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Porous graphene doped with Fe/N/S incorporated Fe$_3$O$_4$ nanoparticles for efficient oxygen reduction reaction

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Rational construction of carbon base with porous structure incorporated with effective dopants is an intriguing and challenging strategy to develop advanced electrocatalysts for oxygen reduction reaction (ORR). Herein, we synthesize a novel efficient electrocatalyst of three-dimensional (3D) porous graphene doped with Fe/N/S incorporated Fe$_3$O$_4$ nanoparticles (Fe$_3$O$_4$/FeNSG), using melamine formaldehyde resin playing the dual-functional roles of soft template and nitrogen-abundant source. Rational design of the Fe$_3$O$_4$/FeNSG-3 with 3D porous architecture, abundant of active sites (Fe-N-C, Fe$_3$O$_4$, pyridinic N, C-S-C, et al.), and large surface area (530.5 m$^2$ g$^{-1}$), makes it an efficient electrocatalyst towards ORR. The Fe$_3$O$_4$/FeNSG-3 catalyst shows a much positive ORR onset potential (0.951 V) and half-wave potential (0.810 V), comparable to the commercial Pt/C in alkaline media. Furthermore, the catalyst exhibits a four-electron transfer pathway, superior methanol tolerance and stability. This work paves the way to prepare low-cost, active, and stable non-Pt group metal catalysts through regulating the catalytic active sites on 3D graphene with porous architecture.

1. Introduction

Deriving from the high performance of oxygen reduction reaction (ORR), precious metal of the platinum (Pt)-based catalysts crucially enable numerous emerging technologies such as hydrogen production, metal-air batteries, catalytic converters and fuel cells (FCs).$^{1-7}$ However, their prohibitive cost and low natural abundance impose restrictions on widespread utilization, which results in highly demanding for searching inexpensive and resource-rich catalysts with attractive electrocatalytic performance. The non-Pt group metal (non-PGM) catalysts have attracted increasing interests in recent years due to their high electrocatalytic activity and low cost.$^{8-16}$ Non-PGM catalysts are generally based on precursors based on earth-abundant elements, such as carbon (C), nitrogen (N), sulfur (S), phosphorus (P) along with transition metals, such as iron (Fe) and cobalt (Co).$^{17-22}$ These promising non-PGM catalysts include the representatives of metal oxides (e.g., Co$_3$O$_4$ and Fe$_3$O$_4$),$^{23, 24}$ metal sulfides (e.g., CoS$_2$ and Co$_9$S$_8$),$^{25, 26}$ metal-nitrogen-carbon materials (M-N-C, M=Fe, Co, etc.),$^{27, 28}$ Fe/Fe$_2$C based materials,$^{29}$ metal free of the heteroatom-doped carbons.$^{30-32}$ The metal oxides and sulfides usually suffer from low electrical conductivity, large particles, small surface area, as well as easy dissolution and further aggregation.$^{23-26, 33}$ With unique core-shell structure, the Fe/Fe$_2$C based catalysts are confronted with synthesis difficulties.$^{29, 34}$ The heteroatom-doped carbons without any metals possess the superiorities of extremely low cost, but its electrocatalytic activity is still limited according to previous reports.$^{14, 16, 35}$ Nevertheless, the M-N-C based materials have been given specific attention and regarded as the most promising of non-PGM catalysts owing to their highly active and stable electrocatalytic performance towards ORR.$^{15, 17-19}$

To date, great efforts have been paid to fabricate novel M-N-C catalysts.$^{17-19, 27}$ Piotr Zelenay’s research group reported a high-performance PGM-free ORR catalyst, which could be ascribed to the FeN$_4$ active sites associated with specific lattice-level carbon structures together with the large surface area (~1500 m$^2$ g$^{-1}$) and porous architectures.$^{17}$ Yang et al. reported the Fe/Co-containing polypyrrole hydrogel derived ORR catalyst, which presented high ORR performance due to the homogeneous incorporation of highly active Fe/Co-N-C species.$^{35}$ Chen et al. developed a reactive and stable isolated single-atom Fe/N-doped porous carbon catalyst, which exhibited excellent ORR activity owing to the unique structure of isolated Fe atoms incorporating with N.$^{36}$ Based on the analysis of above classic reports, it can be noted that rational design of abundant active sites, three-dimensional (3D) porous structures, and large surface areas offers great opportunities to create more state-of-the-art M-N-C catalysts.$^{17, 18, 19}$ In order...
to acquire the homogeneously dispersed active sites along with well-tuned porous structures, some hard templates such as ordered mesoporous silica SBA-15 and silica colloid are used to aid the preparation of these M-N-C catalysts.\textsuperscript{18, 24} However, the hard template-assisted method on one hand inevitably includes infiltration of precursors, on the other hand suffers from the difficulties to remove the template.\textsuperscript{21, 24} Therefore, it is still highly needed and remains a challenge to design this kind of M-N-C materials by new synthesis method.

