p-FePc was first confirmed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) imaging, respectively (Fig. S1 and S2†). Atomic force microscopy (AFM) imaging reveals a height of ~ 2.5 nm for representative thin p-FePc flakes

(Fig. S3†). It is noted that the irreversible oxidative polymerization of monomers is kinetically controlled, which makes it difficult to form a highly ordered crystalline structure.²⁵ In addition, p-FePc tends to stack into thick flakes due to strong π interaction between phthalocyanine units as revealed by both SEM and AFM images. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and the corresponding X-ray energy dispersive spectroscopy (EDS) elemental maps of p-FePc show that Fe and N atoms are distributed uniformly in the polymerized film (Fig. S4†).

The restacking of p-FePc into thick sheets not only results in a poor electrical conductivity but also makes the majority of FeN_4 active sites inaccessible to the reactants. To overcome these issues, multiwalled CNTs (an average diameter of ~ 30 nm, Fig. S5†) with large specific surface area and excellent electrical conductivity are introduced during the synthesis of p-FePc. NH_2 -FePc molecules with a large conjugated π system tend to adsorb on the surface of CNTs *via* π - π interaction and subsequently undergo *in situ* polymerization upon introducing the oxidant (Fig. 1b). As a result, the crystalline wall of CNTs is intimately and conformably coated with a polymer-like structure, with thickness ranging from approximately 1 to 2 nm (Fig. 1c). The Fe content in p-FePc/CNTs is determined to be 0.89 wt% using inductively coupled plasma atomic emission spectroscopy (Table S1†). As shown in Fig. 1d, the atomic-resolution scanning transmission electron microscopy (STEM) image demonstrates that Fe atoms are atomically dispersed on CNTs without aggregation.

It is expected that the oxidation of the aniline-like structure in NH_2 -FePc can form two different moieties, namely the azobenzene or pyrazine structure. We then used Fourier-transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) to probe the chemical structure of the as-formed polymer. The FT-IR spectrum (Fig. 2a) reveals a new absorption peak at ~ 1645 cm^{-1} after polymerization, which can be assigned to the $\text{C}=\text{N}$ bond in the pyrazine structure.²⁶ In addition, the azo group related absorption peak (typically ~ 1430 cm^{-1}) is absent in p-FePc.²⁷ These observations suggest that pyrazine rings are formed as the linker between FePc units, consistent with the previous report.²⁴ The FT-IR spectrum of p-FePc/CNTs resembles that of p-FePc, indicating a successful polymerization of monomers on CNTs to form the p-FePc/CNTs hybrid.

The XPS results of p-FePc, FePc and NH_2 -FePc are shown in Fig. 2b and S6,† respectively. Two kinds of nitrogen atoms in FePc (bridging aza and pyrrole nitrogen atoms) with similar binding energies result in a single peak at 398.7 eV.²⁸ In contrast, NH_2 -FePc exhibits an additional peak at 400.0 eV, which can be assigned to the amino group.²⁹ Upon polymerization, the amino group related peak vanishes. Instead, one broadened peak is observed at ~ 398.8 eV. The pyrazine related peak is reported to be at 398.9 eV, which unfortunately overlaps with the feature of FePc.³⁰ It is thus difficult to distinguish these two components in the XPS spectrum of p-FePc. N K-edge near edge X-ray absorption fine structure (NEXAFS) measurement is used to further probe the chemical environment of N atoms in p-FePc (Fig. 2c). The N K-edge XAS spectrum of p-FePc exhibits

