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Article

An effective FeCl_3 template assisted synthesis of nitrogen, sulfur and iron-tridoped carbon nanosheets from a protic salt for oxygen reduction electrocatalysis

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ABSTRACT

Doping heteroatoms into carbon matrix was an efficient strategy to achieve a high-performance non-precious metal oxygen reduction electrocatalyst. Herein, an in situ templated synthesis strategy has been demonstrated to fabricate nitrogen, sulfur and iron-tridoped mesoporous carbon nanosheets (NSFC) with FeCl_3 as the two-dimensional template. And a protic salt was used as the carbon, nitrogen and sulfur source, which realized one-step preparation of catalyst materials and the co-doping of various heteroatoms simultaneously. As a result, the optimized NSFC catalyst possessed comparable catalytic activity and selectivity, while superior durability and methanol permeability resistance to commercial 30 wt% Pt/C catalyst in alkaline media. Such excellent performance should be ascribed to the efficient multiple-element doping into the large-specific-surface-area and highly stable carbon nanosheets realized by the in situ synthesis route with a novel FeCl_3 template.

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1. Introduction

The fuel cell as a sustainable and clear energy technology has been seriously investigated to deal with continuously increasing global energy and environmental problems. Nonetheless, the performance of fuel cells was mainly limited by the intrinsic characteristic of sluggish kinetics for oxygen reduction reaction (ORR) on the cathode. Pt-based materials were recognized as the state-of-the-art electrocatalysts for ORR [1,2]. Unfortunately, they had disadvantages of limited resource reserve, high cost, poor durability, and huge difficulty to recycle [3–5], which significantly hinder the large-scale application of fuel

cell. Therefore, developing a low-cost ORR electrocatalyst with comparable performance to Pt-based materials is critically important for large-scale applications of this new energy devices [6,7].

In recent years, heteroatom-doped carbon materials (HCM) have been developed as greatly promising ORR electrocatalysts due to their unique advantages of low cost, excellent catalytic properties, long-term stability and excellent resistance to methanol crossover effects [8–10]. The heteroatom doping strategy has been proved effectively to improve the ORR electrocatalytic activity of carbon materials by controllable manipulation of the electronic delocalization of the carbon framework.

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Some recent reports suggested that carbon materials mixed with a variety of elements (N, B, S and P etc.) had better catalytic activity than the single atom doped carbon because of synergetic effects of co-doping [11–13]. In particular, the doped carbon materials decorated with transition metal(s) such as Co and (or) Fe were identified to be the most active non-noble metal catalysts [14]. Great efforts have been devoted to pursuing efficient fabrication strategies in order to obtain advanced HCM materials with highly open structure and appropriate doping location. Many previously reported results suggested that the choice of precursor and doping method should play a much more important role in intrinsic introducing active sites of HCM materials [7,15–17].

For traditional synthesis strategies, it is still very difficult to obtain the co-doped carbon materials with superior nanostructure simultaneously and effective heteroatom doping states. Recently, Watanabe's group [18,19] demonstrated a neutralization strategy between amines and acids to form novel protic salt complexes with controllable element composition which can be directly used as ideal precursors for fabricating a series of heteroatoms-doped carbon materials. Unfortunately, the HCM materials generated from directly pyrolysis of these complexes usually possess low surface area and a micropore-dominated nanostructure, which extremely weaken the utilization of active sites and mass transfer during electrocatalytic process. Han's group recently developed a novel template synthesis strategy for efficient transformation of biomass to high-quality graphene [20]. Although the graphene fabricated by this method has made it more possible to facilitate achieve a highly-opened carbon skeleton, but can't provide excellent electrochemical activity for oxygen reduction [16,21–23].

Herein, we successfully combined the FeCl_3 template synthesis strategy and novel protic salt precursors of P-phenylenediamine sulphate (PPS) to achieve N, S, Fe-tridoped mesoporous carbon nanosheets (NSFC) for oxygen reduction electrocatalysis. We have achieved the simultaneous optimization of the microscopic structure and surface functionality of the catalyst by controlling the ratio of FeCl_3 template and PPS. As a non-precious metal electrocatalyst, the optimized NSFC-3 showed the nearly catalytic ability and selectivity, while superior excellent resistance to crossover effects to commercial 30 wt% Pt/C catalysts in KOH solution (0.1 mol/L).

2. Experimental

2.1. Preparation

P-phenylenediamine (2.16 g, PPDA) dissolved in ethanol (40 mL) was gradually added into dilute sulfuric acid (4 g, 98 wt%, 20 mL water) under a N_2 atmosphere and kept in an ice-water mixture. The mixture was then stirred for 2 h at room temperature. Finally the solvent was removed with heating at 80 °C for 24 h, giving a pink solid which named PPS.

