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Communication

# Highly active and stable single iron site confined in graphene nanosheets for oxygen reduction reaction



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# ABSTRACT

Exploring high performance non-precious metal catalysts to substitute Pt for oxygen reduction reaction (ORR) has stimulated wide research interest recently, but it remains a great challenge. Herein, we report a single iron site confined in graphene catalyst via 4N atoms, forming flat FeN<sub>4</sub> structure in the matrix of graphene. The optimized catalyst shows a high ORR activity, almost coming up to the activity of commercial 40% Pt/C catalyst, but a significantly higher stability and tolerance to SO<sub>x</sub>, NO<sub>x</sub> and methanol with respect to 40% Pt/C. This welldefined structure provides an ideal model to study the catalytic origin of iron-based catalysts. DFT calculations indicate that the high ORR activity origins from highly dispersed and high-density coordinatively unsaturated Fe centers, and the excellent stability origins from the unique confinement of the graphene matrix via 4N atoms. This reaction can proceed easily to H<sub>2</sub>O via a four electron transfer path way on the single iron site, which is further confirmed by the experiment. This experimental and theoretical study provides a further insight into the nature of the Fe/N/C catalyst and also introduces a reference for designing high efficient catalysts in electrocatalysis.

## 1. Introduction

Oxygen reduction reaction (ORR) is a key process in the cathode of  $H_2$ /methanol- $O_2$  fuel cells [1–4] and metal-air batteries [5–7]. So far Pt-based materials are known as the best catalysts and are widely practiced for ORR [8-10]. However, the commercialization of the above devices is still hindered due to the high cost of the Pt-based catalysts. Therefore, significant efforts are being devoted to replacing Pt catalyst with earthly abundant materials, i.e. non-precious metals and carbon-based materials containing separately or collectively transition metal/hetero-atom/carbon elements [3,11-20]. Among them, metal-N4 macrocycles have been considered as one of the best substitutions for Pt [21]. Since the discovery of high ORR activity of metal-N<sub>4</sub> chelates by Jasinsky in 1964 [22], there has been an increasing interest and research effort in the design, characterization and functionalization of these materials [21,23,24]. However, the activity and stability of the isolated Metal-N<sub>4</sub> chelate electrocatalysts are still limited due to its high electric resistance and the chemical attack by the reaction medium and the intermediate  $H_2O_2$  released during oxygen reduction [21]. Immobilization of metal-N4 macrocycles onto carbon substrates, such as activated carbon [25] and carbon black [26] upon liquid-phase

method, followed by a thermal treatment usually at 400-1000 °C [24] can improve the catalyst stability as well as its activity. However, the metal-N<sub>4</sub> macrocycles are prone to sublimate during the thermal treatment, which leads to the loss of the active sites in the final sample and therefore reduces the activity. In addition, the limited electron conductivity and weak resistance to chemical corrosion of carbon black and activated carbon also impede the final performance. Graphene, as one of the allotropes of carbon, has attracted great attention in electrocatalysis recently due to its large specific surface area, high conductivity and mechanical strength [15,17,27-31]. However, it is difficult to use perfect  $sp^2$  hybridized graphene as the support for metal-N<sub>4</sub> macrocycles because of the weak interaction between them.

Recently, we reported a one-step method for highly dispersed single FeN4 center with coordinatively unsaturated (CUS) Fe sites confined in graphene nanosheets (FeN4/GN) via direct ball milling of iron phthalocyanine (FePc) and graphene nanosheets (GN) [32]. The obtained FeN<sub>4</sub>/GN sample showed high performance in the direct catalytic oxidation of benzene to phenol at room temperature. DFT calculations indicated that the confined FeN4 center can efficiently activate O species. Therefore, we anticipate that the FeN<sub>4</sub>/GN catalyst can be utilized for efficient oxygen reduction reaction considering the high

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electron conductivity of graphene and the high density of the active FeN<sub>4</sub> center. Here, we prepared a series of FeN<sub>4</sub>/GN catalysts with different Fe content via direct ball milling. The optimized catalyst shows a high ORR activity, and a significantly higher stability and tolerance to  $SO_{xy}$ ,  $NO_x$  and methanol with respect to 40% Pt/C.

#### 2. Experimental section

## 2.1. Raw materials

Graphite flake (99.8%, metals basis) was purchased from Alfa Aesar. Iron phthalocyanine (96%) was purchased from Acros organics.