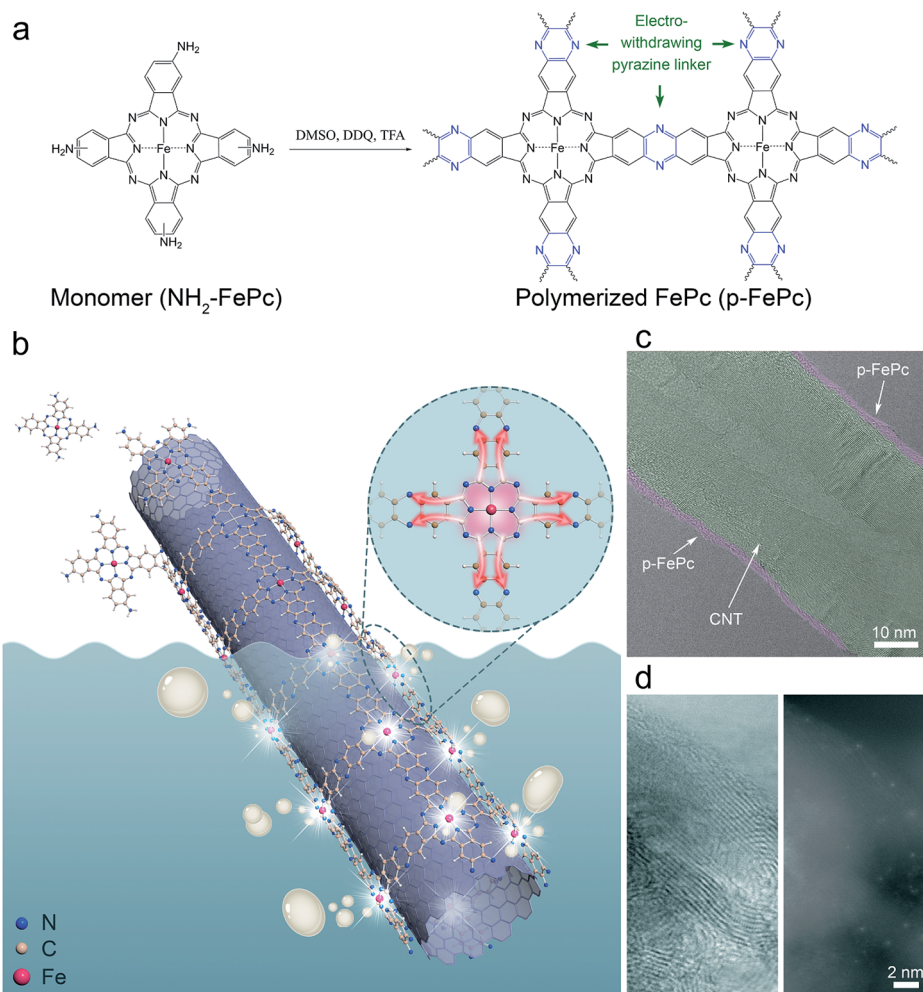


Fig. 1 Schemes for the synthesis of the FeN₄/CNTs SAC via *in situ* polymerization. (a) The schematic illustration of the chemical synthesis of p-FePc from a monomer (NH₂-FePc). (b) The schematic illustration of *in situ* polymerization of monomers over CNTs to form a superior FeN₄/CNTs SAC (p-FePc/CNTs hybrid). (c) High magnification TEM image of p-FePc/CNTs synthesized in this work. (d) Annular bright field (left) and dark field (right) STEM images of p-FePc/CNTs.

an additional absorption peak at 399.0 eV, which is absent in that of FePc; this absorption feature can be ascribed to the transitions to π^* states associated with the pyrazine group.^{31,32} This further demonstrates that the linkers between FePc units are pyrazine groups. In addition, thermogravimetric analysis (TGA) data (Fig. S7†) indicate that p-FePc has a higher decomposition temperature (~ 250 °C) than NH₂-FePc (~ 175 °C), suggesting higher thermal stability of p-FePc.