It is reported that introducing abundant active sites (e.g., Fe/N/C, C-S-C, etc.) into porous carbon can greatly enhance the catalysts’ ORR activity.\textsuperscript{15, 37-40} Doping Fe/N/C with heteroatoms, specifically S has been demonstrated displaying a great potential in enhancing the ORR reactivity.\textsuperscript{38-40} Regarding S, the reported work has discovered that S species (e.g., thiophene-S) at the zigzag and armchair edges of the carbon framework could induce “electron spin” redistribution, showing contributions in boosting ORR performance.\textsuperscript{41} Similar to N, S atom is a p-block element, but its electronegativity and atomic radius are different. On one hand, S with the relative big atomic radius is likely to induce more defects on carbon framework.\textsuperscript{40} On the other hand, the electronic structures of the Fe-N active centers can be modified by S because of its lower electronegativity.\textsuperscript{15} Therefore, the S doping is a possible way to further improve the ORR activity of Fe-N-C based catalysts.

To tackle the above-mentioned issues, melamine formaldehyde resin (MFR) was selected as a nitrogen-rich soft template to assist the formation of porous structures, because it could be not only easily synthesized by a hydrothermal method, but simply decomposed by pyrolysis treatment.\textsuperscript{31, 37, 42} Significantly, during the pyrolysis process, MFR could give rise to the N-doped carbon.\textsuperscript{43} As a new type of graphene sheet, 3D honeycomb-like structured graphene (HSG) exhibits distinct honeycomb-like architecture, high conductivity, structural defects and desirable initial surface area along with porous architecture, and has been demonstrated showing great superiorities in catalysts’ carbon alternatives.\textsuperscript{4, 45, 46}

Hence, it is very interesting to simultaneously introduce the N, S and Fe into HSG by using the MFR, benzyl disulfide (BD) and a cheap Fe precursor of ferric chloride. Therefore, for the first time, we prepare a novel efficient electrocatalyst of 3D porous graphene doped with Fe/N/S incorporated FeO\textsubscript{4}/FeNSG nanoparticles (FeO\textsubscript{4}/FeNSG) by a pyrolysis method.\textsuperscript{31, 44} The schematic preparation of the FeO\textsubscript{4}/FeNSG is shown in Scheme 1. The originalities of our work mainly embody in: i) 3D porous graphene with unique structure and large initial surface area was used as the carbon source; ii) the MFR was employed as not only the N source for doping, but also the surface area contributor; iii) acid-leaching process can be used to remove the unstable reagents (e.g., FeS, uncovered FeO\textsubscript{4}, etc.); and leave the well-preserved iron-containing species (e.g., Fe/N/C, FeO\textsubscript{4}, etc.) in the hybrid.\textsuperscript{15, 17} More importantly, the obtained optimal FeO\textsubscript{4}/FeNSG-3 catalyst shows high ORR performance and comparable to the Pt/C in alkaline media. With regard to this excellent electrocatalytic activity towards ORR, the FeO\textsubscript{4}/FeNSG-3 hybrid can be considered as a novel and promising non-PGM catalyst.

2. Experimental

2.1 Catalyst preparation

The 3D honeycomb-structured graphene (HSG) was prepared according to our previously reported work.\textsuperscript{45} For the synthesis of the hybrid, certain melamine was firstly added into formaldehyde (37 wt%, 0.18 mL) followed by adding 0.82 mL of deionized (DI) water. The mixture was then sonicated for 5 min to get melamine well-dispersed. Next, the well-dispersed melamine together with 1 g of ferric chloride (FeCl\textsubscript{3}, 6H\textsubscript{2}O) were added into the homogeneous HSG suspension (1.5 mg/mL, 10 mL) with vigorous stirring for 2 h followed by sonication for 10 min. Afterwards, the above mixture was transferred into an autoclave and kept in an oven at 180 °C for 12 h. The S source of benzyl disulfide (BD) was added into the obtained mixture with drastic stirring and heated to 75 °C for 1 h. The solid powder can be acquired after thermally dried at 90 °C for overnight. After that, pyrolytic and acid-etching processes are needed. In detail, the as-prepared solid powder was first pyrolyzed at 850 °C with flowing Ar for 2 h and then subjected to 0.5 M H\textsubscript{2}SO\textsubscript{4} at 80 °C for 10 h. Subsequently, the acid-treated sample was needed to centrifuge for several times using DI water and ethanol then thermally dried at 90 °C for overnight. Specifically, the feeding ratios between melamine, BD and HSG were confined to 3:5:1, 5:5:1 and 5:3:1, respectively. They have been marked as FeO\textsubscript{4}/FeNSG-X (X=1, 2 and 3), correspondingly. For comparison, S-co doped HSG (NS-HSG), Fe, S-co doped HSG without N (FeO\textsubscript{4}/FeSG), and Fe, N-co doped HSG without S (FeO\textsubscript{4}/FeNSG) were also prepared by the similar procedures, and the precursors’ mass ratio is similar with the FeO\textsubscript{4}/FeNSG-3.