#### 2.2. Synthesis of graphene nanosheets (GN)

GN was prepared following the same procedure in our previous report [32]. In a typical experiment, 2.0g graphite flake and 60g steel balls (1-1.3 cm in diameter) were put into a hardened steel vial inside a glove box and purged with high purity Ar (99.999%) for 20 min before the vials were sealed. The ball milling was carried out at 450 rpm for 20 h.

## 2.3. Synthesis of FeN<sub>4</sub>/GN

FeN<sub>4</sub>/GN synthesis is the same as our previous report [32]. Briefly, 2.0 g FePc and GN composites with a desired ratio, and 60 g steel balls (1–1.3 cm in diameter) were ball milled following the same procedure as synthesis of GN. A series of samples with different Fe content were prepared, including FeN<sub>4</sub>/GN-1.5 (1.5 indicates 1.5% Fe measured by inductively coupled plasma (ICP), the same below), FeN<sub>4</sub>/GN-2.7 and FeN<sub>4</sub>/GN-4.0, from the precursor FePc and GN with a ratio of 15%, 30%, and 45%, respectively.

#### 2.4. Characterization

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were performed on a JEOL ARM200F equipped with double aberration correctors and a cold field emission gun operated at 80 kV. STEM images were recorded using a HAADF detector with a convergence angle of 30 mrad and a collection angle between 90 and 370 mrad. Under these conditions, the spatial resolution is ca. 0.08 nm.

### 2.5. The rotating disk electrode (RDE) measurements

The RDE measurements were employed to assess the activity, duration and anti-poison performance of the catalysts in ORR, which were evaluated on a 2273 potentiostat/galvanostat equipped with a three-electrode electrochemical cell and gas flow control systems. Mercury/mercuric oxide electrode (Hg/HgO) (1 M NaOH-filled) was used as the reference electrode, and a Pt wire as the counter electrode. The Hg/HgO reference electrode was calibrated in H<sub>2</sub>-saturated 1 M NaOH solution, reversible hydrogen electrode(RHE) was converted by equation E(RHE)=E(Hg/HgO)+0.914. A glassy carbon rotating ring disk electrode with a diameter of 5 mm (0.196 cm<sup>2</sup>) covered by a thin film of the catalyst was used as the working electrode. Typically, 5 mg catalyst was ultrasonically suspended in 2 mL ethanol and 50 µL of Nafion solution (5 wt%, Du Pont) to form a homogeneous ink. Then 25 µL of the ink was spread onto the surface of the glassy carbon with a micropipette followed by drying under room temperature. Experiments were conducted in 1 M NaOH solution, which were saturated with oxygen at 25 °C. A rotation rate of 2500 rpm and a scan rate of 10 mV/ s were employed.

### 2.6. The rotating ring disk electrode (RRDE) measurements

The RRDE measurements were employed to assess the H<sub>2</sub>O<sub>2</sub> yield and the electron transfer number during ORR, which were performed on a computer-controlled Pine bipotentiostat (Pine Company), with a modulated speed rotator with a working electrode fitted with a glassy carbon disk (diameter of 5.7 mm) and a polycrystalline platinum ring. Mercury/mercuric oxide electrode (Hg/HgO) (1 M NaOH-filled) was used as the reference electrode, and a Pt wire as the counter electrode. The working electrodes were prepared using the same method and the same dosage of the catalyst with the RDE measurements. To perform the RRDE tests, cyclic voltammetry (CV) scans were performed on the disk from -0.8 to 0.2 to -0.8 V (vs. Hg/HgO) in O<sub>2</sub> - saturated 1 M NaOH solution at a scan rate of 10 mV/s and a rotation speed of 1600 rpm at 25 °C, while the potential of the platinum ring was held at 0.8 V (vs. Hg/HgO). The hydrogen peroxide yields in the ORR were calculated from the RRDE experiments as XH2O2% =(2Iring/N)/  $(I_{disk}+I_{ring}/N)$ . The collection efficiency of the ring electrode (N=0.38) was calibrated by the K<sub>3</sub>Fe(CN)<sub>6</sub> redox reaction. The electron transfer number was estimated according to n=2X<sub>H2O2</sub>%+4X<sub>H2O</sub>%=4 I<sub>disk</sub>/  $(I_{disk}+I_{ring}/N).$ 

