Fe-N-doped porous carbon from petroleum asphalt for highly efficient oxygen reduction reaction

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ABSTRACT

Fe-N-doped porous carbon derived from petroleum asphalt (NPCA) was prepared via a facile template synthesis method, with urea as nitrogen source while α-Fe2O3 nanoparticles as template and Fe source. The as-prepared NPCA calcined at 900 °C (NPCA-900) exhibits excellent electrocatalytic performance with high diffusion-limiting current density and stability comparable to those of commercial Pt/C catalysts in alkaline environment. The remarkable ORR performance of NPCA could be ascribed to the abundant porosity, large specific surface area (1060 m² g⁻¹), as well as the doping of Fe-N (especially pyridinic N). The NPCA derived from cheap petroleum asphalt has good application future in the field of catalysis, while it may pave a new way to realize the clean and high value utilization of heavy oils.

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1. Introduction

Oxygen reduction reaction (ORR), as a critical reaction of the renewable and sustainable energy source-fuel cells, has gained extremely crazy attention. Commercial Pt/C catalyst of ORR cannot be widely used due to its shortage and poor durability, thus earth-abundant elements as the alternatives are urgently needed to be explored, such as C, N, Fe, Co, Mn, etc. [1–3]. Various carbon materials have been utilized as ORR catalysts and demonstrated remarkable electrocatalytic performance, among which N-doped carbon materials performed superiorly [4–9]. It has been manifested that the embedded nitrogen atoms can modify the local electron density of neighboring carbon atoms and facilitate oxygen adsorption and dissociation [10,11]. What’s more, the extra addition of non-noble transition metals can further improve the performance. Fe was reported to perform as part of the active sites to form Fe-N-C ORR catalysts [12–14]. A variety of Fe-N doped carbon structures have been used as ORR catalysts, such as Fe-N-doped mesoporous carbon microspheres [15], Fe/N/C catalysts in monolayer graphene [16], mesoporous Fe-N-doped carbon nanofibers [17], Fe/N co-doped graphitic carbon bulb [18], etc.

Besides the doped heteroatoms, the resultant electrocatalytic performance of ORR catalysts is also closely associated with the properties of the carbon support, such as specific surface area, porosity and the degree of graphitization. It is supposed that optimal electrocatalytic activity is correlated to the large specific surface area and suitable pore size, which can facilitate the mass and charge transfers across electrode-electrolyte interface efficiently. Mesopores with the pore size in the range of 20–30 nm is considered to be the optimal porosity for mass transport of ORR [19]. At the same time, the higher graphitization is crucial in accelerating electron transfer process with lower charge-transfer resistance [20,21]. Taken above mentioned into account, how to facilely develop efficient Fe-N-doped carbon based ORR catalyst from cheap raw materials is still a big challenge.

As a kind of by-product of the oil refinery process, petroleum asphalt with annual output around million tons is mainly utilized as waterproof or paving materials in construction industry, or as fuel. However, it is promising to serve as carbon sources for various dimensional carbon materials due to the high contents of carbon and aromatic groups, which can act as bricks to build carbon buildings. A lot of efforts have been devoted to fabricating various carbon materials from petroleum asphalt for adsorption and energy storage [22–26], however, no report has focused on ORR.

Herein, we prepared Fe-N-doped porous carbon (NPCA) by employing petroleum asphalt and urea as carbon and nitrogen sources respectively. Fe₂O₃ nanoparticles were employed not only...
as template to form porous structure, but also as the precursor of Fe for Fe-N doping. The electrocatalytic performances of the as-prepared NPCA were investigated and its potential application was envisaged.

2. Experimental

2.1. Chemicals

Petroleum asphalt was obtained from China National Offshore Oil Corporation (17.63 wt.% saturates, 31.13 wt.% aromatics, 38.21 wt.% resins and 6.40 wt.% asphaltenes). 30 nm α-Fe2O3 nanoparticles was purchased from Macklin Biochemical Co., Ltd. HCl (36–38 wt.%), urea (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. KOH (90 wt.%), Nafion solution (5 wt.%) and commercial 20 wt.% Pt/C catalyst were purchased from Aladdin Industrial Corporation.

