



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 facilitate 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

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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 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, PCA was 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 K α radiation ($\lambda = 1.518 \text{ \AA}$). 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-010 Raman spectrometer. X-ray photoelectron spectroscopy (XPS) analyses were conducted on a Kratos Axis Ultra instrument (Chestnut 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), $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V} + 0.0591 \text{ pH}$. 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 pipetted 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.

$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_L} = \frac{1}{j_K} + \frac{1}{B\omega^{-1/2}} \quad (1)$$

$$B = 0.62nFD^{2/3}\nu^{-1/6}C_0 \quad (2)$$

where j , j_K , and j_L denote the measured, kinetic and diffusion-limiting current densities (mA cm⁻²), respectively. ω 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 O₂ in 0.1 M KOH ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$); ν is the kinetic viscosity (0.01 cm² s⁻¹), and C_0 is the concentration of O₂ ($1.2 \times 10^{-3} \text{ mol L}^{-1}$).

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, Fe₃O₄, FeO and Fe can be effectively removed with acid. The NPCA samples fabricated at different temperatures exhibit similar XRD patterns with PCA (Fig. 2b).

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 distributions 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

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