To further probe the local structure of the iron atom in the p-FePc/CNTs, we carried out X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements. The Fe K-edge XANES spectrum of p-FePc (Fig. 2d) shows an absorption edge between those of Fe₂O₃ and FeO, which reveals that single iron atoms exhibit an oxidation state between Fe²⁺ and Fe³⁺. The pronounced pre-edge peak at 7113 eV suggests that a considerable proportion of the Fe center is in a non-centrosymmetric environment, presumably due to O₂ adsorption.^{33–35} Compared with FePc, the absorption edge of p-FePc shifts towards higher energy,

although the p-FePc sample adsorbs fewer O₂ molecules as indicated by a lower intensity of the pre-edge peak. This suggests that the single-atom Fe active center in p-FePc exhibits a higher oxidation state due to the presence of the electron-withdrawing pyrazine linkers. Additional structural information can also be inferred from EXAFS spectra at the Fe K-edge. As shown in Fig. 2e, the Fourier transformed (FT) $k^3\chi(k)$ spectra of p-FePc and FePc exhibit similar features, suggesting that the structure of central FeN₄ moieties remains approximately unchanged after polymerization. The dominant peak centered at 1.47 Å can be attributed to the Fe–N bonds of the FeN₄ moieties. The absence of the peak at 2.18 Å (corresponding to the Fe–Fe bond) confirms the atomic dispersion of isolated Fe atoms in p-FePc. We then performed density functional theory (DFT) calculations in combination with a least-squares EXAFS fitting to determine the coordination configurations of the FeN₄ moieties in p-FePc. As shown in Fig. S8,† DFT calculation indicates that the most stable configuration for the case of O₂ adsorbed over p-FePc is the “end-on” configuration, and