N,S-codoped porous carbon (NSPC) was prepared by heating PPS at 900 °C for 2 h with ramp rate of 3 °C/min in N_2 .

PPS was directly mixed with FeCl_3 template according to 1:1, 1:3, 1:5 (PPS: FeCl_3 mass ratio) by grounding in an agate

mortar for 5 min, then the mixture was dried at 80 °C for 24 h in porcelain boat and resulted to black solid. Then the mixture was heated at 900 °C for 2 h with the ramp rate of 3 °C/min in N_2 . The resultant composite was etched with a HCl solution (2 mol/L) at 80 °C for 8 h with the stirring to remove the superfluous Fe. NSFC-X (X = the mass ratio of FeCl_3 template and PPS, X = 1, 3, 5) was obtained after drying overnight at 80 °C.

2.2. Characterization

The X-ray diffraction (XRD) instrument was examined at 40 kV and 40 mA (BRUKER D8, $\text{Cu K}\alpha$) to analyze composition. X-ray photoelectron spectroscopy (XPS) measurements were carried out on Kratos AXIS Ultra spectrometer with a source gun of Al $\text{K}\alpha$ and spot size of 400 μm . The morphology of as-prepared catalysts was investigated by scanning electron microscopy (SEM) (Hitachi S-4800), transmission electron microscopy (TEM) (Philips Tecnai 12). The Brunauer-Emmett-Teller (BET) was characterized with a Micromeritics ASAP2020 analyzer (USA) at –196 °C to get specific surface area, pore size distribution, and pore volume of materials.

2.3. Electrochemical measurements

The all cyclic voltammetry (CV), rotating disk electrode (RDE), and rotating ring-disk electrode (RRDE) were tested using the catalyst ink which was prepared from 2.0 mg of prepared catalyst or commercial 30 wt% Pt/C catalyst dispersed in 1.0 mL Nafion ethanol solution (0.05 wt%) by sonication for 1 h. Then, 25.0 μL of the prepared catalyst ink or 12.5 μL of commercial 30 wt% Pt/C ink was dropped on a RDE glass carbon electrode with a diameter of 5.00 mm to prepare the working RDE electrode. And 31.5 μL of the prepared catalyst ink or 16.0 μL of commercial 30 wt% Pt/C ink was dropped on an RRDE glass carbon electrode with a diameter of 5.61 mm to prepare the working RRDE electrode. Electrochemical measurements were conducted by a three-electrode cell and used saturated calomel electrode (SCE) and a platinum sheet as the reference and counter electrodes, respectively. 0.1 mol/L KOH electrolyte was used to carry out CV, RDE, and RRDE tests on a CHI760D electrochemical workstation assembled with MSR Electrode Rotator (Pine Research Instrumentation) at room temperature. The obtained electrochemical curves in O_2 -saturated electrolyte have been corrected by subtracting the obtained electrochemical curves in N_2 -saturated electrolyte, considering the contribution of the electrical double layer capacity for current response. The four-electron selectivity was evaluated based on the electron transfer number (n) and HO_2^- yield, calculated from the following equations.

$$\text{HO}_2^- (\%) = 200 \times \frac{I_{\text{R}}/N}{I_{\text{R}}/N + I_{\text{D}}} \quad (1)$$

$$n = 4 \times \frac{I_{\text{D}}}{I_{\text{R}}/N + I_{\text{D}}} \quad (2)$$

Here, I_{D} and I_{R} are the disk and ring currents, respectively, and N is the ring collection efficiency (0.37).

3. Results and discussion

The synthetic process for NSFC-X has been shown in Fig. 1. According to previous reports, FeCl_3 has been developed as an efficient template for fabrication of 2D carbon nanomaterials due to the formation of layered crystal structure during recrystallization process at 80 °C [20]. Therefore, PPS as the sources of C, N, and S can be confined in the laminated structure of FeCl_3 . After high temperature pyrolysis and acid treatment, the NSFC-X with a layered structure and N, S, Fe-tridoped states was achieved.

PPS was first directly carbonized at high temperature to get the product (denoted with NSPC). The SEM image of NSPC was shown in Fig. 2(A). It can be obviously observed that PPS was transformed into bulk carbon with promiscuous agglomerate without the assistant of FeCl_3 template.

