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Creating Hybrid Coordination Environment in Fe-Based Single Atom Catalyst for Efficient Oxygen Reduction

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Tailoring the local chemistry environment to optimize the geometric and electronic properties of single atom catalysts has received much attention recently. Yet, most efforts have been devoted to establishing the preferable binding between the solid support and the single metal atom. In this work, a hybrid coordination environment was created for Fe-based single atom catalysts, comprising inorganic anchoring site from the support and organic ligands from the precursor. Using N,S co-doped graphene oxide as the support, Fe phthalocyanine was selectively anchored by the N/S sites, creating the unique N/ S–Fe–N4 active sites as evidenced by extended X-ray absorption fine structure and Mössbauer spectrometry. Compared with other analogues with different metal centers or support, N/ S–Fe–N4 showed much improved activity in oxygen reduction reaction, delivering onset and half-wave potentials of 1.02 and 0.94 V. This was superior over the state-of-the-art 20 wt% Pt/C and the classic Fe–N4 carbon catalysts. Density functional theory calculations revealed that the interaction between phthalocyanine ligands and heteroatom dopant from the support pushed electrons of Fe site to para-position, facilitating O2 adsorption and activation. This work shows the exciting opportunities of creating a hybrid coordination environment in single atom catalysts and paves a new avenue of improving their catalytic performance.

Introduction

The oxygen reduction reaction (ORR) electrode is at the heart of fuel cells and metal–air batteries directly determines the efficiency and cost of these energy devices.[1] Pt-based catalysts remain the best option and have been extensively examined due to their excellent O2 activation capability. However, the scarcity and the associated high cost impede the industrial application on a large scale.[2] Therefore, finding a good Pt-free ORR electrocatalyst with low cost, high activity, and high stability is urgent yet remains a challenge. Recently, nanocarbon materials with sp2-hybridized carbon basal planes, such as graphene oxide (GO), emerged as a promising catalyst for a couple of reactions including ORR.[3] However, the pristine nanocarbons are usually inactive for catalysis because of the stable electronic configuration of the (0001) surface orientation.[4] Heteroatom (such as N and S) dopants break the sp2 hybrid structure, leading to the electronic localization and create non-neutral sites that are active for ORR.[5] However, such metal-free catalysts are not comparable with the state-of-the-art Pt catalysts in terms of activity.

To address this limitation, constructing single atom catalysts (SACs) on these carbon materials comes under the spotlight. Such isolated metal atoms, coordinated with heteroatom in carbon, simultaneously share the advantages of heterogeneous and homogeneous catalysts.[4b,6] SACs based on nitrogen-doped carbon consisting of Fe–N4 active sites (planar structure of a Fe atom coordinated by four N atoms) remain the most promising option for ORR. The nitrogen atoms stabilize the metal atoms and contribute to the modulation of the electronic structures of the active sites, boosting the catalytic activity in ORR. Despite the recent progress on tuning the coordination environment of Fe–N4 active sites, such as by introducing a second heteroatom (S or P), there are still remaining research questions and challenges.[6a] If we treat these catalysts as the “molecular catalyst” analogues, the nitrogen moieties from the carbon support will be the “inorganic ligands” of the single metal center. It is yet unclear how these “molecular catalyst analogues” will behave if an additional organic ligand is introduced to the coordination environment. In fact, this intuitive imagination comes from the inspiration of Nature’s catalysis by enzyme. For instance, Cytochrome c oxidase catalyzes 4-electron ORR to water involving an iron center accompanied with a bimetallic copper cofactor.[7] Unlike the classic Fe–N4 active site in SACs for electrochemical ORR, the active Fe site here in the enzyme has a unique coordination number of five, containing a five-coordinated Fe-porphyrin...
configuration with histidine as axial ligand. Research by synthetic model also revealed that the axial ligand is critical for O₂ binding and assists the O–O bond cleavage.⁹ The important roles of the coordination environment is also seen in many catalytic systems.⁹ Another associated challenge is to rationally create the well-defined single site on carbon materials. Today, most of the large-scale synthesis of these SACs relies on the high-temperature treatment to convert the single atom precursor into single metal sites on carbon. The local chemistry environment of these metal sites varies as some metal atoms can be coordinated by heteroatoms in carbon while others might be anchored by the intrinsic defects of carbon. It is thus challenging to elucidate the catalytic behavior of each site by experimental approaches.