2.2. Synthesis

2.2.1. Synthesis of Fe-doped porous carbon from asphalt (PCA)

3 g g petroleum asphalt was dissolved in 100 mL methylbenzene. Then 12 g α-Fe2O3 nanoparticles (30 nm in diameter) was added into the solution under vigorous stirring, and the mixture was dried at 90 °C and then carbonized at 800 °C for 1 h under N2. The composite obtained after carbonization (noted as PCA0) was double treated with 2 M HCl at room temperature and 90 °C for 12 h respectively to remove the template. Then the material was filtrated, washed with deionized water until neutral, and finally dried at 80 °C as PCA. For comparison, petroleum asphalt was carbonized at 800 °C for 1 h under N2 without the addition of α-Fe2O3 template and the obtained sample was named as CA.

2.2.2. Preparation of Fe-N-doped porous carbon form asphalt (NPCA)

1.5 g urea was dissolved into 3 mL deionized water, which was added into 0.3 g as-prepared PCA. After ultrasonic dispersing for 30 min and vacuum drying for 3 h at 80 °C, the obtained mixture was subsequently calcined at different temperatures (800, 900, 1000 °C) for 2 h under N2, named as NPCA-800, NPCA-900 and NPCA-1000, respectively. For comparison, calcined at 800, 900 and 1000 °C for 2 h under N2 without the addition of urea, and noted as PCA-800, PCA-900 and PCA-1000, respectively.

2.3. Characterization

The crystal property and phase composition of the as-prepared products were investigated by X-ray diffraction (X’Pert PRO MPD, Holland) with Cu Kα radiation (λ = 1.518 Å). The specific surface area was measured using the Brunauer-Emmett-Teller (BET) method on a sorptometer (Micromeritics, ASAP 2020, America). Transmission electron microscopy (TEM) (JEM-2100UHR, Japan) and field emission scanning electron microscopy (FE-SEM) (Hitachi S-4800, Japan) were used to identify the microstructures and morphologies of the samples. The crystallinity of as-made samples was labeled by Raman analysis carried out by a Jobin–Yvon Labram-G10 Raman spectrometer. X-ray photoelectron spectroscopy (XPS) analyses were conducted on a Kratos Axis Ultra instrument (Chesnut Ridge, NY).

2.4. Electrochemistry

Electrochemical measurements were performed on an electrochemical workstation (CHI 760E, CH Instrument, China) with a three-electrode cell system, using Ag/AgCl (saturated KCl) electrode as reference electrode and Pt wire as the counter electrode. All the potentials were referred to a reversible hydrogen electrode (RHE), ERHE = EAg/AgCl + 0.197 V + 0.0591 pH. A rotating ring-disk electrode (RRDE) with a glassy carbon disk (GCE, 4 mm in diameter) was loaded with the as-prepared catalysts, serving as working electrode. 2 mg of the obtained samples was dispersed in 0.8 mL ethanol and 0.005 mL of 5 wt.% Nafion solution under sonication for 30 min to prepare catalyst inks. 15 μL of the suspension was pipette onto the GCE and dried in air at a catalyst loading of 0.30 mg cm−2. For comparison, commercial Pt/C was loaded onto the GCE by the same means (also at the loading of 0.30 mg cm−2). ORR test was performed in an O2 saturated 0.1 M KOH aqueous solution (70 mL). For the durability test of methanol, 47.5 μL methanol dissolved in 1 mL of 0.1 M KOH was added to the O2-saturated 0.1 M KOH aqueous solution at 300 s, and the current was collected at 0.565 V vs. RHE with a rotation rate of 1600 rpm. The ORR kinetics was analyzed with the Koutecky–Levich (K–L) plots based on K-L equations as below.

\[
\frac{1}{J} = \frac{1}{j_K} + \frac{1}{j_L} = \frac{1}{j_K} + \frac{1}{B^{0.5}} \tag{1}
\]

\[
B = 0.62nFD^2\nu^{-2}C_O \tag{2}
\]

where \( j \), \( j_K \), and \( j_L \) denote the measured, kinetic and diffusion-limiting current densities (mA cm−2), respectively. \( \omega \) is the electrode rotating speed in rad s−1. \( B \) is the reciprocal of the slope determined from the slope of Koutecky-Levich plots and \( n \) is the number of electrons transferred per oxygen molecule. \( F \) is the Faraday constant (96485 C mol−1); \( D \) is the diffusion coefficient of \( O_2 \) in 0.1 M KOH (1.9 × 10−5 cm2 s−1); \( \nu \) is the kinematic viscosity (0.01 cm2 s−1), and \( C_O \) is the concentration of \( O_2 \) (1.2 × 10−3 mol L−1).