2.2 Materials characterization

Scheme 1 Schematic preparation of the FeO\textsubscript{4}/FeNSG hybrid.
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Scanning electron microscopy (SEM) images were performed using a JEOL JSM-7800F instrument. High-resolution transmission electron microscopy (HR-TEM) equipped with energy dispersive spectroscopy (EDS) were measured on Tecnai G2 F30 S-Twin electron microscopy to characterize the material morphology and elemental mapping. X-ray diffraction (XRD) patterns were acquired on a PW1700 diffractometer equipped with a Cu Kα (λ= 1.5405 Å) source. X-ray photoelectron spectra (XPS) were characterized by K-alpha (Thermos Fisher, UK). Thermofisher Raman spectrometer with 532 nm wavelength incident laser light at 5 mW was utilized to collect Raman spectra. The surface area was tested on a NOVA300e 250 volumetric adsorption instrument through N2 using the Brunauer-Emmett-Teller (BET) method, and pore size distribution was calculated by density functional theory (DFT) method.

2.3 Electrochemical testing

ORR performance was tested in a three-electrode system including a working electrode (glassy carbon disk), an Ag/AgCl reference electrode, and a counter electrode (Pt wire, protected by salt bridge). In order to well disperse the catalyst, the solvent was prepared using DI water, iso-propanol (99.5%) and Nafion (5 wt%) with a volume ratio of 8:2:0.05. The working electrode should be pre-polished before making the catalyst film. Herein, the electrode loadings of the as-prepared catalysts and the contrast of commercial Pt/C (20 wt%) were deposited to be 0.2 mg cm⁻² and 0.1 mg cm⁻², respectively. After dried at 60 °C for 30 min, the catalyst film can be achieved for further measurement. For the ORR tests, cyclic voltammetry curves (CVs) were recorded in a N₂-saturated 0.1 M KOH or 0.5 M H₂SO₄ solution with a scanning rate of 50 mV s⁻¹. The rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) experiments were measured in an O₂-saturated 0.1 M KOH or 0.5 M H₂SO₄ solution at diverse rotation rates from 225 to 2500 rpm with a scanning rate of 10 mV s⁻¹. The RDE and RRDE tests were conducted on the working electrode of glassy carbon disk with effective area of 0.196 and 0.247 cm², respectively. The testing potentials were confined to a specific region from -1.0 to 0.2 V (vs. Ag/AgCl), which have switched to values versus the reversible hydrogen electrode (RHE) in all presented figures. Thereby, the HSG possesses a desirable S_BET (~144.6 m² g⁻¹, Fig. S1), and higher than our previously reported 3D graphene (~90.9 m² g⁻¹) prepared by freeze-drying method. The unique structure and desirable surface area for HSG make it be a promising electrocatalytic carbon candidate and NPs supporter. Similar with NS-HSG (Fig. 2a), the hybrids remain obvious 3D porous structures (Fig. 2b-d). But the morphologies of Fig. 2b-d are indeed different from that Fig. 1a and Fig. 2a due to the MFR derived microstructure. Compared with TEM image of NS-HSG (Fig. 2a*), some NPs can be seen on the TEM images for Fe₃O₄/FeNSG hybrids (Fig. 1c and Fig. 2c*), resulting in their aggregations and difficulties in well-incorporated with graphene sheets. Interestingly, the Fe₃O₄/FeNSG-3 shows the uniformly morphology (Fig. 1c). There are no big nanoparticles and particle aggregates can be found because of the optimal precursor mass ratios in our experiment. The HRTEM image of Fe₃O₄/FeNSG-3 in Fig. 1d presents typical particles with ~17 nm embedded in graphene sheets, showing the lattice fringes. The lattice distance of 0.297 nm (left bottom) and 0.209 nm (right bottom) could be coincident with that of (220) and (400) planes of Fe₃O₄, respectively, suggesting the existing of few

3. Results and discussion

As depicted in Fig. 1a, the graphene sheets for HSG connect to each other and come into being a 3D honeycomb-like structure, which can be further demonstrated by TEM image (Fig. 1b). It can be seen that the crater-structured cells with nanoscale on 3D graphene corrugate from the basal plane, which could lead to increased S_BET of each sole graphene sheet. Therefore, the HSG possesses a desirable S_BET (~144.6 m² g⁻¹, Fig. S1), and higher than our previously reported 3D graphene (~90.9 m² g⁻¹) prepared by freeze-drying method. The unique structure and desirable surface area for HSG make it be a promising electrocatalytic carbon candidate and NPs supporter. Similar with NS-HSG (Fig. 2a), the hybrids remain obvious 3D porous structures (Fig. 2b-d). But the morphologies of Fig. 2b-d are indeed different from that Fig. 1a and Fig. 2a due to the MFR derived microstructure. Compared with TEM image of NS-HSG (Fig. 2a*), some NPs can be seen on the TEM images for Fe₃O₄/FeNSG hybrids (Fig. 1c and Fig. 2c*), resulting in their aggregations and difficulties in well-incorporated with graphene sheets. Interestingly, the Fe₃O₄/FeNSG-3 shows the uniformly morphology (Fig. 1c). There are no big nanoparticles and particle aggregates can be found because of the optimal precursor mass ratios in our experiment. The HRTEM image of Fe₃O₄/FeNSG-3 in Fig. 1d presents typical particles with ~17 nm embedded in graphene sheets, showing the lattice fringes. The lattice distance of 0.297 nm (left bottom) and 0.209 nm (right bottom) could be coincident with that of (220) and (400) planes of Fe₃O₄, respectively, suggesting the existing of few
remained Fe₃O₄ NPs. To verify the uniformity of the element distribution, STEM measurement is used to test the elemental mappings (Fig. 1e). It can be seen that N and S atoms are well-distributed throughout the graphene sheets. Particularly, combining with the element mappings of Fe and O, it can be noted that there have emerged some brighter particles with same locations on graphene sheets, which could further demonstrate the existed Fe species involving few Fe₃O₄ NPs. The existing of all the elements can be further demonstrated by the EDS spectrum (Fig. S2).

