



Short communication

Tailoring the porous structure of N-doped carbon for increased oxygen reduction reaction activity

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ABSTRACT

A facile one-pot method using molten salt medium is developed to fabricate an open structured N-doped carbon (ONC) derived from biomass. SEM and TEM show the ONC is made up of interconnected thin amorphous carbon layers. N₂ isotherm shows that ONC has hierarchical porous structure with a high specific surface area of 1893.5 m² g⁻¹. Compared to commercial Pt/C (20 wt%), the ONC has comparable ORR activity and better durability. Due to its high ORR activity and durability, producing an opened N-doped carbon in this molten salt medium can provide a promising approach for synthesizing heteroatom doped carbons with electrochemical performance.

1. Introduction

High energy density systems, such as metal-air batteries and fuel cells, are highly expected to be used in transportation and electricity generation, which are currently dominated by using fossil fuels. Unfortunately, sluggish kinetics of oxygen reduction reaction (ORR) at the cathode of fuel cells and metal-air batteries required high Pt-loadings, impeding their practical applications, which has stimulated the researchers to exploit low-cost alternative to Pt-based catalysts with better performance or equivalent to the Pt standard [1–3].

Recently, nitrogen-doped (N-doped) carbon materials have attracted more and more attention due to its low-cost, abundance, inert to methanol and relative high ORR activity [4]. Among them, N-doped carbons with an open structure represented by a honeycomb-like appearance have gained tremendous attention since the open structure provides highly opened three-dimensional channels for facilitating mass diffusion of the electrolyte [5–7]. A series of methods have been developed to tailor the open structure in N-doped carbon materials, for instance, using templates, such as nano-sized silica [8], nickel foam [9], MCM-48 [10] or ordered metal oxides [11]. It was also reported that the open structure in N-doped carbon network could be made using KOH etching agent at elevated temperature [12]. It is quite difficult to scale up from cost and environmental point of views because some extremely corrosive chemicals are required to etch part of the carbon or to remove the templates. Recently, opened N-doped carbons have also been prepared from the polymer in molten salt medium, which has a much less impact on the environment [13,14]. However, most of N-

doped carbons prepared in molten salt medium did not present the open structure, although they have rich micropores or/and mesopores [15,16]. It indicates that the obtained open structure in N-doped carbons is still a challenging task. When applied in ORR 4e procedure, optimized porosity in heteroatom-doping carbon is favorable for mass transfer. While in the doped N species, pyridinic-N provides a pair of electrons to bond with the *p*-conjugated rings and graphitic-N can bring about lower overpotential for ORR [17,18]. The latter density can be improved by trace addition of transition metal salts, such as Fe ones.

NaNO₃ is a low-cost salt, which had been used as etching agent to mechanochemically super-polish the surface of diamond as decomposed oxygen from NaNO₃ can chemisorb on the surface of diamond and react with carbon to form CO and CO₂ [19]. Inspired by this work, in this study, NaNO₃ was introduced into the NaCl/ZnCl₂ molten salt medium as surface etching agent to prepare N-doped carbon with open structure. A biomass waste, soybean dregs (SD), was selected as the carbon and nitrogen sources, which was carbonized at elevated temperature with NaCl/ZnCl₂/NaNO₃. The as-prepared opened N-doped carbons (ONC) were tested as electrocatalyst for ORR, and showed a comparable ORR activity to commercial Pt/C with outstanding durability.

2. Experimental

The detailed procedure of preparing ONC is as follows: SD was first dried at 80 °C in oven for 4 days, and then the dried SD was sifted through a 80 mesh sieve to remove the large particles. 1 g of dried SD

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was mixed with 10.5 g of NaCl/ZnCl₂/NaNO₃ (mass ratio 60.16%, 35.08% and 4.76% respectively) mixture and ball milled in a zircon jar at 600 rpm for 6 h. After that, the mixture was loaded into a ceramic crucible and then located in an inert gas tube furnace. The temperature was elevated to 900 °C with a heating rate of 2.5 °C min⁻¹ under nitrogen atmosphere, and kept at this temperature for 60 mins. Subsequently, the temperature was cooled down to 50 °C with a cooling rate of 5 °C min⁻¹. The obtained product was immersed into 400 ml H₂O and magnetically stirred for 6 h, then filtered out and dried at 80 °C in a vacuum oven for 12 h. Afterwards, 1 g of the above products with 1 g of FeCl₃ were dissolved in 5 ml of water, dried at 60 °C for 12 h and then heated at 900 °C for 1 h. The obtained product was treated HNO₃ to remove unstable Fe species. After acid-treatment, the sample was rise with water until pH of filtrate was neutral, and the dried at 60 °C for 12 h, at last labeled as ONC. For comparison, SD without above salt mixture was also carbonized with the same procedure of preparing ONC. The final product was labeled as NC.

X-ray diffraction (XRD) patterns were performed on Shimadzu XD-3A with CuK α radiation. The morphology of carbon samples was studied by scanning electron microscopy (SEM, Carl Zeiss Ultra Plus) and transmission electron microscopy (TEM, JEM-2000 FX). Specific surface area was determined by the nitrogen adsorption region of relative pressure from 0.05 to 0.25, and the total pore volume was measured at 0.99. The pore size distribution was obtained with density functional theory (DFT) method using the QSDFT model for slit shaped pores provided by Quantachrome data reduction software QuadraWin Version 2.02 [20]. X-Ray Photoelectron Spectroscopy (XPS) spectra were generated with a PHI-5702 multifunctional X-ray photoelectron spectrometer (Physical Electronics).