3. Results and discussion

Fig. 1 describes the preparation procedure of NPCA. Firstly, petroleum asphalt was mixed with 30 nm α-Fe2O3 nanoparticles and carbonized at 800 °C in N2 to obtain PCA0. And then PCA was prepared by washing the as-prepared PCA0 with 2 M HCl to remove the sacrificial template. At last, the PCA was infused with urea solution and doped at different temperatures to obtain final NPCA samples.

As shown in Fig. 2a, the XRD pattern of PCA is mainly composed of two broad peaks around 23.9° and 43.2° corresponding to the (002) and (100) diffractions of amorphous carbon, as well as the small sharp peak at 26.4° assigned to the (002) diffraction of graphitic carbon. Fe2O3 nanoparticles not only act as usual hard template, but also have activation effect and graphitization catalysis effect for creating pores and graphitic structure [27,28]. The coexistence of amorphous and localized graphitic structures may be ascribed to the graphitization catalysis effect of nano-Fe2O3. Through the XRD comparison of PCA and PCA0, Fe2O3, FeO and Fe can be effectively removed with acid. The NPCA samples fabricated at different temperatures exhibit similar XRD patterns with PCA.

The pore structure of as-prepared PCA and NPCA-900 were investigated with nitrogen adsorption. From Fig. 2c, type IV isotherms with obvious hysteresis loops can be observed for both PCA and NPCA-900, suggesting the existence of abundant mesopores, which can also be demonstrated by the pore size distribution of PCA and NPCA-900 (Fig. 2d). The pore size distribution of PCA centered at 25 nm and 35 nm consists with the size of nano-Fe2O3 template, illustrating the good template effect of α-Fe2O3. There are
also a small portion of micropores and macropores in PCA, probably resulted from the activation and aggregation of nano-Fe₂O₃ template during the calcination, respectively [28]. Compared with PCA, NPCA-900 possess a similar pore size distribution but with relatively more micropores and macropores while less mesopores. The specific surface area of NPCA-900 is 1060 m² g⁻¹, including 305 m² g⁻¹ of micropore area, which is larger than that of PCA (708 m² g⁻¹ with a micropore area of 126 m² g⁻¹). N-doping may increase the defects of carbon structure, accompanied with the formation of pyrrolic and pyridinic N [29], which may also lead to the increase of micropores and specific surface area. The increased specific surface area and abundant pore structure of NPCA-900 could be very favorable for its electrocatalytic activity. Furthermore, the effect of N-doping can be demonstrated by the Raman spectra of PCA and NPCA samples (Fig. S1). The I_D/I_G of NPCA samples are around 0.89, much higher than 0.82 of PCA, manifesting that the defects can be effectively introduced into the carbon structure by N-doping.

The smooth surface without visible porous structure of CA can be identified in its SEM image (Fig. S2a). TEM image of PCA₀ (Fig. S2b) exhibits closely packed Fe-based nanoparticles wrapped by carbon layers. After removing template, the closely packed mesoporous structures of PCA with pore size around 30 nm can be obviously seen according to the SEM and TEM images (Fig. S2c, d), demonstrating the significant template and activated effects of nano-Fe₂O₃. More macropores can be observed in the SEM and TEM images of NPCA-900 (Fig. 3a and b) in comparison to PCA, which is in agreement with the pore size distribution of NPCA-900. The abundant porous structure of NPCA-900 can also be obviously observed in TEM image (Fig. 3c). The HRTEM image of NPCA-900 (Fig. 3d) shows that only amorphous crystallite carbon can be observed, without any Fe-based particles. The SAED pattern of NPCA-900 (the inset of Fig. 3d) shows the ring rather than diffraction spot, revealing the low crystallinity, which coincide with
the HRTEM image. Whereas, the TEM elemental mapping results in Fig. 3e reveal that residual iron species still remain and distribute homogeneously in NPCA-900. It can be inferred that some iron species including Fe-N are stable and can keep in NPCA-900 even after acid washing (Fig. 4). Besides, as shown in Fig. 3e, nitrogen species were indeed doped into the porous carbon structure uniformly. Thus, the form of Fe can be speculated to be very small clusters like Fe-N coordination embedded in porous carbon with high dispersion rather than Fe-based nanoparticles [30,31].