To obtain a well-defined and continuous mesoporous carbon material, PPS was simply mixed with FeCl_3 template. As SEM shown in Fig. 2(B), the NSFC-3 had a separated lamellar structure and the thickness of about 12.2 nm. FeCl_3 was evidently functional as the template which could exfoliate the carbide products of PPS into ultra-thin two-dimensional nanosheets. The TEM shown in Fig. 2(C) further showed that the surface of NSFC-3 was not smooth under the field of vision. A large amount of folds and crisscross connected channels at the edge have been formed and couldn't see any obvious metal particles on the material surface which instructed that the most part of Fe introduced by FeCl_3 have been acid etched. The folds and channels can not only improve the specific surface area of NSFC-3, but also increase the exposure degree of catalytic active sites. As shown in Fig. 2(D), the high resolution TEM (HRTEM) image of NSFC-3 sample demonstrated abundant microporous and mesoporous structures, which were probably formed by the irregular 2D template structures as well as acid etching of Fe-containing compounds (Fe , Fe_3C , and FeS_x etc.). The above results indicated that the FeCl_3 did serve as an efficient 2D template in the process of recrystallization, and the standard slice structure and abundant pore channels, micropores and mesopores were formed.

Changing the ratio of FeCl_3 and PPS would influence the microstructure and ORR catalytic activity of NSFC, so a series of NSFC-X has been synthesized and measured. As shown in Fig.

Fig. 1. Schematic illustration for the synthesis process of NSFC-X from a novel protic salt.

Fig. 2. (A) SEM image of NSPC sample; SEM (B) and TEM (C) images of NSFC-3 sample; (D) HRTEM image of NSFC-3.

3(A) and (C), NSFC-1 (the ratio of FeCl_3 and PPS was 1:1) presented a two-dimensional slice layer structure, but these patches were confined to the uneven surface, illustrating that less FeCl_3 couldn't make them form integrated two-dimensional template, only some nanoscale fragments displayed in the image. As shown in Fig. 2(B) and (C), when the ratio was increased to 3:1, NSFC-3 presented a micron grade 2D nanoscale lamellar structure with around 12 nm in thickness. The inerratic two-dimensional nanosheets were taken shape, and there were many connected channels on the surface of NSFC-3. While the connected channels vanished, and perfectly smooth lamellas were formed when the ratio of FeCl_3 and PPS was increased to 5:1 as shown in Fig. 3(B) and (D). Although NSFC-5 had the same complete laminar structure as NSFC-3, but the smooth surface severely limited the exposure area of catalytic active sites. The above comparison showed that only the appropriate ratio of FeCl_3 and PPS could optimize the structure and surface function simultaneously. It was expected that the NSFC-3 had a perfect two-dimensional struc-

Fig. 3. SEM (A, B) and TEM (C, D) images of NSFC-1 (A, C) and NSFC-5 (B, D).

ture and a relatively rough surface for larger specific surface area and better active site exposure.

To further study the effect of FeCl_3 to the carbonization product of PPS, we tested the samples using the BET method, XRD and XPS. As the BET measurements of NSPC and NSFC-3 shown in Fig. 4(A) and (B), the obtained NSPC had a specific surface area of $139 \text{ m}^2/\text{g}$ and pore volume of $0.159 \text{ cm}^3/\text{g}$. By contrast, the NSFC-3 had a specific surface area of $702 \text{ m}^2/\text{g}$ and pore volume of $0.559 \text{ cm}^3/\text{g}$, which were nearly 5 times and 3.5 times of NSPC, respectively (Fig. 4(A)). These results demonstrated that the specific surface area and pore volume were significantly improved with the addition of FeCl_3 . This result was mainly attributed to the function of two-dimensional template of FeCl_3 , and the connected channels and the abundant micropores and mesopores formed in the pyrolysis process, simultaneously. FeCl_3 was uniform mixed with the precursor then inserted the layer stripping and catalyzed the formation of cotton-like two-dimensional carbon nanofilms in heating treatment. The presence of micropores and mesopores further enhanced the specific surface area of the product. The

Table 1

BET surface area and pore volume of NSPC and NSFC-X.

Sample	$S_{\text{BET}} (\text{m}^2/\text{g})$	$V_{\text{tot}} (\text{cm}^3/\text{g})$	$D_{\text{ave}} (\text{nm})$
NSPC	139	0.159	4.58
NSFC-1	547	0.347	2.54
NSFC-3	702	0.559	3.19
NSFC-5	813	0.541	2.66

graph of pore diameter distribution proved this point convincingly (Fig. 4(B)), the $dV/d\log D$ numerical values of NSPC and NSFC-3 both were greater than zero ranging from 1 to 100 nm, which indicated that they had hierarchical porous structure incorporating micropores, mesopores and macropores simultaneously, and the number of aperture sizes of various sizes of NSFC-3 was larger than NSPC, especially within the range 4.5 to 6.7 nm.

For further exploring the influence of the template dosage on NSFC-X, the NSFC-X was analyzed by BET measurement (Fig. 4(C), (D) and Table 1). As the absorption and desorption curve of nitrogen shown in Fig. 4(C), the specific surface area of

Fig. 4. N_2 adsorption-desorption isotherms (A, C) and DFT pore size distribution curves (B, D) of NSPC (A, B) and NSFC-X (C, D).