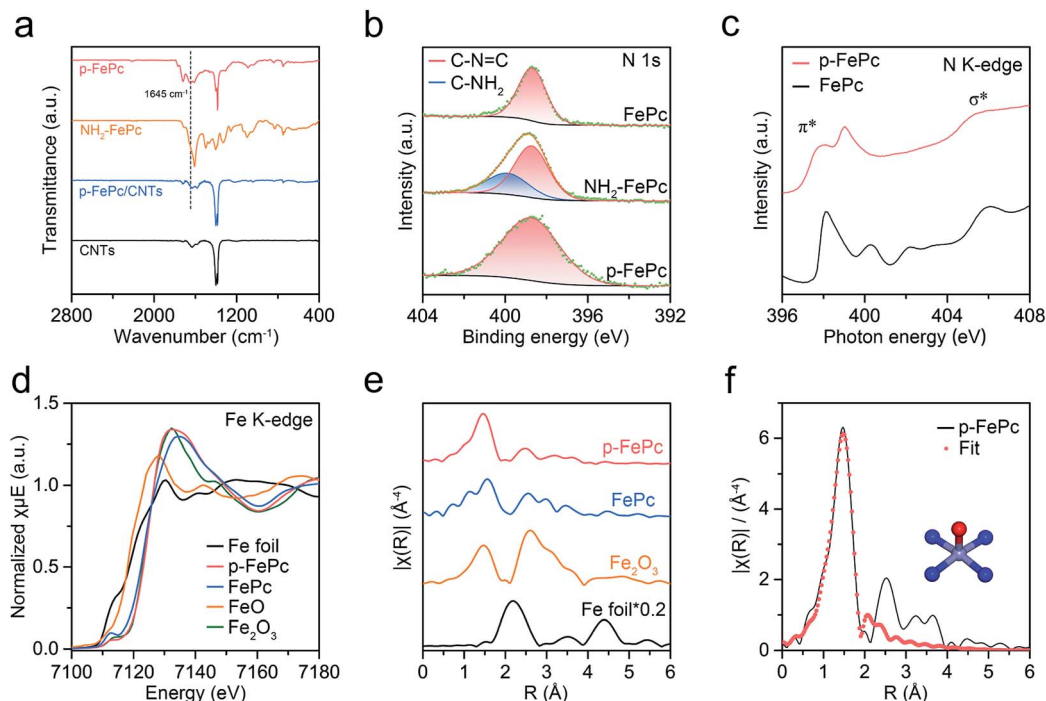


Fig. 2 Structural characterization of the FeN₄/CNTs SAC (p-FePc/CNTs). (a) FT-IR spectra of p-FePc, NH₂-FePc, p-FePc/CNTs and CNTs. (b) The high-resolution XPS N 1s spectra of FePc, NH₂-FePc and p-FePc. (c) N K-edge NEXAFS spectra of p-FePc and FePc. (d) Normalized Fe K-edge XANES spectra of Fe foil, p-FePc, FePc, FeO, and Fe₂O₃. (e) FT-EXAFS spectra of p-FePc, FePc, Fe₂O₃ and Fe foil. (f) Comparison of the experimental FT-EXAFS curves with the calculated data of p-FePc. Purple, blue and red spheres represent iron, nitrogen and oxygen atoms, respectively.

this optimized structure is used for EXAFS fitting. The EXAFS spectrum of p-FePc is fitted with two single scattering paths (Fe–N and Fe–O), and the best-fitting spectrum (Fig. 2f) is nearly identical to the experimental spectrum.

The electrocatalytic ORR activity of these samples is first evaluated by cyclic voltammetry (CV) in 0.1 M KOH solution (Fig. S9†). The p-FePc/CNTs hybrid exhibits an onset potential of 0.98 V and a peak potential of 0.90 V vs. RHE, which are comparable to those of commercial 20 wt% Pt/C. The enhanced ORR activity of the p-FePc/CNTs hybrid compared with pristine p-FePc can be ascribed to the CNTs support with enhanced conductivity and enlarged specific surface area. As shown in Fig. S10,† the Nyquist plots of electrochemical impedance spectroscopy (EIS) demonstrate that p-FePc/CNTs catalyst exhibits a much smaller charge transfer resistance than pristine p-FePc, suggesting a better conductivity of p-FePc/CNTs than pristine p-FePc.

Then, rotating-disk electrode (RDE) measurement was used to reveal the ORR kinetics of our p-FePc/CNTs catalyst. The Koutecky–Levich plots of p-FePc/CNTs and Pt/C are shown in Fig. S11.† The linearity and the near parallelism of the fitted line indicate first-order reaction kinetics for the dissolved oxygen with similar electron transfer numbers at different potentials. The electron transfer number of p-FePc/CNTs is calculated to be 3.9 at 0.60–0.75 V vs. RHE from the slopes of the Koutecky–Levich plot, suggesting that p-FePc/CNTs catalyst favors a four-electron oxygen reduction process. The linear sweep

voltammetry (LSV) polarization curves (Fig. 3a) reveal a half-wave potential of 0.88 V vs. RHE at 1600 rpm for the p-FePc/CNTs catalyst, which is more positive than that of FePc/CNTs (0.86 V vs. RHE) and the Pt/C catalyst (0.86 V vs. RHE). The excellent ORR performance of p-FePc/CNTs is either superior or comparable to the performance of a majority of previously reported phthalocyanine-based electrocatalysts (Table S2†). The mass-transport corrected Tafel curves (Fig. 3c) show that p-FePc/CNTs and FePc/CNTs exhibit almost the same Tafel slope of ~31 mV dec^{−1} in the low over-potential region, consistent with the previous result on tetrasulfonated FePc adsorbed on a graphite electrode.³⁶ We also prepared a sample *via* physical mixing for comparison, namely the p-FePc + CNTs mixture catalyst (Fig. S12a and b†). Compared with p-FePc/CNTs, the p-FePc + CNTs mixture exhibits a more negative half-wave potential, presumably due to the poor dispersity of p-FePc on CNTs with few FeN₄ active sites exposed. A series of p-FePc/CNTs catalysts with different Fe contents were also prepared to optimize the catalyst component. As shown in Fig. S13,† the p-FePc/CNTs catalyst with an Fe content of 0.89 wt% exhibits the highest ORR activity. This result indicates that a lower Fe loading fails to provide sufficient active sites for the ORR, and higher Fe loading with an excess amount of polymer on the surfaces of CNTs decreases the conductivity of hybrid materials.