The activities were performed using CHI650D (CH Instruments) with a glass carbon (GC) electrode of diameter 5 mm as the working electrode, a Pt wire as the counter electrode and Ag/AgCl (saturated KCl) as the reference one. Each carbon suspension was prepared by making 2 mg activated carbon dispersed in 0.4 ml nafion/ethanol (0.25% Nafion) solution. After sonication for 20 min, 10 μ l of the ink was applied onto the GC electrode, and then dried under room temperature. The geometric area of working electrode is about 0.196 cm², and the mass loading of each carbon materials as well as commercial 20 wt% Pt/C is about 0.255 mg cm⁻². The Pt-loading on the ring electrode was 51 μ g_{Pt} cm⁻².

3. Results and discussion

SEM picture of ONC presented in Fig. 1a showed a very open morphology with very thin walls. For comparison, SEM of NC is shown in Fig. S1a, in which irregularly shaped blocks in the range of about one micron and even tens of microns with a compact structure are found. TEM was performed to investigate their detail structures (Fig. 1b and Fig. S1b). As shown in Fig. 1a and b, interconnected macroporous network with open structure are observed in ONC. Moreover, the walls of this structure were made up of thin carbon layers, especially in its TEM image, which shows thin amorphous carbon layers were found. Its high resolution in Fig. S2 reveals thicker walls (about three layers)

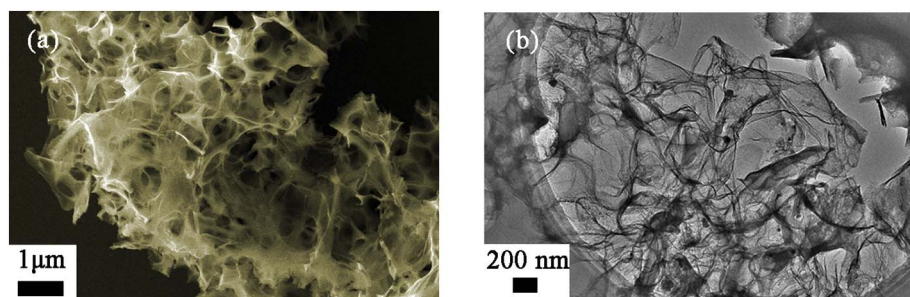


Fig. 1. SEM picture (a) and TEM image (b) for ONC.

surround pores. The thickness of ONC is less than 1.1 nm. In the case of NC, a relatively compact structure was revealed in Fig. S1b. SEM and TEM images clearly display the open structure can be fabricated in ONC via this molten salt method at high temperature.

Nitrogen isotherm was adopted to study the porous structures of as-prepared carbons (Fig. S1c). In the case of NC, its N₂ isotherm exhibits a typical type I adsorption/desorption behavior with a small uptake at low relative pressure, indicating that there are small amount of micropores existed in NC [21]. The N₂ isotherm of ONC belongs to a mixed type, namely type I at relative low pressure and type IV at relative intermediate to high pressure. An obvious uptake appeared in the initial part, which is the characteristic of micropores. At the relative intermediate and high pressure, a certain hysteresis slope was found in the isotherms, indicating there are mesoporous existed, and a rapid N₂ uptake at relative high pressure implies the existence of macropores [22]. The pore size distribution of ONC and NC presented in Fig. S1b clearly shows coexistence of micropore and mesopore in the two samples, and the amount of micro and meso pores in ONC is higher than that of NC. A large amount of mesopores in the range of 2.3 to 5 nm was formed in ONC which results from the etching of NaNO₃ at high temperature. The BET specific surface area of ONC is 1893.5 m² g⁻¹, which is about 21 times that of NC (89.6 m² g⁻¹). Meanwhile, total pore volume of ONC was 1.708 m³ g⁻¹, larger than that of NC (0.096 m³ g⁻¹).

The XRD patterns of ONC and NC (Fig. S3a) show two diffraction peaks at 2 θ values of ca. 25° as well as 43°, which are quite similar to that of graphite [23], but the two peaks are broad, suggesting that the graphitization of the two samples is quite low.

XPS was performed to study the surficial chemical state of the elements. In Fig. S3b, both NC and ONC contain C, N and O elements. Although there was little FeCl₃ added in ONC preparation process, no obvious Fe signal has been detected, indicating its washing out thoroughly. Furthermore, the faint signal centered around 200.0 eV for sample ONC should result from Cl 2p. While according to Table S1, there is no obvious Na auger signal. Even if there is any auger Zn signal, it will be overlapped by O signal. In Fig. S3c, there is no signal of Na or Zn. It can be concluded that ZnCl₂ will be trapped in closed pore inside ONC if there is a trace amount of ZnCl₂ existed. However, the effect of ZnCl₂ on electrochemical performance can be neglected [24]. To investigate N elemental chemical state which play an important role in the catalytic activity of N-doped carbon, its fine spectra were also conducted. As shown in Fig. S3d, there are six types of nitrogen species on the surfaces of both samples, namely, pyridinic-N at 398.3 eV, pyrrolic-N at 399.9 eV, graphitic-N at 401.2 eV, pyridinic N-oxide at 402.4 eV, π - π^* satellite at 404.8 eV, and entrapped NO_x at 406.3 eV [25,26]. Detailed percentage of these N species in ONC and NC are illustrated in Fig. S3e. The percentage of graphitic-N and pyridinic N in ONC is much higher than that of NC. High amount of graphitic-N and pyridinic N has been proved to bring about lower over-potential for ORR [27], which could result in a better ORR performance.

To investigate the electrochemical performance of as-prepared samples, cyclic voltammograms were carried out and presented in Fig. 2a. The CV curve of ONC showed a reversible, featureless and

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