The valence states and elemental compositions of PCA and NPCA samples were analyzed by XPS measurements. The survey spectra in Fig. 4a suggests the existence of C, N and O, corresponding to the peaks in 284.6, 401.0 and 532.0 eV. The amount of Fe could also be identified to be ca. 0.30 at.%. Because of the low content of Fe, the peaks of Fe are invisible in the survey spectra. With the increase of calcination temperature from 800 to 1000 °C, the peaks of N and O tend to be weaker, which are in agreement with the elemental contents in Table 1. Furthermore, based on the deconvolution of the high-resolution N 1s spectra (Fig. 4c and Fig. S3), five nitrogen species exist in PCA and NPCA samples, including N-Fe (398.8 eV), pyridinic N (399.8 eV), pyrrolic N (400.6 eV), quaternary N (402.0 eV) and N-O (404.0 eV). The concentrations of N species can be visualized according to Fig. 4b and Table 1. Pyridinic N could largely favor mass and charge transfer, as well as the electrochemical reaction [32–35]. Although the total N content of NPCA-900 is 2.80 at.%, lower than 4.83 at.% of NPCA-800, the proportion of pyridinic N in NPCA-900 is the largest among the four materials. The characteristic peak of N-Fe gives strong evidence to the incorporation of Fe species and the mutual charge transfer between Fe and pyridinic N-doped carbon structure, which is conducive to the improvement of the ORR performance of the materials [36]. The high-resolution Fe 2p spectra of NPCA-900 (Fig. 4d) can be divided into two pairs of peaks for Fe$^{3+}$ and Fe$^{2+}$, which can also indicate the existence of Fe-Nx in the materials.

The as-prepared materials were utilized as ORR electrocatalyst to test their electrocatalytic performance. The cyclic voltammetry (CV) of PCA and NPCA samples were firstly performed in 0.1 M KOH solution saturated with Ar or O$_2$ at a scan rate of 0.1 V s$^{-1}$ (Fig. 5a). CV curves of the materials in Ar-saturated solution display no obvious redox peak, while those in O$_2$-saturated solution exhibit
well-defined cathodic peaks, illustrating the effective electrochemical reduction of oxygen on the materials, especially NPCA-900.

Furthermore, linear sweep voltammograms (LSVs) of CA, PCA0, PCA, NPCA samples and Pt/C were recorded in 0.165–1.015 V (vs. RHE) with the rotation rate of 1600 rpm for comparison (Fig. 5b). The ORR performances of CA and PCA0 are evidently inferior to that of PCA, indicating the necessity of introducing templates to create pores and removing them after carbonization to expose active sites. It is obvious that both the onset potential and the diffusion-limiting current density of NPCA samples are apparently facilitated compared with those of PCA, verifying the necessity of the N-doping process and the critical role of the nitrogen species embedded in the carbon structure. Specifically, compared with PCA, the higher specific area and more defects of NPCA-900 can not only increase the density of active sites, but also enable more accessible contact between active sites and the dissolved O2, thus enhancing ORR [15]. Besides, as analyzed in the previous section, the co-doping of N and Fe species and the mutual charge transfer between the Fe and N-doped carbon structure also contribute to ORR performance. The LSVs of NPCA-800, NPCA-900 and NPCA-1000 display a similar trend, while NPCA-900 performs the most positive onset potential (0.93 V vs. RHE) and the highest diffusion-limiting current density. The diffusion-limiting current density of NPCA-900 is comparable to that of 20 wt.% Pt/C, suggesting the excellent ORR electrocatalytic performance of NPCA-900. As demonstrated in the analysis of XPS spectra, higher calcination temperature would lead to the decrease of N-doped content and the change of N species. The increase of pyrolysis temperature could normally result in higher graphitization degree of carbon materials and effectively enhance the efficiency of electron transfer [21,37,38]. As shown in Fig. S4, PCA-800, PCA-900 and PCA-1000 prepared without N-doping under the same calcination exhibit medium ORR performances between PCA and NPCAs, which further indicates that both the nature of nitrogen and degree of graphitization is supposed to be the essential factors of carbon catalysts of ORR. The ORR performance of NPCA should be a balance of above two factors [39]. Therefore, NPCA-900 with relatively optimum balance exhibits better ORR performance than NPCA-800 and NPCA-1000.

**Table 1**

Elemental contents and concentrations of N species in PCA and NPCA catalysts determined by XPS measurements.