Fig. 2 (a-d) SEM images of the NS-HSG and different Fe₃O₄/FeNSG-X (X=1, 2 and 3) hybrids, respectively, (a‘-d‘) are their corresponding TEM images.

The microstructures of Fe₃O₄/FeNSG hybrids were measured by XRD (Fig. 3). For comparison, pure HSG and NS-HSG were also investigated. A peak can be observed at 2θ = 24.8° for HSG (Fig. 3a), which corresponds to the (002) diffraction peak of graphitic carbon. The characteristic peak of carbon for NS-HSG has transferred to 13.5° (Fig. 3a), indicating the increased interlayer spacing, which may be caused by the introduced N, S atoms and oxygen-containing species. After further introduced into Fe species, XRD patterns of the composites (Fig. 3) are different from HSG and NS-HSG, especially when the 2θ exceeds 40°. The peak (Fig. 3b) appearing at 43.1° is indexed to the (400) reflection of Fe₃O₄ (JCPDS: 65-3107), which is consistent with the HRTEM analysis mentioned above (Fig. 1d). This consequence is coincident with one previous report, in which the Fe₃O₄ encapsulated within the carbon layers can be remained after acid-leaching. Moreover, the peaks at 20-30° of the diverse Fe₃O₄/FeNSG products could be attributed to C (002) of graphene. Small differences between these peaks are possibly attributed to their divergent doping constitutions in graphene framework, deriving from the precursors’ variation.

XPS spectra were tested to investigate the chemical composition of the Fe₃O₄/FeNSG products. As expected, XPS survey spectra of the composites show peaks for C, N, O, S, and Fe (Fig. 4a), illuminating the co-doping of carbon with N and S, as well as the introduced Fe species. Introducing both N and Fe species into carbon base is beneficial for forming strong Fe-N interaction, and thus N atoms could be retained during the annealing process. The element contents of different Fe₃O₄/FeNSG samples were summarized in Table 1. Different mass ratios of N and S precursors show different influence on the compositions of products. The total N content in Fe₃O₄/FeNSG gradually increases, with the increase of mass ratios between melamine and BD. And the Fe₃O₄/FeNSG-3 exhibits the highest content of S (2.11 at. %), N (1.72 at. %), and Fe (0.60 at. %) at the ratio between melamine and BD of 5:3. This result indicates that more Fe atoms have been remained in the hybrid of Fe₃O₄/FeNSG-3. In contrast, the Fe₃O₄/FeNSG-1 and Fe₃O₄/FeNSG-2 samples show similar contents of Fe and S (Table 1). XPS (Fig. 4b-f) shows the detailed chemical composition and bonding configuration of the Fe₃O₄/FeNSG-3. It can be seen that the C 1s spectrum (Fig. 4b) is deconvoluted for several bonds of C=C/C=C (284.8 eV), C=N/C=O (286.7 eV), as well as C=O/C=N (289.0 eV), correspondingly. This suggests that N and S atoms have been introduced into the carbon matrix. The N 1s scan (Fig. 4c) illumnates the three typical forms of N, including pyridinic N/Fe-N (398.7 eV), pyrrolic N (400.1 eV), and graphitic N (401.9 eV). Previous reports have proven that pyridinic N and pyrrolic N are regarded as the active sites for ORR activity. In these three products, the Fe₃O₄/FeNSG-3 has the highest amount of the two active N species (74.4%, in Fig. 5a), implying that it probably has the improved ORR performance. In the case of O 1s, the XPS spectrum (Fig. 4d) is deconvoluted for FeO/C-O (532.3 eV) and C=OH/C-O-C (533.7 eV), which further
indicate the formation of Fe–O bond, originating from Fe₃O₄.²⁴
The S 2p signals of Fe₃O₄/FeNSG-3 could be deconvoluted