### 2.7. Density functional theory calculations

All calculations were performed using the Vienna Ab-initio Simulation Package (VASP) with the projector augmented wave method and a cutoff energy of 400 eV [33-39]. The generalized gradient approximation method with Perdew-Burke-Ernzerhof (PBE) functional for the exchange-correlation term [40,41] were used. The vacuum thickness in the c direction of the FeN4/GN model was set to 10 Å. The Monkhorst-Pack k-point sampling scheme was adopted [42]. Spin-polarization was considered for all calculations. The free energies of the reaction intermediates were obtained by  $G = E_{total} + ZPE - TS$ , where E<sub>total</sub> is the total energy of species, ZPE is the zero point energy and S is the entropy. The effect of water was considered in calculating the free energy of the reaction intermediates by adding a correction on the formation energy of reaction intermediates using the method in our previous studies [28,30]. The effect of a bias was included in calculating the free energy change of elementary reactions involving transfer of electrons by adding  $\Delta G(U)$ =neU, where n is number of electrons transferred and U is the electrode potential [43]. The transition states of each elementary reaction was searched using the constrained minimization approach in the presence of a few water layers with pre-optimized structures [28,30,44-46]. The effect of bias on the activation energy is not considered in our simulations. In a previous study of the ORR mechanism on N-doped graphene, the bias effect on the reaction mechanism is marginal and does not affect the relative difficulty of elementary steps, and hence it is neglected in this work [28,30].

# 3. Results and discussion

The typical morphology of FeN<sub>4</sub>/GN is presented by HAADF-STEM as shown in Fig. 1a. One can see well dispersed white dots in the graphene nanosheets as tagged by arrows, corresponding to the Fe atoms which are confined by N atoms as conformed by our previous work by combining high-angle annular dark-field scanning transmission electron microscopy with low temperature scanning tunneling microscopy [32].

Cyclic voltammetry (CV) measurements in 1.0 M NaOH were performed to assess the ORR activity of the catalyst. The FeN<sub>4</sub>/GN sample exhibits a pronounced peak at 0.84 V versus reversible hydrogen electrode (RHE) in O<sub>2</sub>-saturated electrolyte in contrast to N<sub>2</sub>saturated electrolyte (Fig. 1b), indicating there a significant ORR around this potential. We first optimized the catalyst component and found only a moderate Fe content in graphene nanosheets, i.e. the



**Fig. 1.** Morphology and electro catalytic performance of FeN<sub>4</sub>/GN samples. (a) HAADF-STEM image of FeN<sub>4</sub>/GN-2.7. The area with red cycles shows some typical single Fe atoms in the nanosheets. The insert in the upper shows the scheme of the atomic structure of a FeN<sub>4</sub> center in graphene. (b) CVs of FeN<sub>4</sub>/GN-2.7 in N<sub>2</sub>-saturated (dotted) and O<sub>2</sub>-saturated (solid) 1.0 M NaOH at the scan rate of 100 mV/s<sup>-1</sup>. (c) Oxygen reduction voltammograms of graphite, GN, FePc, FeN<sub>4</sub>/GN-1.5, FeN<sub>4</sub>/GN-2.7, FeN<sub>4</sub>/GN-2.7, FeN<sub>4</sub>/GN-4.0% and 40% Pt/C in O<sub>2</sub> saturated 1.0 M NaOH at the scan rate of 10 mV/s<sup>-1</sup>. (d) The ORR activity of FeN<sub>4</sub>/GN-2.7% and 40% Pt/C after 7000 cycles. Different potential cycling was carried out between 0.11 and 1.11 V (vs. RHE) at 100 mV/s before the test of RDE polarization curves. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).



Fig. 2. Durability test of FeN<sub>4</sub>/GN-2.7% and 40% Pt/C for ORR in the presence of methanol, NO<sub>x</sub> and SO<sub>2</sub>. (a) 40% Pt/C and (b) FeN<sub>4</sub>/GN-2.7 in ORR in the presence of methanol (100 mM), NO<sub>x</sub> (100 mM NaNO<sub>2</sub>) and SO<sub>2</sub> (10 mM Na<sub>2</sub>SO<sub>3</sub>) in O<sub>2</sub> saturated 1.0 M NaOH at a scan rate of 10 mV/s.