<table>
<thead>
<tr>
<th></th>
<th>C (at.%)</th>
<th>O (at.%)</th>
<th>N (at.%)</th>
<th>Fe (at.%)</th>
<th>N-O (%)</th>
<th>Quaternary N (%)</th>
<th>Pyrrolic N (%)</th>
<th>Pyridinic N (%)</th>
<th>N-Fe (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCA</td>
<td>91.76</td>
<td>6.68</td>
<td>1.26</td>
<td>0.30</td>
<td>0.18</td>
<td>0.02</td>
<td>0.03</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>NPCA-800</td>
<td>89.71</td>
<td>5.14</td>
<td>4.83</td>
<td>0.32</td>
<td>0.07</td>
<td>0.04</td>
<td>0.04</td>
<td>0.43</td>
<td>0.33</td>
</tr>
<tr>
<td>NPCA-900</td>
<td>93.35</td>
<td>3.55</td>
<td>2.80</td>
<td>0.30</td>
<td>0.04</td>
<td>0.04</td>
<td>0.40</td>
<td>0.59</td>
<td>0.29</td>
</tr>
<tr>
<td>NPCA-1000</td>
<td>96.36</td>
<td>2.06</td>
<td>1.34</td>
<td>0.24</td>
<td>0.02</td>
<td>0.47</td>
<td>0.21</td>
<td>0.28</td>
<td>0.02</td>
</tr>
</tbody>
</table>

**SCN**⁻ is usually adopted as an ORR inhibitor to coordinate Fe (2⁺/3⁺) ions [40–42]. In order to further demonstrate the role of Fe
species during the ORR process, SCN⁻ was employed to decrease the availability of Fe active centers for ORR. According to the result shown in Fig. S5, compared with NPCA-900 without KSCN, the onset potential and the diffusion-limiting current density of NPCA-900 dropped to some extent after introduction of 5 mM KSCN. Thus, it can be inferred that Fe species act as a part of ORR active sites, even the Fe content of NPCA-900 is only 0.30 at.% determined by XPS measurements.

The LSVs of the samples in O₂-saturated 0.1 M KOH with various rotation rates from 400 rpm to 2500 rpm were also recorded (Fig. 5c, Figs. S6a, S7a, S8a and S9a). The ORR kinetics was analyzed with the Koutecky–Levich (K–L) plots (Fig. 5d, Figs. S6b, S7b, S8b and S9b) based on K-L equations. The as-calculated n of PCA, NPCA-800, NPCA-900 and NPCA-1000 are 3.07, 3.42, 3.63 and 3.39, respectively. The n of NPCA-900 is much closer to that of Pt/C (n = 4) than other samples, indicating a more efficient electron pathway of NPCA-900.

The stability of NPCA-900 as ORR electrocatalyst was also investigated through current-time chronoamperometric responses at 0.465 V vs. RHE over 40000 s (Fig. 5e), indicating a good durability comparable to that of commercial Pt/C catalyst. LSV curves of NPCA-900 before and after cycling for 3000 times can also demonstrate the good stability of NPCA-900, as shown in Fig. S10. Besides, the durability of methanol crossover effect is an important factor to evaluate the performance of ORR catalyst. As shown in Fig. 5f, commercial Pt/C catalyst suffered a notable loss in current density after the injection of methanol at the time of around 300 s, while the influence to NPCA-900 was not obvious, demonstrating the remarkable resistance to methanol crossover of NPCA-900.

To sum up, the optimal performance of NPCA-900 may be attributed to the following two factors. On one hand, the abundant porosity and the large specific surface area provide high speed mass
transport for reactants towards the active sites. On the other hand, the optimal balance between the type and content of nitrogen and the degree of graphitization benefits the ORR performance. The relatively high degree of graphitization can enhance the efficient electron transfer, while the doping of Fe-N, especially the relatively high amount of pyridinic N, gives rise to more defects and active sites, and contribute to the improvement of ORR performance. In the near future, we will do experiments to clarify the detailed roles of Fe-N and N types of NPCA on ORR.

4. Conclusion

In summary, we demonstrated a facile strategy to fabricate Fe-N-doped porous carbon from petroleum asphalt for ORR via template method and subsequent urea-doped assistant calcination. Fe$_2$O$_3$ nanoparticles act not only as template and activation agent to form porous structure, but also as the precursor of Fe for Fe-N. The abundant porosity, large specific surface area, pyridinic N, and the co-doping of Fe-N. Therefore, NPCA-900 has good application future as an effective alternative to the commercial ORR catalyst. Besides, it can also pave a new way to realize the clean and high value utilization of petroleum asphalt.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.carbon.2017.10.004.

References