In this work, we created a hybrid coordination environment, comprising inorganic anchoring site from the support and organic ligands from the precursor, in carbon-based SACs by accommodating metal phthalocyanine complexes (MPC) on N,S co-doped graphene oxide material (SNGO/MPC, M = Fe, Co, Cu, or Sn). Particularly, Fe phthalocyanine was selectively anchored by the N/S sites, creating the unique N/S–Fe–N₄ active sites as evidenced by the extended X-ray absorption fine structure (EXAFS) and Mössbauer spectroscopy. The new active sites demonstrated superior ORR performance in both three-electrode system and the 160 h longevity test in Zn–air battery compared to the conventional Fe₈ positions, facilitating O₂ activation.

To understand the anchoring sites on carbon, we first performed Raman spectroscopy. A decrease of D bands intensity of SNGO/FePc sample was observed (Figure S6). As a result, the I_D/I_G of SNGO/FePc (1.05) is slightly lower than that of SNGO (1.07). This is ascribed to the fact that FePc was immobilized on the energetically favored defect sides of SNGO, causing the area decrease of the defect domains. The chemical composition and elemental states of SNGO and SNGO/FePc were analyzed by X-ray photoelectron spectroscopy (XPS). The survey spectrum of SNGO/FePc shows signals of 5p₂ (162.8 eV), S 2s (226.1 eV), C 1s (284.2 eV), N 1s (398.2 eV), O 1s (531.2 eV), and Fe 2p (709.3 eV, Figure S7 and Table S1).

Results and Discussion

Hybrid coordination environment

The synthesis process of SNGO/MPC (M = Fe, Co, Cu, or Sn) is illustrated in Figure 1. SNGO was firstly synthesized by a simple pyrolysis of the mixture of GO and non-toxic 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([Bimi][TF₂N]) ionic liquid, serving as N and S sources. SNGO/MPC catalysts were subsequently obtained via dropwise addition of a homogeneous DMF solution of MPC into a suspension of SNGO. The anchoring of MPC onto the carbon matrix typically involves π–π stacking interactions between large conjugate rings and is enhanced by the interaction of metal center with heteroatom dopant from the carbon support. For comparison, MPCs were also dispersed on N- and S-doped GO (NGO/MPC and SGO/ MPC), respectively. Besides, single Fe atom embedded in N,S co-doped carbon (SNGO/Fe) was also prepared by a well-established method (Figures S1 and S2).

The anchoring of FePc on SNGO was first evidenced by the characteristic vibrations from the Fourier-transform infrared (FTIR) spectrum of the SNGO (Figure S3). This result was also illustrated by the Fe peak in the energy-dispersive X-ray spectroscopy (EDS) analysis (Figure S4). No obvious agglomeration of either SNGO sheet or FePc on the surface was identified from X-ray diffraction (XRD) patterns (Figure S5). To understand the configuration of the anchored FePc, we first obtained the thickness profile of SNGO/FePc using atomic force microscopy (AFM) (Figure 2a). In the wide-range scan (300 nm), the height was maintained at around 3.1 ± 0.1 nm. The small thickness variation implied that all FePc molecules were indeed “lay on the back” on the surface of SNGO as proposed on Figure 1 without agglomeration or “stand-up” (note the vertical FePc on the surface would be > 1.2 nm). This conclusion was further confirmed by the aberration-corrected transmission electron microscopy (TEM) using the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) mode. As shown in Figure 2b, the bright dots are recognized as well-dispersed Fe single atoms, validating that the Fe species are atomically isolated on the SNGO.

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X-ray absorption near-edge structure (XANES) and EXAFS spectra can further determine the coordination environment between SNGO and FePc. The pre-edge peak at 7113 eV in FePc is due to the square planar and centrosymmetric Fe–N₄ structure (D₄h symmetry) resulting from the transition of the 1s → 4p, ligand with metal charge transfer. In contrast, the edge peak of SNGO/FePc is shifted to the right and the peak is smoother, indicating a possible change in symmetry of the

![Figure 1. Synthesis process and structure of SNGO/MPC.](Image)
structure of the planar Fe–N4 structure (Figure S8a). The k3-weighted Fourier transform spectrum of the Fe K-edge EXAFS of SNGO/FePc shows a main peak at 1.50 Å, which can be attributed to the scattering interaction between Fe and N in the coordination shell of SNGO/FePc (Figure S8b). Interestingly, the peak intensity of the Fe–N peak of SNGO/FePc is higher than that of the Fe–N peak in FePc, implying the possible occurrence of additional coordination between FePc and N and/or S mieties in SNGO. The fine coordination environment of Fe site was further determined by EXAFS curve-fitting, and found that the experimental data are highly consistent with the N/S–Fe–N4 configuration (Figure 2e and Table S2). We thus concluded that the hybrid N/S–Fe–N4 coordination environment was indeed established.