FeN<sub>4</sub>/GN-2.7 (2.7 wt% Fe) shows the highest ORR activity among all these FeN<sub>4</sub>/GN composites (Fig. 1c). We speculate that a lower Fe content, e.g. FeN<sub>4</sub>/GN-1.5 (1.5 wt% Fe), cannot provide enough active sites for ORR, while too much Fe content, e.g. FeN<sub>4</sub>/GN-4.0 (4.0 wt% Fe) may lower the dispersion of FeN<sub>4</sub> centers and reduce the overall electronic conductivity of the sample and hence reduce the electrocatalytic activity. As references, graphite, GN, FePc, and commercial 40 wt% Pt on Vulcan carbon black (from Johnson Matthey Corp.) (40%

Pt/C) were also measured. Although FePc was previously reported with a rather high ORR activity, our experiments show it is far less active than the commercial 40%Pt/C, as shown in Fig. 1c. Remarkably the FeN<sub>4</sub>/GN-2.7 catalyst shows higher ORR activity approaching that of commercial 40% Pt/C catalyst as both the onset potential and the limiting current are almost similar. The ORR activity of FeN<sub>4</sub>/GN samples are much higher than previously reported N-doped grapheme [47,48] and is comparable to the most active Fe/N/C catalysts [49,50].



**Fig. 3.** Theoretical analysis of the catalytic reaction process by DFT calculations and experiments. (a) The dissociative adsorption energy  $(E_{a(dis)})$  of oxygen on different sites of the FeN<sub>4</sub>/GN structure, in reference to the gas phase O<sub>2</sub>. (b) Projected density of states of Fe, N, and C atoms of the corresponding FeN<sub>4</sub>/GN structure in the inset of (a). (c) Free energy diagram of the evolution of the FeN<sub>4</sub>/GN structure under reaction condition (green line, O<sub>2</sub>+H<sub>2</sub>O +2e<sup>-</sup> $\rightarrow$ O<sub>(ads)</sub>+2OH<sup>-</sup>) and different oxygen reduction reaction pathways (black, blue, and red lines) on the iron site. (d) The H<sub>2</sub>O<sub>2</sub> yield and the corresponding electron transfer number of FeN<sub>4</sub>/GN-2.7, FePc, 40% Pt/C and GN according to the RRDE measurements. All tests have been carried out in O<sub>2</sub>-saturated 1.0 M NaOH at a rotation rate of 1600 rpm and a scan rate of 10 mV/s. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

More importantly, this  $FeN_4/GN-2.7$  catalyst exhibits a greater stability under ORR conditions than 40% Pt/C. As shown in Fig. 1d and S1, both the onset potential and the limiting current of 40%Pt/C catalyst decline significantly after cycling for 7000 cycles between 0.11 and 1.11 V (vs. RHE) at 100 mV/s in O<sub>2</sub>-saturated electrolyte. In contrast, the onset potential only decreases slightly with respect to its initial one for FeN<sub>4</sub>/GN-2.7 and the decrement in the limiting current

is obviously smaller than that over Pt/C (Fig. 1d and S1). After 7000 CVs cycling, FeN<sub>4</sub>/GN-2.7 exhibits a significantly higher activity than 40% Pt/C catalyst at both the onset potential and limit current (Fig. 1d), suggesting a better stability of FeN<sub>4</sub>/GN-2.7 in ORR.

It is known that Pt is readily poisoned by even trace  $SO_x$  and  $NO_x$  in air, which can significantly reduce the activity and the durability of H<sub>2</sub>-O<sub>2</sub> fuel cells [20,51,52]. In addition, in direct methanol fuel cells, Pt/C

is also sensitive to trace methanol crossing from the anode through the membrane [4]. As expected, 40% Pt/C shows a drastic decrease in the ORR activity in the presence of trace  $SO_x$  (10 mM Na<sub>2</sub>SO<sub>3</sub>), NO<sub>x</sub> (100 mM NaNO<sub>2</sub>) and methanol (100 mM) (Fig. 2a). In contrast, FeN<sub>4</sub>/GN-2.7 remains almost intact under the same conditions (Fig. 2b), exhibiting an excellent tolerance to  $SO_x$ , NO<sub>x</sub> and methanol compared with Pt/C catalyst, which might be owing to the preferential adsorption of O<sub>2</sub> over SO<sub>x</sub>, NO<sub>x</sub>, and methanol on the Fe site of FeN<sub>4</sub>/GN.