NSFC-1 reached 547 m²/g when the mass ratio of FeCl₃ and PPS was 1:1, nearly 4 times as much as NSPC. The results indicated that even small quantity of FeCl₃ could significantly improve the specific surface area and pore volume of NSPC adequately. When the mass ratio of FeCl₃ and PPS increased from 1:1 to 3:1 and then further increased to 5:1 gradually, the specific surface area of NSFC-X correspondingly increased from 547 to 702 m²/g and further to 813 m²/g. As shown in Fig. 4(D), it would form more mesoporous ranging from 2 to 20 nm because of more FeCl₃ template was used.

Detailed analysis of XPS was carried out as shown in Fig. 5, to research the impact on surface chemical composition and bonding state of NSPC by FeCl₃. The survey spectra of NSPC showed four peaks typical of C 1s, N 1s, O 1s, and S 2p in all the carbon materials indicating the presence of N, O, and S dopants, and the atomic ratio respectively were 88.89%, 6.75%, 3.97% and 0.39% as shown in Table 2. Comparably the survey spectra of NSFC-3 showed five peaks typical of C 1s, N 1s, O 1s, S 2p and Fe 2p indicating the presence of N, O, S and Fe dopants occupying 88.99%, 3.30%, 6.36%, 0.91% and 0.44% respectively. The diversified and abundant element composition was benefit from the neutralization strategy. N, O and S were effective and homogeneous doped into NSPC using PPS as precursor, and the collaborative doping of various elements was realized by the in situ doping method. The results also indicated that the FeCl₃ template changed the surface chemical composition of NSPC. The contents of O and S increased while that of N decreased simultaneously. More importantly, there were Fe elements occurred in NSFC-3 from scratch. To further testify the existing form of Fe in NSFC-3, the XRD pattern was demonstrated in Fig.

Table 2

XPS of NSPC and NSFC-3.

sample	C (at%)	N (at%)	O (at%)	S (at%)	Fe (at%)
NSPC	88.89	6.75	3.97	0.39	
NSFC-3	88.99	3.30	6.36	0.91	0.44

5. There were only two typical diffraction peaks of carbon (002) and (101) planes at 24° and 43.5° (Fig. 5(A)) and no peaks of pure Fe or other Fe compound species, which showed that no free Fe was introduced and accorded with the SEM and TEM of NSFC-3. This conclusion was further proved in the Fe 2p spectrum shown in Fig. 5(C), the peaks at 709.5 and 713.1 eV can be assigned to the binding energies of the 2p_{3/2} orbitals of Fe²⁺ and Fe³⁺ species, respectively. The peak at 722.5 and 725 eV were attributed to the binding energy of Fe²⁺ and Fe³⁺ for the 2p_{1/2} band. According to previous reports, the Fe²⁺ and Fe³⁺ species were beneficial to the catalytic activity of oxygen reduction [24]. In addition, the C 1s spectra shown in Fig. 5(D) indicated that the NSPC and NSFC-3 both contained C=C, C-C and C-O peaks at the binding energies of 284.7, 285.6 and 286.5 eV respectively.

Increased performance not only depended on presence of the Fe²⁺ and Fe³⁺ species but also depended on the use of active nitrogen-doped sites and sulfur-doped sites [21,25]. The binding states of these sites in the resulting products were revealed by high-resolution by high-resolution N 1s XPS spectra of NSPC and NSFC-3 as shown in Fig. 5(E). The spectra of both of NSPC and NSFC-3 could be deconvoluted into four types of nitrogen: pyridinic N (≈398.1 eV), pyrrolic N (≈399.0 eV), graphitic N

Fig. 5. (A) XRD pattern of NSFC-3; (B) Survey XPS spectra of NSPC and NSFC-3; High-resolution Fe 2p (C), C 1s (D), N 1s (E), and S 2p (F) XPS spectra of NSFC-3.

Fig. 6. Nitrogen contents and types in NSPC and NSFC-3. ^aThe relative value of different typed nitrogen vs. total nitrogen content. ^bThe relative value of different typed nitrogen vs. total atom content.

(≈ 400.9 eV) and oxidized nitrogen at (≈ 402.7 or 405 eV) [26]. The proportion of them are 17.69%, 8.13%, 62.11%, 12.07% and 11.37%, 8.53%, 69.80%, 10.30% in sequence as shown in Fig. 6. When adding the FeCl_3 template, the pyridinic N was decreased (from 17.69% to 11.37%) and graphitic N was increased inversely (from 62.11% to 69.80%), the two else types were invariant almost. Graphitic N was more important for the ORR catalytic activity of N-doped porous carbon than pyridinic N due to that graphitic N could accelerate the transfer of elec-

trons to O_2 in the crystal lattice of C [27,28].

