Heteroatom-doped hollow carbon material as an electrocatalyst for oxygen reduction reaction

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Abstract. The development of highly efficient and stable non-precious metal electrocatalysts is essential for the oxygen reduction reaction (ORR). In this study, a simple polymerization pyrolysis method is proposed to prepare heteroatom-doped hollow carbon nanospheres (NPSC-800) by using Fe-BDC and phosphorus-containing polymers as precursors. The unique structure allows the catalyst to show good catalytic performance (Initial potential of 0.8786 V, a half-wave potential of 0.7576 V, and a diffusion-limited current density of 4.48 mA cm⁻²). This research provides an effective strategy for the synthesis of heteroatom-doped carbon materials with good ORR catalytic performance.

1. Introduction
The slow kinetics of the oxygen reduction reaction (ORR) is one of the reasons that hinder the wide application of these energy conversion systems (such as zinc-air batteries (ZAB), fuel cells) [1-6]. Pt-based catalysts are effective for ORR, but their high cost, scarcity, and instability limit their large-scale commercial applications [7-10]. In this case, it is important to explore alternative non-precious metal materials.

At present, it has been proved that heteroatom-doped hollow carbon materials (e.g., N, P, S, O, B) show more excellent electrocatalytic performance [11-14]. However, specific atom doping requires specific instruments or methods, and it is difficult to achieve co-doping of multiple heteroatoms at the same time [15-16]. In this context, Metal-organic Frameworks (MOFs) containing metal ions and organic ligands attract a lot of attention. Generally, MOFs have poor electrical conductivity, but they can be further transformed into metal compounds and carbon frameworks through a simple pyrolysis process to improve their performance [17-20]. Moreover, in order to avoid the generation of a large amount of toxic and deadly gases during the calcination process, the use of phosphorus-containing polymers to achieve phosphating of materials seems to be the most effective strategy [21-24]. Therefore, it is necessary to develop a non-toxic and simple preparation method to synthesize multi-heteroatom co-doped carbon materials.

Here, we successfully design a facile method to synthesize hollow carbon nanospheres (NPSC-800) by using Fe-BDC calcined Fe₃O₄ as the core and cyclotriphosphonitrile-co-4,4′-sulfonyl diphenol (PZS) as the shell, followed by high temperature calcination treatment. Due to its simple design and unique structure, the obtained products show good catalytic activity and electrochemical stability towards ORR.

2. Experimental Section

2.1. Material preparations
First, 1.62 g FeCl₃⋅6H₂O and 0.995 g 1,4-dicarboxybenzene (H₂BDC) were dissolved in 30 mL DMF, followed by the rapid addition of 2.4 mL NaOH (2 M), and then transferred to a Teflon-lined autoclave and heated at 100 °C for 15 h. The product was collected and washed several times with DMF, ethanol and dried at 70 °C overnight. The prepared Fe-BDC was calcined at 500 °C under air for 2 h to obtain Fe₃O₄. Second, The Fe₃O₄
was dispersed in methanol (60 mL). Then, the mixture solution of 0.112 g hexachlorocyclophosphonitrile (HCCP) and 0.255 g 4,4'-flavoyldiphenyl sulfone (BPS) in methanol (14 mL) was added dropwise to the above solution. After 15 minutes, the 300 μL triethylamine (TEA) was added dropwise as the catalyst and continued stirring for 10 h. The obtained product (Fe$_2$O$_3$@PZS) was washed with methanol and then dried. Finally, Fe$_2$O$_3$@PZS was annealed at 800 °C under Ar/H$_2$ gas for 2 h (5 °C/min) to obtain the product Fe$_2$O$_3$@PZS-800, which was then immersed in 2 M HCl for 12 h. After drying, the product was calcined again under the same calcination conditions as above to obtain the final product hollow carbon nanospheres (NPSC-800).

2.2. Material Characterization
The morphology of the prepared materials were studied using scanning electron microscopy (SEM, Hitachi S-4800). The structure of the prepared materials were tested using X-ray diffraction (XRD, Rigaku-D/max).

2.3. Electrochemical measurements
To evaluate ORR performance, CV tests were carried out in an O$_2$-saturated 0.1 M KOH solution and the cyclic activation scan rate was set at 100 mV s$^{-1}$. After the test, the linear scanning voltammetry (LSV) test for ORR was continued in the above solution. (10 mV s$^{-1}$). Simultaneous rotating disc (RED) electrodes were added to the rotational speed (400, 625, 900, 1225, 1600 rpm). The number of electron transfers (n) was calculated from the LSV curves of the ORR at different rotational speeds and from the Koutecky–Levich (K-L) equation.

3. Results and discussions

3.1. Synthesis and characterizations

![Synthetic Route of NPSC-800](Fig. 1)

The synthesis process of heteroatom-doped hollow carbon nanospheres (NPSC-800) is mainly divided into two steps (Figure 1). First, the surface of Fe$_2$O$_3$ nanoparticles is coated with a layer of polymer (PZS). The synthesis mechanism of PZS is to polymerize HCCP and BPS in situ on the surface of Fe$_2$O$_3$ nanoparticles under the catalysis of triethylamine. Subsequently, Fe$_2$O$_3$@PZS was pyrolyzed and etched to obtain hollow carbon nanospheres (NPSC-800). In the carbonization process, PZS not only acts as a carbon source but also achieves simultaneous doping of multiple heteroatoms.