Rotating ring-disk electrode (RRDE) measurement was performed to monitor the formation of peroxide species during the

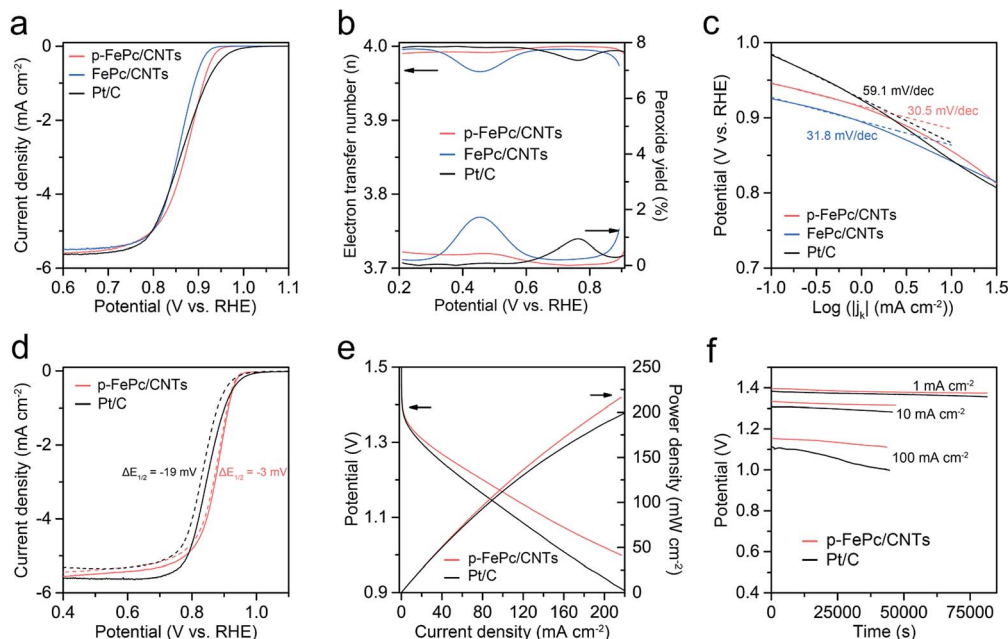


Fig. 3 The evaluation of ORR and Zn–oxygen battery performance. (a) ORR polarization curves of p-FePc/CNTs, FePc/CNTs and Pt/C. (b) Electron transfer number and peroxide yield of p-FePc/CNTs, FePc/CNTs and Pt/C. (c) Tafel plots of p-FePc/CNTs, FePc/CNTs and Pt/C. (d) ORR polarization curves of p-FePc/CNTs and Pt/C before and after 10 000 potential cycles in O_2 -saturated 0.1 M KOH. (e) Discharge polarization curves and the corresponding power densities of Zn–oxygen batteries fabricated with p-FePc/CNTs and Pt/C. (f) Galvanostatic discharge curves of Zn–oxygen batteries fabricated with p-FePc/CNTs and Pt/C at 1, 10 and 100 $mA\ cm^{-2}$.

ORR process (Fig. 3b and S12c†). In the potential range of 0.2–0.91 V vs. RHE, the peroxide yield is less than 1% for both p-FePc/CNTs and Pt/C, and the corresponding electron transfer number is greater than 3.95, which is consistent with the results obtained from the Koutecky–Levich plot. This indicates that the ORR process catalyzed by p-FePc/CNTs is mainly a four-electron process which is critical for practical applications, because the two-electron ORR process cannot completely utilize the chemical energy in the reaction between fuel and oxygen.