The high resolution S 2p XPS peaks were also deconvoluted, mainly into four peaks associated with $-\text{C}-\text{S}-\text{C}-$ and $-\text{C}-\text{SO}_x-\text{C}-$ species as shown in Fig. 5(F). Participation of FeCl_3 templates changed the bonding method of the surface doped S atom by proton salt carbide obviously. The content of $-\text{C}-\text{S}-\text{C}-$ decreased from 78.91% to 51.74%, and the content of $-\text{C}-\text{SO}_x-\text{C}-$ increased from 21.09% to 48.26% on the contrary. According to previous reports, the doped S increased the oxygen reduction activity mainly ascribed to the S-related active sites and the synergistic effect of N, S-codoped [21,29,30].

The electrocatalytic activity of the as-prepared NSPC and NSFC-3 was evaluated first by CV, linear sweep voltammetry (LSV), RDE, and RRDE measurements in KOH solution (0.1 mol/L). The CV and LSV curves have been corrected by subtracting the curves recorded under saturated O_2 from those in saturated N_2 . As shown in Fig. 7(A), a weak cathodic peak for ORR was observed for NSPC, while a strong peak was observed for NSFC-3 as well as 30 wt% Pt/C. Notably, the peak position for NSFC-3 was more positive than that of 30 wt% Pt/C, suggesting the best oxygen reduction electrocatalytic activity of NSFC-3 among these prepared catalysts. As the Id curves shown in Fig. 7(B), the onset potential (E_{onset} , the potential when catalytic current density reaches 0.20 mA/cm^2) for NSPC was -0.15 V versus SCE, while -0.03 V for NSFC-3, which was quite comparable to that of 30 wt% Pt/C (-0.05 V). Meanwhile, NSFC-3 showed a similar current density at -0.3 V (5.05 mA/cm^2) to 30 wt% Pt/C (5.59 mA/cm^2), but much superior to

Fig. 7. CVs in O_2 - and N_2 -saturated 0.1 mol/L KOH solutions (A), Id and Ir curves (B), electron transfer number, and HO_2^- yield (C) of the carbons derived from NSPC, NSFC-3 and commercial 30 wt% Pt/C; (D) LSVs of NSFC-3 and commercial 30 wt% Pt/C in O_2 -saturated KOH electrolyte recorded during the cycling durability test; (E) Chronoamperometric responses of NSFC-3 and commercial 30 wt% Pt/C in N_2 -saturated 0.1 mol/L KOH solutions, followed by addition of saturated O_2 and 3 mol/L methanol successively at 600 and 1200 s, respectively.

Fig. 8. (A) CVs in O_2 - and N_2 - saturated 0.1 mol/L KOH solutions; (B) Polarization curves of ORR on RDE rotating at 1600 r/min; RRDE curves (C), electron transfer number, and HO_2^- yield (D) of the carbons derived from NSFC-X.

that of NSPC (3.1 mA/cm^2). Furthermore, NSFC-3 had a more positive half potential ($E_{1/2}$) of -0.142 V , which was 41 mV more than that of 30 wt% Pt/C (-0.181 V).

RRDE LSV measurements were further employed to uncover the reaction pathways of the as-prepared catalysts, which detected the formed peroxide (HO_2^-) intermediate during the ORR process as shown in Fig. 7(C). The electron transfer number (n) calculated from the ring and disc currents was greater than 3.9 for NSFC-3 over the entire potential range, which indicated that ORR proceeded mainly through a four-electron (O_2 to OH^-) reduction pathway. In contrast, n for NSPC was lower than 3.7, even at a high potential of up to -0.8 V . Furthermore, the calculated peroxide yield (HO_2^- %) from the RRDE data was lower than 3% for NSFC-3 over the range of -0.8 to 0 V , which was significantly lower than that of NSPC.

Besides, the stability and methanol-tolerance ability of NSFC-3 were also measured by the cycling durability test and chronoamperometry [31]. In Fig. 7(D), NSFC-3 showed no obvious decrease in onset potential over 1,000 cycles of constant operation, while a decrease both in onset potential and current

density was observed for Pt/C catalyst, suggesting that NSFC-3 had superior durability over commercial Pt/C catalyst. On the other hand, as shown in Fig. 7(E), Pt/C catalyst exhibited an obvious current decay immediately after the injection of 3 mol/L methanol, indicating the occurrence of the methanol oxidation reaction. Whereas no noticeable change of current response was observed on NSFC-3. The results demonstrated that NSFC-3 catalyst possessed considerably better tolerance to methanol crossover than 30 wt% Pt/C.