The fine structure of Fe site was further analyzed by the 57Fe Mössbauer spectroscopy analysis. The Mössbauer spectrum of SNGO/FePc can be divided into two doublets (Figure 2f). The Doublet 1 peaks were assigned to the square-planar FeN4 species from the primary coordination sphere, the Doublet 2 peaks were the N-FeN4 sites with O2 molecule adsorption (N–FeN4–O2). The N–FeN4–O2 configuration was formed with central Fe atom in FePc coordinating to the N atom in SNGO, and then the Fe atom adsorbs the O2 molecules on the para-position. This shows the local symmetry undergoes a shift from a square plane to a five- ligand system in the presence of support–catalyst interaction. As for FePc, only one doublet was fitted observed, which could be attributed to the FeN4 structure of FePc. No obvious O2 adsorption peak was observed from FePc, proving the interaction between Fe site and doping atom enhances the adsorption of Fe site to O2 in SNGO/FePc sample.

Catalytic roles of metal center and coordination environment

To identify the electrocatalytic activity of the prepared catalysts for ORR, the linear sweep voltammetry (LSV) was firstly carried out in 0.1 M KOH electrolyte solution using the standard three-electrode system. As presented in Figure 3a, SNGO/FePc presents remarkable onset potential (E0) of 1.02 V (vs. reversible hydrogen electrode, RHE) and half-wave potential (E1/2) of 0.94 V, which are much superior to FePc (E0 = 0.83 V, E1/2 = 0.75 V) and the state-of-the-art Pt/C catalyst (E0 = 1.00 V, E1/2 = 0.85 V). Notably, E1/2 for the SNGO/FePc is more positive by around 190 and 90 mV than that for FePc and Pt/C catalyst, respectively. To identify the effect of coordination sites created by carbon substrate, the performance of NGO/FePc and SGO/FePc was also evaluated under the identical conditions. Interestingly, SNGO/FePc exhibits significantly better ORR performance than NGO/FePc and SGO/FePc with positive shift of 80 and 110 mV for E1/2, respectively (Figure 3b and Figure S9). Yet, it should be noted that the Fe–N4 sites created by Pt complex is also vital for catalysis, the control group of anchoring iron atom on SNGO (SNGO/Fe) clearly shows worse ORR activity (E0 = 0.96 V, E1/2 = 0.85 V), in agreement with various reports of Fe SACs ORR catalyst in the literature (see Table S3). We thus concluded that both coordination spheres substantially affect the activity of the iron center in ORR.

The metal center is another important factor controlling the activity in ORR. We prepared a series of analogue including SNGO/CuPc, SNGO/CuPc, and SNGO/SnPc, all of which show improved ORR performance compared with the bare MPC molecule immobilized on carbon (see the summary in Figure S10). Yet, SNGO/FePc remains the best, which is also reflected by the smallest Tafel slope of 56.1 mVdec−1 (Fig-
Figure 3. (a) LSV curves of as-prepared materials in 0.1 M KOH solution. (b) $E_1$ and $E_{1/2}$ of different catalysts. (c) Kinetic current density ($J_k$) and electron transfer number ($n$) of various materials at 0.2 V (vs. RHE). (d) $H_2O_2$ yield and $n$ of Pt/C and SNGO/FePc.

ure S11), better than that of the analogues and the commercial Pt/C (61.3 mV dec$^{-1}$) catalyst.