The electrochemical double-layer capacitance (C_{dl}) of electrocatalysts was measured to determine the electrochemical surface area (ECSA) via performing CV at different scan rates (Fig. S14†). The C_{dl} and ECSA of p-FePc/CNTs were calculated to be 2.47 $mF\ cm^{-2}$ and 61.8, respectively. The ORR activities of the electrocatalysts were assessed and compared based on turnover frequency (TOF). The TOF values were calculated assuming that all the single Fe atoms participate in the ORR process and one Fe atom contributes to one active site. As shown in Fig. S15 and Table S1,† the TOF values of p-FePc/CNTs at 0.95 and 0.90 V vs. RHE are at least 2.5 times higher than that of FePc/CNTs and NH_2 -FePc/CNTs. The difference in the TOF value at 0.85 V vs. RHE gets smaller, which is attributed to the restriction of mass transport.

Stability is also an important factor in electrocatalysis. To simulate the practical working conditions of a Zn–air battery, an accelerated stability test was conducted between 0.75 and 1.05 V vs. RHE (corresponding to the potential range of the ORR peak in the CV curve). As shown in Fig. 3d, after 10 000 potential cycles, the half-wave potential of p-FePc/CNTs shows a very

small negative shift of 3 mV, while that of Pt/C is negatively shifted by 19 mV, suggesting that the p-FePc/CNTs catalyst has higher cycling stability than Pt/C during the ORR process. The excellent stability of p-FePc/CNTs can be ascribed to the π – π interaction between cross-linked p-FePc and CNTs.

In the differential pulse voltammetry (DPV) curves of p-FePc and FePc (Fig. S16†), a reduction peak appears at 0.86–0.88 V vs. RHE, which can be assigned as the reduction peak of Fe(III). It is noted that Fe(II) is suggested as the real active center, because Fe(III) will be poisoned by strongly adsorbed OH^- species.³⁸ The onset potential of this reduction peak is very close to that of the ORR. This indicates that Fe(II) generated by the reduction of Fe(III) can act as the active center to catalyze the ORR.

For a proof-of-principle demonstration of the practical use, a primary Zn–oxygen battery is constructed. Carbon fiber paper loaded with p-FePc/CNTs is used as a gas diffusion layer for the cathode, and Zn foil and 6 M KOH solution are used as the anode and electrolyte (Fig. 3e). The backside of the gas diffusion layer faces oxygen gas, and the front side faces the electrolyte. In addition to a high open-circuit voltage of 1.45 V, the p-FePc/CNTs-based battery can supply discharge current densities of 80 and 215 $mA\ cm^{-2}$ at the voltages of 1.2 and 1.0 V, respectively, which are ~ 20 and 50 $mA\ cm^{-2}$ larger than those of the battery that uses benchmark Pt/C as a catalyst. Meanwhile, the p-FePc-based battery also exhibits excellent durability (Fig. 3f). When discharged at a constant current density of 1 $mA\ cm^{-2}$ for 22 hours or 10 $mA\ cm^{-2}$ for 12 hours, negligible decay in voltage is observed owing to the excellent stability of p-FePc/CNTs during the ORR process. After continuous discharge at a very

high current density of 100 mA cm^{-2} for 12 hours, the voltage drops significantly, but it still can supply a voltage of 1.11 V. All of these performance indicators are superior to those of the Zn–oxygen battery constructed with the Pt/C catalyst.

We then carried out DFT calculations to understand the different catalytic activities between p-FePc and FePc. Here, a four-step associative mechanism for oxygen reduction in alkaline media was considered (see Fig. S17 and S18†).^{39,40} We constructed the energy profile of the ORR as a function of electrode potentials, including zero potential ($U = 0 \text{ V}$), the equilibrium potential ($U = 1.23 \text{ V}$), and the maximum potential to make elementary steps downhill (Fig. S19† and 4a). We find that the potential applied is limited by the formation of $^*\text{OH}$. As shown in Fig. 4a, the oxygen reduction process over p-FePc is barrier-free at a potential of 0.73 V, whereas an energy barrier of 0.05 eV for the $^*\text{O}$ protonation can be observed over FePc. An analysis of the binding energies of the intermediate $^*\text{O}$ shows that FePc ($E_{\text{b},^*\text{O}} = 1.59 \text{ eV}$) has a similar oxygen binding strength to Pt ($E_{\text{b},^*\text{O}} = 1.57 \text{ eV}$).³⁷ However, the binding of oxygen over p-FePc is weaker by 0.18 eV ($E_{\text{b},^*\text{O}} = 1.77 \text{ eV}$) than that over FePc.