Table 1 Summary of the element contents for different Fe₃O₄/FeNSG hybrids.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>O</th>
<th>S</th>
<th>Fe</th>
<th>Pyridinic N</th>
<th>Pyrrolic N</th>
<th>Graphitic N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃O₄/FeNSG-1</td>
<td>89.95</td>
<td>6.77</td>
<td>1.93</td>
<td>0.43</td>
<td>0.26</td>
<td>0.36</td>
<td>0.30</td>
</tr>
<tr>
<td>Fe₃O₄/FeNSG-2</td>
<td>89.77</td>
<td>6.69</td>
<td>1.93</td>
<td>0.39</td>
<td>0.41</td>
<td>0.35</td>
<td>0.46</td>
</tr>
<tr>
<td>Fe₃O₄/FeNSG-3</td>
<td>87.09</td>
<td>8.48</td>
<td>2.11</td>
<td>0.60</td>
<td>0.31</td>
<td>0.44</td>
<td>0.97</td>
</tr>
</tbody>
</table>

for Fe–S (163.4 eV), C–S (2p₃/₂, 164.7 eV and 2p₁/₂, 165.9 eV),
C-SO₃ (168.3 eV) and C-SO₄ (169.5 eV).³¹ It is generally
acknowledged that the Fe species have high thiophilic ability.
Therefore, the powerful interaction between Fe²⁺ and S species
could give rise to the production of FeS, resulting in the
residual Fe–S bond.³⁹, ⁵¹ It is well known that the porous
structure can be formed after acid-leaching FeS, which probably increases the surface area of product.⁵¹ The existed
C-S-C bond demonstrates that the S atoms have been bound in
aromatic carbon structures, which is reported as the thiofeine-S of catalytic active sites.⁴⁰ The additional peaks of
SO₃-C and SO₄-C groups are also responsible for improving ORR
performance through the enhanced spin density of carbon
material.¹⁵ Fig. 4f exhibits two main peaks at approximately
712.1 and 726.5 eV, which matches well with the Fe 2p₃/₂ and
Fe 2p₁/₂ orbitals, respectively.⁵² According to the peak fitting
results, Fe atoms in peak 712.1 eV can be deconvoluted into
the form of Fe³⁺ (711.7 eV), and Fe²⁺ (714.1 eV), indicating that
Fe mainly exists in the ionic state.³⁷–³⁹ Consequently, combining with HRTEM and elemental mappings
together with XRD and XPS analysis, it can be concluded that
the 3D porous graphene with well-doped N and S atoms, as well as Fe species (Fe-N-C, Fe-S-C, and Fe₃O₄ NPs) has been achieved.

The disordered graphitic structures of carbon and structural defects in HSG, NS-HSG, and Fe₃O₄/FeNSG samples
were investigated by Raman spectra, as shown in Fig. 5b. All
the samples have the representative D band (~1360 cm⁻¹) and
G band (~1580 cm⁻¹) of graphene, which corresponds to the
presence of defects and graphitic sp² hybridized carbon,
respectively.⁵⁵, ⁵⁶ The peak intensity ratios (I₆/I₇) of different
samples have been summarized in Table S1. The (I₆/I₇) values
for NS-HSG (1.046) and all Fe₃O₄/FeNSG samples (ca. 0.961-
0.992) are higher than that of pure HSG (0.956), since the
introduction of hybrid atoms including N, O, S and Fe.³⁷ The
results indicate that more total contents of melamine and BD
tend to result in more defects for the hybrids. Besides,
when compared with NS-HSG, fewer defects have been introduced
into the Fe₃O₄/FeNSG, which may be attributed to the influence of incorporation between doped N, S atoms and
introduced Fe species.¹⁵ Herein, the N and S co-doping could
transfer the surface charge/defect distributions of carbon
matrix, while the Fe species protected by graphene sheets play
a pivotal role in cooperating with the binary heteroatom-
doped graphene.³⁸, ⁴⁰ Fig. 5c shows that the N₂ adsorption/desorption isotherms of NS-HSG and different
Fe₃O₄/FeNSG products measured based on BET method.⁵⁷
Fig. 5 Relative content of three types of N in different Fe$_{3}$/FeNSG hybrids (a), Raman spectra for different samples of Fe$_{3}$/FeNSG-X (X=1, 2, and 3), HSG and NS-HSG (b), N$_{2}$ adsorption/desorption isotherms (c), and the corresponding pore size distributions for diverse samples of Fe$_{3}$/FeNSG-X (X=1, 2, and 3), and NS-HSG (d).