Because of iron doping in the NSFC-3, there is a question that how iron improved the catalytic performance. There were mainly two different hypotheses about the active sites in the Fe-N/C catalyst in previous works. One is that the $Fe-N_x$ may act as the major active sites [32,33] and the other means that it is same as the nonmetal N/C catalyst [34,35]. The NSFC-3 was most probably considered to follow the former hypothesis, and the poor catalytic activity of NSPC could confirm the viewpoint that the $Fe-N_x$ played a key role in the high catalytic activity of NSFC-3. The NSPC had higher N content (6.75%) than NSFC-3 (3.3%), while the ORR activities of the NSPC were much poorer

than those of the NSFC-3. Particularly, a quite high percentage of Fe^{2+} in the NSFC-3 according to the Fe 2p XPS spectrum could provide $\text{Fe}^{2+}\text{-N}_4$ active sites [32]. Although the Fe-N_x active sites weren't confirmed yet, the obvious improvement of ORR activity had been brought by Fe-N_x species [36].

Based on the above results, we could conclude that the NSFC-3 possessed excellent activity as well as selectivity compared with NSPC and 30 wt% Pt/C. As has been mentioned above, the excellent performance of NSFC-3 should be ascribed to the simultaneous optimization of the microscopic structure and surface functionality. The two-dimensional nanosheets, crisscross connected channels with rich micropores and mesopores provided by the FeCl_3 template made the NSFC-3 possessed of enough specific surface area and the exposure area of catalytic active sites. And the abundant and various active sites which ascribed to the protic salt method have provided concerted catalysis to the NSFC-3 [37].

The RDE and RRDE measurements of NSFC-1, NSFC-3, and NSFC-5 were shown in Fig. 8, tested after the mass ratio of FeCl_3 and PPS had been changed. As shown in Fig. 8(A), the reduction peak potential of the cyclic voltammetry curve was moving positive before negative shift as the ratio of FeCl_3 and PPS increases, which illustrated the best oxygen reduction electrocatalytic activity of NSFC-3 among these prepared catalysts. The result was further confirmed by RDE LSV curves as shown in Fig. 8(B), the onset potential (E_{onset}) and positive half potential ($E_{1/2}$) for NSFC-3 were 60 and 46 mV more than for NSFC-1, 50 and 30 mV more than for NSFC-5, respectively. These results further proved the excellent electrocatalytic activity for NSFC-3. The RRDE LSV measurements were further employed to demonstrate the distinction of reaction pathways and the formed peroxide (HO_2^-) intermediate of the as-prepared catalysts as shown in Fig. 8(C) and (D). The results of the RRDE test of NSFC-X were consistent with the RDE test results, the initial potential, half wave potential and limiting current density of NSFC-3 were superior to NSFC-1 and NSFC-5. NSFC-3 also had the optimal electron transfer number (n) and calculated peroxide yield ($\text{HO}_2^- \%$) over the range of -0.8 to 0 V compared with NSFC-1 and NSFC-5. The excellent performance of NSFC-3 should be ascribed mainly to the perfect two-dimensional structure and a relatively rough surface for larger specific surface area and better active site exposure.

Comprehensive comparing of electrochemical test results, it went without saying that it's vital to select the template and preparation method. The participation of FeCl_3 template in the preparation process made NSPC have improved electrocatalytic performance for oxygen reduction. And NSFC-3 had the best electrocatalytic performance when appropriate ratio of FeCl_3 and PPS was chosen.

4. Conclusions

We have successfully designed and constructed a two-dimensionally ordered mesoporous carbon nanosheet catalyst through FeCl_3 assisted template method. During this process, P-phenylenediamine sulphate was successfully explored as a single, small-molecule precursor to simply but effi-

ciently control the element composition of obtained catalysts. In comparison with traditional polymer precursors, the protic salt precursor not only simplified the synthetic procedure by direct neutralization reaction, but also incorporated N and S heteroatoms into the carbon skeleton in situ. After optimization, NSFC-3 had preponderant microstructure, great specific surface area, excellent pore volume, and rich active sites, therefore possessing similar ORR catalytic activity in both reaction current density and onset potential as well as four-electron selectivity, while superior long-term durability and methanol crossover resistance to commercial 30 wt% Pt/C catalyst in alkaline media. Notably, the excellent catalytic performance was achieved via such a simple fabrication process using inexpensive, available resources, which could significantly reduce production costs and had huge advantages for large-scale production.