To further examine the reaction pathway, a series of polarization curves were tested in $O_2$-saturated 0.1 M KOH solution using rotated disk electrode (RDE) (Figure S12). SNGO/FePc exhibits an enhanced limiting current ($J_L$) of 32 mA cm$^{-2}$ compared with Pt/C of 28 mA cm$^{-2}$ (Figure 3c). SNGO/FePc exhibited a current density of 11.0 mA cm$^{-2}$ (Figure S13) at 0.9 V far exceeding that of Pt/C (2.0 mA cm$^{-2}$) and SNGO/Fe (1.8 mA cm$^{-2}$). The electrochemical surface area (ECSA) was measured by double-layer capacitance method (Figure S14), and SNGO/FePc (1057.5 cm$^2$) shows a slightly higher ECSA than that of SNGO/Fe (812.5 cm$^2$) implying an intrinsic enhancement in ORR performance for SNGO/FePc. The calculated electron transfer number ($n$) for SNGO/FePc reached 3.99, close to 4.0 for the Pt/C catalyst (Figure 3c), confirming that the ORR process was carried out in a four-electron manner. This conclusion was aligned with the results from the rotating ring disk electrode (RRDE) measurement (Figure S15). The $H_2O_2$ selectivity of SNGO/FePc (>$99\%$) was significantly higher than that of FePc, comparable with that of Pt/C.

SNGO/FePc is a robust catalyst as proven by the accelerated durability testing (ADT, see Figure S16a). In the potential dynamic study, the half-wave potential of SNGO/FePc negatively shifted by merely 15 mV after 5000 redox cycles. In contrast, the commercial Pt/C performed poorly by suffering a 53 mV shift (see Figure S16b). In the potentiostatic test, the durability of SNGO/FePc was evaluated by a chronocoulometric (CA) test biased at 0.7 V. SNGO/FePc retained 91\% relative current after 25000 s, higher than that of 81\% for Pt/C in the same conditions (Figure S17a). In addition, no obvious change in $i-t$ curve was observed after adding 3 M methanol to electrolyte for SNGO/FePc (Figure S17b), indicating a better methanol tolerance of SNGO/FePc. In order to further confirm the stability of SNGO/FePc, XRD, XPS, and TEM characterizations were conducted after the durability test. No obvious changes in structure and composition (Figures S18 and S19) were found after durability test, consistent with electrochemical results.

In order to further explore the contribution of heteroatoms on activity, the electronic localization function distribution of different samples was performed by DFT calculations. Graphene oxide-supported iron phthalocyanine (GO/FePc) presents a typical FeN$_4$ plane symmetrical structure (Figure 4a), which is not conducive to O$_2$ adsorption due to the uniform distribution of electrons.$^{[15b,19]}$ In contrast, the electron distribution on Fe site was pushed to the para-position by interaction between Fe site in FePc and N atom of the dopied support resulting an axially asymmetric electron distribution at the N-FeN$_4$ site (Figure 4b). The asymmetric electron distribution was further enhanced by introducing S heteroatom, because the strong electron-donating property of S facilitated the "push effect" (Figure 4c). For SNGO/Fe, the charge symmetry distribution of the central Fe atom was slightly distorted by the introduction of S heteroatoms (Figure S20). The asymmetric electron distribution was well consistent with the catalytic performance in the same order (SNGO/FePc > NGO/FePc > SNGO/Fe > GO/FePc). In addition to the observed axial asymmetry in the electron distribution of Fe, the Gibbs free energy of each basic step of ORR was further conducted to reveal the mechanism of the superior catalytic activity of the prepared catalysts (Figures 4d and S21). For GO/FePc, NGO/FePc, and SNGO/FePc, $O_2$ intermediates formation was the rate-determining step (RDS, Figure 4d).
with limiting potentials of 2.55, 2.34, and 1.78 eV, respectively. The energy barriers for RDS are in the same trend as asymmetric electron distribution and catalytic performance. Therefore, the mechanism of performance enhancement was proposed that the doped N in supports pushes electrons of Fe site to the para-position and thus breaks the symmetric electron distribution of the FeN$_4$ site, and collaborative doping of N and S in SNGO/FePc enhances this push effect. Actually, the push effect has been known for natural ORR catalyst cytochrome c oxidases, where electron of the axial histidine imidazole group was pushed to catalytic Fe site and subsequently facilitates O$_2$ binding and activation by increasing pK$_a$ of oxygen atoms of the resulted Fe–O$_2$ adduct.