Table 2 Summary of ORR activity of the different as-prepared catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{1/2}$ (V vs. RHE)</th>
<th>$J_L$ (mA cm$^{-2}$) at 0.2 V vs. RHE</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS-HSG</td>
<td>0.910</td>
<td>-4.62</td>
<td>ca. 3.81</td>
</tr>
<tr>
<td>Fe$_{3}$/FeSG</td>
<td>0.837</td>
<td>-3.28</td>
<td>ca. 3.26</td>
</tr>
<tr>
<td>Fe$_{3}$/FeNG</td>
<td>0.838</td>
<td>-4.98</td>
<td>ca. 3.71</td>
</tr>
<tr>
<td>Fe$_{3}$/FeNSG-1</td>
<td>0.908</td>
<td>-4.78</td>
<td>ca. 4.00</td>
</tr>
<tr>
<td>Fe$_{3}$/FeNSG-2</td>
<td>0.913</td>
<td>-5.06</td>
<td>ca. 4.00</td>
</tr>
<tr>
<td>Fe$_{3}$/FeNSG-3</td>
<td>0.951</td>
<td>-5.00</td>
<td>ca. 3.85</td>
</tr>
<tr>
<td>Pt/C</td>
<td>0.923</td>
<td>-5.33</td>
<td>ca. 3.80</td>
</tr>
</tbody>
</table>

The major parameters of the surface area and pore volume have been summarized in Table S2. It is noted that the surface areas are calculated to be 406.4, 429.9, 658.6, and 530.5 m$^2$ g$^{-1}$ for NS-HSG, Fe$_{3}$/FeNSG-1, Fe$_{3}$/FeNSG-2, and Fe$_{3}$/FeNSG-3, respectively, which have been improved dramatically in contrast with pure HSG (144.6 m$^2$ g$^{-1}$, Fig. S1). The enhanced surface area may be ascribed to the formed FeS. Further, the Fe$_{3}$/FeNSG hybrids are also enhanced, because Fe-based sulfides can be easily removed by acid-leaching treatment, thus acting as a sacrificial pore-forming agent. Furthermore, DFT method is used to calculate the pore size distributions of the above-mentioned products (Fig. Sd), which exhibit porous structures mainly consisting of mesopores, and macropores. These pores with efficient heteroatoms doping could not only lead to transmission of oxygen and electrolyte, but supply sufficient active sites for accelerating the electrochemical kinetics of ORR.

The ORR activity of Fe$_{3}$/FeNSG products were first analyzed by CV, and compared with NS-HSG, Fe$_{3}$/FeSG, Fe$_{3}$/FeNG, as well as commercial Pt/C. As shown in Fig. 6a, all the catalysts exhibit a well-defined reduction peak in O$_{2}$-saturated 0.1 M KOH solution, whereas no reduction peaks are found in N$_{2}$-saturated electrolyte. The ORR peak potential (0.817 V) of the Fe$_{3}$/FeNSG-3 is almost the same as the peak potential of Pt/C (0.814 V), and more positive than the other catalysts (0.740 V for the Fe$_{3}$/FeNSG-1, 0.763 V for the Fe$_{3}$/FeNSG-2, 0.699 V for the Fe$_{3}$/FeNSG-2, 0.729 V for the Fe$_{3}$/FeNG, and 0.765 V for NS-HSG), implying its superior ORR catalytic activity. To gain further insight into the ORR process, the as-prepared catalysts are investigated by RDE measurement illustrated in Fig. 6b. The key parameters$^{20}$ of onset potential ($E_{o}$), half-wave potential ($E_{1/2}$) and diffusion limiting current density ($J_L$) have been summarized and compared in Table 2. The Fe$_{3}$/FeNSG-2 and NS-HSG show similar ORR activity, as demonstrated in Fig. 6b, while Fe$_{3}$/FeNSG-1 is less active with 22 mV more anodic overpotential in comparison to Fe$_{3}$/FeNSG-2 at a current density of 2 mA cm$^{-2}$. On the other hand, the Fe$_{3}$/FeNSG-3 shows the highest ORR performance compared with NS-HSG, and the other Fe$_{3}$/FeNSG catalysts, having an onset potential of 0.951 V and half-wave potential of 0.810 V, and better than Pt/C ($E_{o}=0.923$ V, and $E_{1/2}=0.800$ V) (Fig. 6f and Table 2). In contrast, the Fe$_{3}$/FeNSG catalyst without N doping and Fe$_{3}$/FeNG catalyst without S doping (Fig. 6b) display much lower ORR activities. The N and S co-doping can improve the ORR activity of catalyst, which is highly consistent with the previous work$^{15, 39, 40, 52}$ in this work, the improved activity by introducing S is attributed to two possible reasons. On one hand, the formed FeS plays an important role in formation of porous structure and the increase of surface area after acid leaching. On the other hand, S doping has provided with more active sites including Fe-S-C, and C-S-C. It is worth mentioning that the observed results for the Fe$_{3}$/FeNSG-3 catalyst are superior or close to many of the given recent reports on Fe (Co)-based carbons (Table 3)$^{12, 23, 38, 50, 59-64}$. These RDE polarization results further indicate highly active nature of the Fe$_{3}$/FeNSG-3 catalyst towards ORR.