References

- [1] L. Ye, G. L. Chai, Z. H. Wen, *Adv. Funct. Mater.*, **2017**, 27, 1606190.
- [2] X. X. Yuan, L. Li, Z. Ma, X. B. Yu, X. F. Wen, Z. F. Ma, L. Zhang, D. P. Wilkinson, J. J. Zhang, *Sci. Rep.*, **2016**, 6, 20005.
- [3] D. Malko, A. Kucernak, T. Lopes, *Nat. Commun.*, **2016**, 7, 13285.
- [4] J. Li, Y. J. Song, G. X. Zhang, H. Y. Liu, Y. R. Wang, S. H. Sun, X. W. Guo, *Adv. Funct. Mater.*, **2017**, 27, 1604356.
- [5] X. Liu, M. Park, M. G. Kim, S. Gupta, X. J. Wang, G. Wu, J. Cho, *Nano Energy*, **2016** 20, 315–325.
- [6] J. T. Zhang, L. T. Qu, G. Q. Shi, J. Y. Liu, J. F. Chen, L. M. Dai, *Angew. Chem. Int. Ed.*, **2016**, 55, 2230–2234.
- [7] C. Tang, Q. Zhang, *Adv. Mater.*, **2017**, 29, 1604103.
- [8] S. H. Ahu, A. Manthriam, *Small*, **2017**, 13, 1702068.
- [9] G. H. Wang, H. J. Peng, X. C. Qiao, L. Du, X. H. Li, T. Shu, S. J. Liao, *Int. J. Hydrogen Energy*, **2016**, 41, 14101–14110.
- [10] Q. J. Niu, J. X. Guo, B. L. Chen, J. Nie, X. D. Guo, G. P. Ma, *Carbon*, **2017**, 114, 250–260.
- [11] J. S. Li, S. L. Li, Y. J. Tang, K. Li, L. Zhou, N. Kong, Y. Q. Lan, J. C. Bao, Z. H. Dai, *Sci. Rep.*, **2014**, 4, 5130.
- [12] S. Y. Wang, E. Iyyamperumal, A. Roy, Y. H. Xue, D. S. Yu, L. M. Dai, *Angew. Chem. Int. Ed.*, **2011**, 50, 11756–11760.
- [13] C. H. Choi, S. H. Park, S. I. Woo, *ACS Nano*, **2012**, 6, 7084–7091.
- [14] W. M. Zhang, Y. S. He, S. M. Zhang, X. W. Yang, X. X. Yuan, Z. F. Ma, *Electrochem. Commun.*, **2017**, 81, 34–37.
- [15] K. G. Qu, Y. Zheng, S. Dai, S. Z. Qiao, *Nano Energy*, **2016**, 19, 373–381.
- [16] J. M. You, M. S. Ahmed, H. S. Han, J. Choe, Z. Üstündag, S. Jeon, *J. Power Sources*, **2015**, 275, 73–79.
- [17] X. Z. Li, Y. Y. Fang, S. L. Zhao, J. T. Wu, F. Li, M. Tian, X. F. Long, J. Jin, J. T. Ma, *J. Mater. Chem. A*, **2016**, 4, 13133–13141.
- [18] S. G. Zhang, M. S. Miran, A. Ikoma, K. Dokko, M. Watanabe, *J. Am. Chem. Soc.*, **2014**, 136, 1690–1693.
- [19] S. G. Zhang, K. Dokko, M. Watanabe, *Chem. Mater.*, **2014**, 26, 2915–2926.
- [20] B. B. Zhang, J. L. Song, G. Y. Yang, B. X. Han, *Chem. Sci.*, **2014**, 5, 4656–4660.
- [21] S. G. Zhang, A. Ikoma, K. Ueno, Z. J. Chen, K. Dokko, M. Watanabe, *ChemSusChem*, **2015**, 8, 1608–1617.
- [22] Y. Y. Meng, D. Voiry, A. Goswami, X. X. Zou, X. X. Huang, M. Chhowalla, Z. W. Liu, T. Asef, *J. Am. Chem. Soc.*, **2014**, 136, 13554–13557.
- [23] Y. L. Liu, C. X. Shi, X. Y. Xu, P. C. Sun, T. H. Chen, *J. Power Sources*,

Graphical Abstract

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An effective FeCl_3 template assisted synthesis of nitrogen, sulfur and iron-tridoped carbon nanosheets from a protic salt for oxygen reduction electrocatalysis

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Nitrogen, sulfur and iron-tridoped mesoporous carbon nanosheets (NSFC) was fabricated using FeCl_3 template from the protic salt PPS. The NSFC possessed comparable electrochemical catalysis with commercial 30 wt% Pt/C catalyst.