Previous studies suggested that slightly weakening the oxygen binding strength is advantageous to improve the oxygen reduction activity of Pt.³⁷ Thus, in this work, the lower energy barrier of the $^*\text{O}$ protonation on p-FePc can also be attributed to its relatively weaker interaction with oxygen.

The binding strength of oxygen species on FeN_4 sites is correlated with the electronic structures of the Fe center, which can be altered by the substituent group at the periphery of the phthalocyanine ring.⁴¹ The Bader charge analysis indicates that the Fe in p-FePc loses more electrons ($+1.28e$) than that in FePc ($+1.15e$), due to the electron-withdrawing effect arising from the pyrazine group in p-FePc. The electron-deficient character of Fe in p-FePc can also be demonstrated by a more positive $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ redox potential in DPV measurement (Fig. S16†). As shown in Fig. 4b and e, differential charge density distributions of the O adsorbed cases indicate that the Fe–O bond exhibits polar covalent bond characteristics with electron transfer from Fe to O. Therefore, the fewer number of electrons on the active center Fe leads to the weaker interactions between Fe and O. To gain deeper insight into the Fe–O bond strength, we calculated the

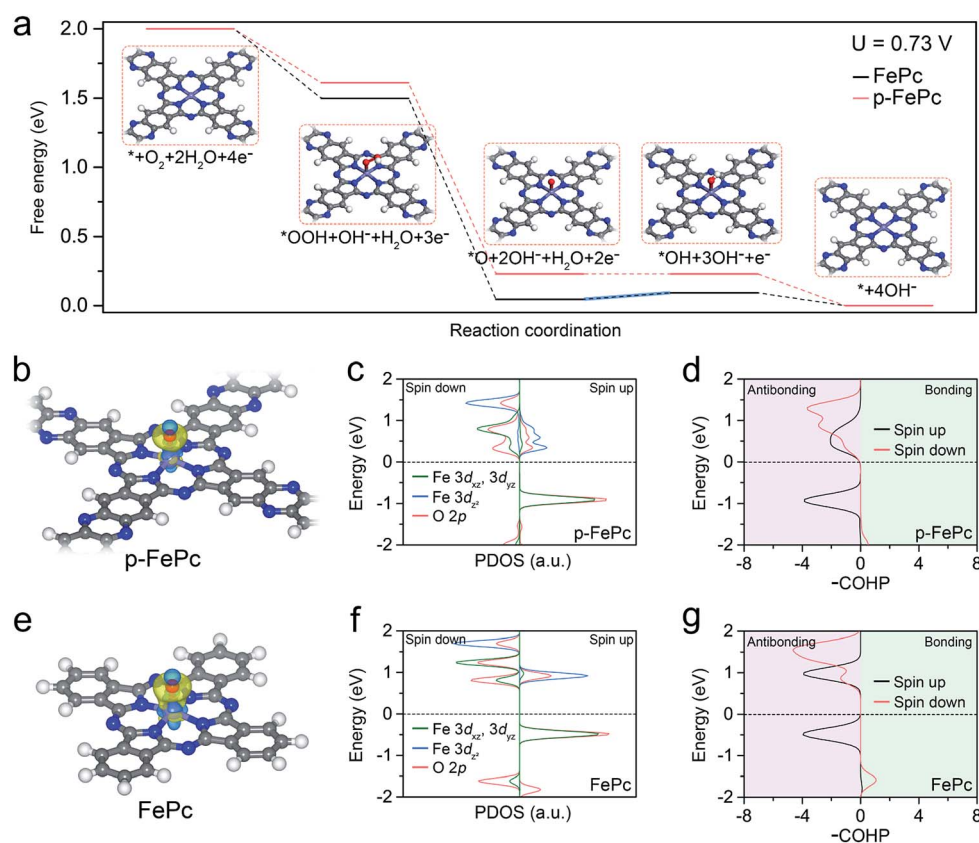


Fig. 4 Probing the catalytic mechanism. (a) Free energy profile for the ORR processes at a U of 0.73 V, where the computational hydrogen electrode (CHE) model was applied. The chemical potential of a proton–electron pair is equal to half of the chemical potential of gaseous H_2 . The gas phase H_2O at 0.035 bar is set as the reference state, where gas phase H_2O is in equilibrium with liquid H_2O at 300 K.³⁷ The asterisk (*) denotes the free adsorption site. p-FePc is a unit cell of a periodic model and FePc is a cluster model, where purple, blue, gray, white and red spheres represent iron, nitrogen, carbon, hydrogen and oxygen atoms, respectively. Differential charge density (yellow color represents a gain of electrons and blue color represents a depletion of electrons) of O adsorbed (b) p-FePc and (e) FePc. Partial DOS (PDOS) of O adsorbed (c) p-FePc and (f) FePc, where the Fermi level is taken as the zero of energy. Crystal orbital Hamilton population (COHP) of Fe–O bonds in (d) p-FePc and (g) FePc, where $-\text{COHP} < 0$ corresponds to antibonding contribution (light red region) and $-\text{COHP} > 0$ represents bonding contribution (light green region).