Optimal ORR activity of the Fe$_{3}$/FeNSG-3 catalyst could be also verified by the smaller Tafel slope (Fig. 6c) of 77 mV dec$^{-1}$ than that measured with the NS-HSG (90 mV dec$^{-1}$), Fe$_{3}$/FeSG (125 mV dec$^{-1}$), Fe$_{3}$/FeNG (130 mV dec$^{-1}$), Fe$_{3}$/FeNSG-1 (109 mV dec$^{-1}$), and Fe$_{3}$/FeNSG-2 (113 mV dec$^{-1}$) catalysts.
Fig. 6 CVs of the FeO$_2$/FeNSG$-X$ (X=1, 2, and 3), NS-HSG, Fe$_2$O$_3$/FeSG, Fe$_3$O$_4$/FeNG, and Pt/C at a scan rate of 50 mV s$^{-1}$ (a); RDE polarization curves of various catalysts at a scan rate of 10 mV s$^{-1}$ and a rotation rate of 1600 rpm (b); Tafel plots derived from the RDE data in Fig. 6b (c); RDE polarization curves on the Fe$_2$O$_3$/FeNSG$-3$ at different rotation rates (d); the corresponding K-L plot of $i^0$ versus $ν^{1/2}$ (e); comparisons of $E_{1/2}$ and the average number of electrons transferred per O$_2$ of the Fe$_2$O$_3$/FeNSG$-3$ and Pt/C (f).

<table>
<thead>
<tr>
<th>Electrode materials</th>
<th>$E_0$ (V vs. RHE)</th>
<th>$E_{1/2}$ (V vs. RHE)</th>
<th>$J_i$ (mA cm$^{-2}$)</th>
<th>Catalyst loading (mg cm$^{-2}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/DAP</td>
<td>0.950</td>
<td>0.742</td>
<td>-5.40</td>
<td>0.20</td>
<td>12</td>
</tr>
<tr>
<td>Co@Co$_3$O$_4$/NC-1</td>
<td>0.918</td>
<td>0.800</td>
<td>-4.50</td>
<td>0.21</td>
<td>23</td>
</tr>
<tr>
<td>Fe-SNC-900</td>
<td>0.979</td>
<td>0.834</td>
<td>-7.20</td>
<td>0.30</td>
<td>38</td>
</tr>
<tr>
<td>Fe$_2$O$_3$/N-MCS-2</td>
<td>1.036</td>
<td>0.861</td>
<td>-5.73</td>
<td>0.32</td>
<td>50</td>
</tr>
<tr>
<td>Fe$_3$O$_4$/N-MCS-2</td>
<td>0.900</td>
<td>0.810</td>
<td>-5.81</td>
<td>0.125</td>
<td>59</td>
</tr>
<tr>
<td>Co@CoO@NC/C</td>
<td>0.920</td>
<td>0.810</td>
<td>-5.25</td>
<td>0.42</td>
<td>60</td>
</tr>
<tr>
<td>D-AC@2Mn-4Co</td>
<td>0.883</td>
<td>0.803</td>
<td>-4.72</td>
<td>0.16</td>
<td>61</td>
</tr>
<tr>
<td>S-Fe/N/C</td>
<td>0.911</td>
<td>0.799</td>
<td>-5.20</td>
<td>0.16</td>
<td>62</td>
</tr>
<tr>
<td>Fe-BC-800</td>
<td>0.940</td>
<td>0.800</td>
<td>-4.18</td>
<td>0.42</td>
<td>63</td>
</tr>
<tr>
<td>Fe-N-C-850</td>
<td>0.920</td>
<td>0.730</td>
<td>-4.10</td>
<td>0.20</td>
<td>64</td>
</tr>
<tr>
<td>Fe$_3$O$_4$/FeNSG-3</td>
<td>0.951</td>
<td>0.810</td>
<td>-5.00</td>
<td>0.20</td>
<td>This work</td>
</tr>
</tbody>
</table>