- 2015, 283, 389–396.
- [24] W. J. Jiang, L. Gu, L. Li, Y. Zhang, X. Zhang, L. J. Zhang, J. Q. Wang, J. S. Hu, Z. D. Wei, L. J. Wan, *J. Am. Chem. Soc.*, **2016**, 138, 3570–3578.
- [25] Q. X. Lai, Y. X. Zhao, Y. Y. Liang, J. P. He, J. H. Chen, *Adv. Funct. Mater.*, **2016**, 26, 8334–8344.
- [26] T. X. Wu, G. Z. Wang, X. Zhang, C. Chen, Y. X. Zhang, H. J. Zhao, *Chem. Commun.*, **2015**, 51, 1334–1337.
- [27] J. R. Pels, F. Kapteijn, J. A. Moulijn, Q. Zhu, K. M. Thomas, *Carbon*, **1995**, 33, 1641–1653.
- [28] Y. Nie, L. Li, Z. D. Wei, *Chem. Soc. Rev.*, **2015**, 44, 2168–2201.
- [29] A. M. El-Sawy, I. M. Mosa, D. Su, C. J. Guild, S. Khalid, R. Joesten, J. F. Rusling, S. L. Suib, *Adv. Energy Mater.*, **2016**, 6, 1501966.
- [30] J. C. Wang, R. G. Ma, Z. Z. Zhou, G. H. Liu, Q. Liu, *Sci. Rep.*, **2015**, 5, 9304.
- [31] Q. X. Lai, Q. Su, Q. W. Gao, Y. Y. Liang, Y. X. Wang, Z. Yang, X. G. Zhang, J. P. He, H. Tong, *ACS Appl. Mater. Interfaces*, **2015**, 7, 18170–18178.
- [32] N. Ramaswamy, U. Tylus, Q. Jia, S. Mukerjee, *J. Am. Chem. Soc.*, **2010**, 135, 15443–15449.
- [33] M. Lefevre, J. P. Dodelet, P. Bertrand, *J. Phys. Chem. B*, **2002**, 106, 8705–8713.
- [34] Y. Nabae, S. Moriya, K. Matsubayashi, S. M. Lyth, M. Malon, L. Wu, N. M. Islam, Y. Koshigoe, S. Kuroki, M. A. Kakimoto, S. Miyata, J. I. Ozaki, *Carbon*, **2010**, 48, 2613–2624.
- [35] R. Silva, D. Voiry, M. Chhowalla, T. Asefa, *J. Am. Chem. Soc.*, **2013**, 135, 7823–7826.
- [36] L. Lin, Q. Zhu, A. W. Xu, *J. Am. Chem. Soc.*, **2014**, 136, 11027–11033.
- [37] J. Liang, Y. Zheng, J. Chen, J. Liu, D. Hulicova-Jurcakova, M. Jaroniec, S. Z. Qiao, *Angew. Chem. Int. Ed.*, **2012**, 51, 3892–3896.

 FeCl_3 模板辅助法由质子盐制备氮、硫、铁三掺杂碳纳米片及其催化氧还原反应

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摘要: 作为一种新型能源技术, 燃料电池具有能源转化效率高、燃料可再生、运行安全清洁等优点, 因而在应对全球持续增长的能源、环境问题方面受到广泛的研究. 但是, 燃料电池的阴极氧还原反应(ORR)存在动力学缓慢的固有特性, 其反应过电位高, 需要在催化剂的辅助下才能顺利发生反应并提供足够的电极电势. 目前ORR催化性能最优的是铂基催化剂, 但其存在着资源稀缺、价格昂贵、循环寿命差等缺陷, 这也是制约燃料电池商业化应用的主要因素. 因而要想实现燃料电池的大规模应用, 寻找新的可替代铂基催化剂、且储量丰富、价格低廉的优秀ORR催化剂成为了研究的热点. 近几年来, 杂原子掺杂的碳材料以其价格低、催化性能卓越、优异的稳定性和抗甲醇性能等优点, 逐渐发展成为最有前景的ORR催化剂.

本文以 FeCl_3 为模板和铁源, 质子盐对苯二胺(PPS)为碳、氮、硫源, 采用简单的一步中和法制备氮、硫、铁三掺杂的

维介孔碳纳米片催化剂(NSFC). TEM和BET结果显示, FeCl_3 不仅起到了二维模板的作用, 同时在热处理过程中与无定形碳发生作用形成了丰富的介孔, 大大提高了材料的比表面积和结构开放性, 为ORR反应提供了反应场所. XPS结果显示, 质子盐中和合成法不仅有效地简化了NSFC的合成步骤, 而且能够灵活地控制材料的元素组成, 实现了氮和硫的原位掺杂, 有效构筑了杂原子掺杂活性位; 同时 FeCl_3 也为催化剂材料引入了Fe元素, 进而形成催化活性更加优异的Fe-N_x活性位. 电化学测试结果表明, 通过调整 FeCl_3 和PPS的比例, NSFC-3催化剂材料在结构形貌和表面功能达到了同时最优化, 获得了与商业30 wt% Pt/C可比的催化性能, 其起始电位和极限电流密度分别达到了 -0.03 V 和 5.05 mA/cm^2 , 同时NSFC-3具有优于商业30 wt% Pt/C的催化选择性、稳定性和抗甲醇性能. 这源于稳定的二维纳米片层结构、丰富的表面介孔结构、大的比表面积和活性位点暴露率以及多种催化活性位点的协同催化效应.

关键词: 氧还原催化剂; FeCl_3 模板; 质子盐; 原位掺杂; 协同催化

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