**Application in device**

In order to explore the practical application, SNGO/FePc was finally employed as the cathode material for a Zn–air battery (ZAB) (Figure 5a).$^{[22]}$ Considering ORR and oxygen evolution reaction (OER) were involved in ZAB, the performance for OER of as-prepared materials was also evaluated. The oxygen electrode activity ($\Delta E$) of SNGO/FePc is only 0.68 V, which is much smaller than other control samples (Table S4 and Figure S22). The cell with SNGO/FePc as the cathode catalyst (1.50 V) showed similar open-circuit potential compared with that employed with Pt/C catalyst (1.48 V) (Figure S19a). The peak power density for SNGO/FePc cell reached 153.3 mW cm$^{-2}$ at a current density of 250 mA cm$^{-2}$, which was better than the Pt/C cell (148 mW cm$^{-2}$). Furthermore, the specific capacities of SNGO/FePc and Pt/C air cathode-based ZAB were evaluated to be 796 mAh g$^{-1}_{Zn}$ (coulombic efficiency: 97.1% of the theoretical capacity, 820 mAh g$^{-1}_{Zn}$) and 725 mAh g$^{-1}_{Zn}$, respectively, according to the quality of Zn consumed by the anode (Figure S23b).

Two liquid Zn–air batteries in series, with SNGO/FePc as the air cathode, successfully powered an LED display (3.0 V) (Figure S24). In the charge–discharge test at a current density of 10 mA cm$^{-2}$ (Figure 5c), the ZAB with SNGO/FePc showed no obvious degradation after 160 h longevity test. In contrast, ZAB with Pt/C showed a significant voltage attenuation after 60 h of cycling.$^{[22b,23]}$ The faster degradation might be ascribed to the corrosion of the electrode during the charging cycle as Pt might also facilitate the carbon corrosion during OER. To the contrary, the Fe center is strongly anchored on the carbon. Even in the charging cycle under the anodic potential, the active metal center is unlikely to be destroyed. All these results clearly showed that the SNGO/FePc catalyst is superior in terms of both electrocatalytic activity and stability.

**Conclusion**

We have demonstrated that the hybrid coordination environment created by heteroatom dopant and phthalocyanine ligands can tune electronic states of catalytic center and therefore boost the oxygen reduction reaction (ORR). The SNGO/FePc was proved to be a highly active ORR catalyst with excellent overpotentials and outstanding long-term stability better than Pt/C catalyst, which was also evidenced in the zinc–air battery test. Density functional theory calculations show heteroatom doping breaks the symmetric structure of FeN$_4$ and enhances the ability of Fe site to adsorb oxygen, and facilitates ORR. This work provides a novel strategy to precisely control the catalytic behavior of heterogeneous catalyst by tuning the coordination environments of active site and can be potentially extended to other proton-coupled electron transfer reactions.

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**Figure 4.** Electron localization functions of (a) GO/FePc, (b) NGO/FePc, and (c) SNGO/FePc (longitudinal section). (d) Free-energy paths of intermediates in ORR on GO/FePc, NGO/FePc, and SNGO/FePc based on $U = 0$ V.
Experimental Section

Materials

GO was obtained from Suzhou Hengqiu Technology Co., Ltd. Urea (CH₄N₂O), ethanol, KOH, NaOH, dibenzyl disulfide (C₁₄H₁₄S₂), and FePc were purchased from Shanghai Dibo Chemical Technology Co., Ltd. [Bimi][Tf₂N] and commercial Pt/C (20 wt %) were purchased from Shanghai Bide Pharmaceutical Technology Co., Ltd.

Synthesis of SGO/MPc, NGO/MPc, and SNGO/MPc

0.05 g GO and 2.5 mL [Bimi][Tf₂N] were mixed and then ultrasonicated for 1 h. The mixture was shifted to a porcelain boat and heated to 900°C keeping 1 h at a rate of 5°C min⁻¹. SNGO was obtained when the temperature was naturally cooled to room temperature. For comparison, following the same steps, SGO and NGO were composed by dibenzyl disulfide and urea as S and N sources, respectively. 5 mg SNGO and 15 mg MPc (M = Fe, Co, Cu, or Sn) were added to a beaker containing 20 mL of DMF respectively, and ultrasonicated for 2 h. Next, the MPc solution was added to the SNGO mixture by dropping and then ultrasonicated for 2 h at 50°C. After that, the mixture was dried at 80°C to obtain SNGO/MPc materials. SGO/MPc and NGO/MPc were prepared according to the same procedure with SGO and NGO as supports, respectively.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.