(96 mV dec$^{-1}$). The Tafel value of Fe$_3$O$_4$/FeNSG-3 catalyst is also comparable to that of Pt/C (71 mV dec$^{-1}$). The above-mentioned results imply that there is an excellent ratio between precursors of melamine and BD for the best catalytic activity towards ORR. The superior ORR activity of Fe$_3$O$_4$/FeNSG-3 catalyst may be collaboratively contributed by the following key aspects. 1) The porous structure and large surface area in Fe$_3$O$_4$/FeNSG-3 result in its uniform distribution of active sites. Especially, the Fe species including Fe$_3$O$_4$ NPs have well embedded in graphene sheets with high homogeneity (Fig. 1c and Fig. 2d*), unlike the large particles and serious aggregations (Fig. 2) on both Fe$_2$O$_3$/FeNSG-1 and Fe$_2$O$_3$/FeNSG-2. 2) Compared with the other two Fe$_2$O$_3$/FeNSG catalysts, the optimal catalyst possesses more amount percentage of active N species (74.4%), and S doing (2.11 at. %). All the active species of pyridinic N along with graphitic N, Fe-N-C, and S doing could alter the electron distribution because of the diverse electronegativity of C, N and S atoms, and thus improving the reactivity of the sites. 3) Large surface area and unique porous structure with homogeneous dopants are responsible for interactions between O$_2$ and abundant approachable active sites and supply multiple electrode-electrolyte interfaces for improving the catalytic performance. In order to reveal the pathway and kinetics of ORR, K-L plots of the NS-HSG (Fig. S3), Fe$_2$O$_3$/FeSG (Fig. S4), Fe$_2$O$_3$/FeNG (Fig. S5), Fe$_3$O$_4$/FeNSG-1 (Fig. S6), Fe$_3$O$_4$/FeNSG-2 (Fig. S7), Fe$_3$O$_4$/FeNSG-3 (Fig. 6e), and Pt/C (Fig. S8) obtained from RDE measurements have recorded at various rotation rates (225-2500 rpm) in O$_2$-saturated 0.1 M KOH solution. The K-L plots present a good linearity for all potentials in different catalysts. The average values of electron transfer number are calculated to ca. 3.81 for NS-HSG, ca. 3.26 for Fe$_3$O$_4$/FeSG, 3.71 for Fe$_2$O$_3$/FeNG, ca. 4.0 for Fe$_2$O$_3$/FeNSG-1, ca. 4.0 for Fe$_3$O$_4$/FeNSG-2, ca. 3.85 for Fe$_3$O$_4$/FeNSG-3, and ca. 3.80 for Pt/C catalysts (Fig. 6f and Table 2), indicating a predominantly four-electron transfer pathway to catalyze O$_2$ and produce the product of water. To evaluate the electrocatalytic activity of the Fe$_3$O$_4$/FeNSG-3 in acid media, the LSV test was conducted on a RDE at a rotating rate of 1600 rpm in an O$_2$-saturated 0.5 M H$_2$SO$_4$ solution (Fig. 7a). For comparison, the commercial Pt/C catalyst was also measured at the same condition. However, the Fe$_3$O$_4$/FeNSG-3 catalyst shows only moderate ORR activity in acid electrolyte. Big gap still exists between the Fe$_3$O$_4$/FeNSG-3 and Pt/C catalysts, indicating that further improvement is demanding.$^{17}$ The production yield of H$_2$O$_2$ on the Fe$_3$O$_4$/FeNSG-3 was explored by RRDE experiment in 0.1 M KOH solution. Fig. 7b shows that the production yields of H$_2$O$_2$ are 1-6% for the Fe$_3$O$_4$/FeNSG-3 in the potential range from 0 to 0.7 V, which is beneficial for the good performance of the sample. The methanol crossover effect is a pivotal aspect of the catalysts in practical fuel cell applications. Tolerance of the Fe$_3$O$_4$/FeNSG-3 and Pt/C to methanol was measured by LSV, shown in Fig. 7c. The Fe$_3$O$_4$/FeNSG-3 shows a superior methanol resistance, with no apparent change when 1 M methanol is added. In contrast, a new peak has emerged on Pt/C, which ascribes to methanol oxidation-reduction, suggesting the catalyst has been poisoned.$^{15}$ In other words, the Fe$_3$O$_4$/FeNSG-3 exhibits high selectivity towards ORR. The long-term stability is also crucial for catalyst in practical fuel cell applications. It can be seen that the initial current...
maintains 71.5% for the Fe$_3$O$_4$/FeNSG-3 catalyst after 30,000 s continuous reaction, whereas only 54.3% of the initial current can be remained in Pt/C (Fig. 7d), illuminating the favorable stability of the Fe$_3$O$_4$/FeNSG-3 product. The above results demonstrate that the Fe$_3$O$_4$/FeNSG-3 catalyst exhibits better methanol resistance and durability compared with commercial Pt/C, which is significant for its realistic application in fuel cells.

4. Conclusions

In conclusion, for the first time, we have synthesized an efficient catalyst of the 3D porous graphene doped with Fe/N/S incorporated Fe$_3$O$_4$ nanoparticles, using a pyrolysis method. 3D porous graphene offers unique architectures, high conductivity, and the large surface area along with structural defects. The soft template of chemically synthesized melamine formaldehyde resin and intermediate product of FeS could be easily decomposed and removed by heat-treatment and acid-leaching process, which gives rise to great enhancement of the surface area. With optimal precursor ratio between melamine and benzyl disulfide, the Fe$_3$O$_4$/FeNSG-3 catalyst has large surface area (530.5 m$^2$ g$^{-1}$), highest amount (74.4%) of active N species (pyridinic N and graphitic N) together with highest contents of S doping (2.11 at. %), as well as the homogeneously embedded Fe species (e.g., Fe-N-C, Fe$_3$O$_4$) in graphene sheets, hence exhibiting the best ORR performance, compared with the other counterparts. Furthermore, this novel Fe$_3$O$_4$/FeNSG electrocatalyst has exhibited much better methanol resistance and stability than commercial Pt/C in alkaline electrolyte, making it a promising non-NPG catalyst.

Conflicts of interest

There are no conflicts to declare.

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The honeycomb-like structured graphene was used to synthesize 3D porous graphene doped with Fe/N/S incorporated Fe$_3$O$_4$ nanoparticles, which showed comparable ORR activity with Pt/C in alkaline media.