partial density of states (PDOS) for O-adsorbed systems, as well as the crystal orbital Hamilton population (COHP) for the Fe–O bond to analyze the bonding and antibonding contributions to the band energy. As shown in Fig. 4c, f and S20,[†] the PDOS of O-p-FePc and O-FePc has a similar structure. The p–d hybridization between O and Fe mainly comes from the Fe- d_{xz} , Fe- d_{yz} and Fe- d_{z^2} orbitals and the O 2p states. A close examination of the PDOS and COHP (Fig. 4d and g) reveals that the peak just below the Fermi level has an antibonding character in both cases. Compared to O-FePc, the occupied antibonding states in O-p-FePc shift down in energy by 0.43 eV, which accounts for the weaker bonding between Fe and O. Thus, the downshift of the filled antibonding levels destabilizes the intermediate *O , leading to a higher ORR activity of p-FePc.

Conclusions

In summary, we have demonstrated a new synthetic route for the design of robust and excellent single-atom FeN₄ catalysts *via in situ* polymerization. The amino-substituted iron phthalocyanine precursors can be directly polymerized on the surface of conductive CNTs, whereby a large number of atomically dispersed Fe single atoms can be accessible to reactants. Monomer polymerization creates electron-withdrawing bridge linkers (pyrazine structure) which further optimize the electronic structures and catalytic performance of the single-atom Fe active center. As a result, the single-atom FeN₄/CNTs catalyst (p-FePc/CNTs) exhibits an outstanding ORR activity and stability, and is superior to the commercial Pt/C catalyst in both the ORR half-reaction and Zn–oxygen batteries. Our DFT calculations also reveal that the Bader charge of Fe is more positive due to the presence of electron-withdrawing pyrazine linkers. This leads to a weakened bonding between Fe and O, primarily responsible for the enhancement of ORR activity. Our findings may open up a new avenue for the design of advanced single-atom electrocatalysts beyond ORR catalysts.

Author contributions

J. Lu supervised the projects. H. Xu, J. W. and J. Lu conceived and designed the experiment. H. Xu and T. S. performed the electrochemical measurement. B. X. performed the XANES and EXAFS measurements. J. Li performed the SEM and AFM characterization. S. L. performed the STEM and EDS characterization under the supervision of Q. H. H. Xu performed the TEM characterization under the supervision of M. L. P. L. and D. Q. performed the N K-edge XAS measurements. W. Y. performed the XPS characterization. J. Z. performed theoretical calculations. H. Xiao assisted with the analysis of the theoretical data. All authors contributed to the scientific discussion and the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

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