To gain further understanding of the ORR reaction process at an atomic and molecular level, we carried out density functional theory (DFT) calculations of the active sites and the reaction mechanism (Fig. 3). We firstly compared the activity of different sites, i.e. Fe, N and C atoms for oxygen adsorption. As indicated in Fig. 3a, the dissociative adsorption of O<sub>2</sub> on the Fe site is much stronger than that on the C sites, owing to the notably higher distribution of density of states of Fe near the Fermi level than that of C atoms (Fig. 3b). O atom does not bind with the N site and moves to the Fe site after structural relaxation. These results suggest that the Fe site most likely serves as the active site for the ORR reaction. Thus we further investigated the reaction progress on the Fe site. In the first stage of the reaction process, the Fe site is readily to form a Fe<sup>=</sup>O structure with a free energy gain of 2.52 eV due to the strong adsorption of O, as shown in the first step (green line) in Fig. 3c. Further hydrogenation of this Fe<sup>=</sup>O producing Fe-OH is energetically unfavorable with an energy loss of 0.41 eV (black line in Fig. 3c), indicating that the formed Fe<sup>=</sup>O structure is quite stable and the adsorbed O is not likely to desorb under the reaction conditions. However, our results show that the other side of the Fe opposite to the pre-adsorbed O of the Fe<sup>=</sup>O structure can serve as the active center for the ORR. The ORR reaction process is accompanied by a dynamic cycling of hydrogenation and dehydrogenation of the intermediate X-Fe=O structure, i.e. X-Fe=O=X-Fe-OH (X refers to reaction intermediates of ORR, which are  $O_{2(ads)}$ ,  $OOH_{(ads)}$ ,  $O_{(ads)}$ , and  $OH_{(ads)}$ ) which promotes the reaction by lowering the activation barrier of O-OH<sub>(ads)</sub> cleavage by 0.48 eV (blue line in Fig. 3c) compared to that without the dynamic process (red line in Fig. 3c). The largest barrier is given by the step of O–OH<sub>(ads)</sub> cleavage producing O<sub>ads</sub> and OH<sup>-</sup> which is 0.59 eV but still moderate for the reaction to proceed with a reasonable rate under room temperature. Therefore, our theoretical results demonstrate that the O2 molecule can readily be reduced to H<sub>2</sub>O molecule via a 4 electron transfer pathway on the Fe site of the FeN<sub>4</sub> structure. The reaction following the 4 electron transfer pathway is ideal while the 2 electron transfer pathway will lead to formation of H<sub>2</sub>O<sub>2</sub>, which will etch the catalyst in a long run and consequently severely reduce the ORR activity and durability.

We also investigated the electron transfer number during ORR in experiment in order to confirm the result of the DFT calculations. As shown in Fig. 3d, the H<sub>2</sub>O<sub>2</sub> yield estimated from the rotating ring disk electrode (RRDE) measurements is less than 0.5% for FeN<sub>4</sub>/GN-2.7, which is obviously lower than 5% for 40% Pt/C at all potentials. The corresponding electron transfer number for FeN<sub>4</sub>/GN-2.7 (Fig. 3d) is about 3.99, close to 4 in the whole process. The above results indicate that graphene nanosheets confining FeN<sub>4</sub> centers significantly enhance the ORR activity in an alkaline medium, which can be as a promising substitution of commercial 40% Pt/C catalyst.

## 4. Conclusions

In conclusion, we demonstrated that the graphene confined coordinatively unsaturated iron atom via 4 N atoms can be used as an efficient ORR catalyst. The optimized FeN<sub>4</sub>/GN-2.7 exhibits high ORR activity which is comparable with the commercial 40% Pt/C catalyst. Especially, the stability and anti-poison ability are even better than the Pt/C catalyst. The DFT calculations found that the high stability can be attributed to strong covalent bonds between C-N-Fe atoms, in which N atoms as "anchors" can bond with C atoms and Fe atoms strongly. And the high activity is tightly correlated with the high density of active sites and also the low reaction energy barrier for ORR on these sites, leading to the easy transformation of  $O_2$  to  $H_2O$  via a 4 electron transfer pathway, which is further confirmed by the experiment. This study is anticipated to promote the applications of this novel material as a high efficient catalyst in electrocatalysis and heterogeneous catalysis involving oxygen activation.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2016.12.056.

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