![SEM Images](Fig. 2)

Fig. 2. SEM images of (a) Fe-BDC, (b) Fe$_2$O$_3$, (c) Fe$_2$O$_3$@PZS, (d) NPSC-800.
The morphology of various products is observed by SEM. It can be found that Fe-BDC exhibits a clear nanorod shape with uniform size distribution (Figure 2a) [14]. After calcination in air, the obtained Fe$_2$O$_3$ sample still retains the rod-like structure (Figure 2b). After the surface polymerization reaction, it can be seen that the surface of Fe$_2$O$_3$@PZS is smooth and the average diameter increases, which proved that PZS was successfully coated on the surface of Fe$_2$O$_3$ nanorods (Figure 2c). When it underwent the carbonization-etching-carbonization process, it could be found that NPSCS-800 showed irregular morphology and produced a distinct hollow structure (Figure 2d).

![XRD patterns](image)

**Fig. 3.** XRD patterns of Fe$_2$O$_3$, Fe$_2$O$_3$@PZS and NPSC-800.

The crystal structure of various samples is proved by XRD patterns. As shown in Figure 3, the complete conversion of Fe-BDC to Fe$_2$O$_3$ after calcination under air conditions agrees well with the simulated diffractogram of the Fe$_2$O$_3$ (PDF#33-0664). The diffraction peaks at about 24.1°, 33.1°, 35.6°, 49.4°, and 54.1° are attributed to (012), (104), (110), (024), and (116) crystal planes, respectively. After the polymerization reaction, it is found that the obvious diffraction peaks in Fe$_2$O$_3$@PZS corresponded to the characteristic peaks of Fe$_2$O$_3$ card (PDF#33-0664), indicating that the original structure of Fe$_2$O$_3$ is not destroyed by PZS coating on the Fe$_2$O$_3$ surface. After two calcinations, the characteristic peaks of NPSC-800 appear at approximately 25° and 44°, corresponding to (002) and (100) crystal planes, respectively. It shows that NPSC-800 has a good degree of carbonization.

### 3.2. Electrochemical characterization

![CV curves](image)

**Fig. 4.** CV curves of NPSC-800 in O$_2$-saturated solution.

The electrocatalytic activity of NPSC-800 as an electrocatalyst for oxygen reduction is studied for the first time. From the CV curves of NSPC-800, a clear reduction peak at 0.72 V can be observed, indicating the significant oxygen reduction activity of NPSC-800 (Figure 4).
Fig. 5. LSV curves of Fe$_2$O$_3$@PZS-800, Fe$_2$O$_3$@PZS-800-etching, NPSC-800, Pt/C at 1600 rpm.

To compare the ORR performance of the samples, the polarization curves of different samples are tested at 1600 rpm. Among them, the NPSC-800 shows excellent electrocatalytic activity. The results show that it has an initial potential ($E_0$) of 0.8786 V, a half-wave potential ($E_{1/2}$) of 0.7576 V, and a diffusion-limiting current density ($J_L$) of 4.48 mA cm$^{-2}$, which is better than Fe$_2$O$_3$@PZS-800 ($E_0$ of 0.8036 V, $E_{1/2}$ of 0.6436 V and $J_L$ of 3.27 mA cm$^{-2}$) and Fe$_2$O$_3$@PZS-800-etching ($E_0$ of 0.8566 V, $E_{1/2}$ of 0.7086 V, and $J_L$ of 4.19 mA cm$^{-2}$) (Figure 5).

Fig. 6. Tafel plots of Fe$_2$O$_3$@PZS-800, Fe$_2$O$_3$@PZS-800-etching, NPSC-800, Pt/C.

In addition, the Tafel slopes of the above catalysts are evaluated. As shown in Figure 6, the values indicate that the Tafel slope of NPSC-800 is 63.06 mV dec$^{-1}$, which is lower than Fe$_2$O$_3$@PZS-800 (133.14 mV dec$^{-1}$) and Fe$_2$O$_3$@PZS-800-etching (96.13 mV dec$^{-1}$) and similar to Pt/C (51.88 mV dec$^{-1}$).
Fig. 7. LSV curves of NPSC-800 at different rotating rates and corresponding K-L plots (inset).

Next, the LSV of NPSC-800 is measured at different rotational speeds (400, 625, 900, 1225, 1600 rpm), and the electron transfer kinetics of NPSC-800 during ORR is discussed (Figure 7). Obviously, with the rotation speed increases, the diffusion limit current density of NPSC-800 also increases, which is due to the faster O\textsubscript{2} diffusion speed at high rotation speeds. In addition, the corresponding Koutecky-Levich (K-L) diagram confirms the first order reaction kinetics of ORR. According to the K-L equation, the electron transfer number (n) can be determined to be 2.71, indicating that NPSC-800 ORR catalyzed through the mixed 2 and 4 electron transfer pathways (inset in Figure 7).

4. Conclusions
In summary, NPSC-800 is successfully synthesized in a simple manner using MOF as the precursor and calcined material as the core, by polymerization method and two calcination processes. The result shows that NPSC-800 has good ORR catalytic activity, with an E\textsubscript{0} of 0.8786 V, E\textsubscript{1/2} of 0.7576 V, and J\textsubscript{L} of 4.48 mA cm\textsuperscript{-2}. The method introduced here can provide a new strategy to design and synthesize catalyst materials with high ORR electrocatalytic performance.

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