



Tuning the extent of porosity and composition of N-doped carbon materials by NaNO₃ and its effect on electrochemical activity

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ABSTRACT

A facile one-pot method using NaNO₃ as etching agent in a molten salt medium is developed to tune the porous structure and composition of N-doped carbon materials derived from biomass at high temperatures. SEM and TEM analyses reveal that by increasing the amount of NaNO₃, the structures of the obtained carbons become more open and graphene-like layers are formed. N₂ adsorption/desorption isotherms show that the hierarchical porous structure could be efficiently tuned by adjusting the amount of NaNO₃ in the salt mixture. It is observed that the specific surface area of the as-prepared N-doped carbon using NaNO₃ can reach 1430.1 m² g⁻¹, a much higher value than that of the sample prepared in the absence of NaNO₃. The micropore ratio decreases with increased amount of NaNO₃, from 49.42% to 9.98%. Whilst the surface composition of the obtained carbon materials is affected by NaNO₃. The N content increases and O decreases respectively, by increasing the amount of NaNO₃. Analysis on the N 1s high resolution reveals that the sum of pyridinic-N and graphitic-N increased, whereas the sum of pyridinic-N oxide and NO_x decreases from NC-0 to NC-0.75. It is also found that the changes of the porous structure and the oxygen-containing groups from NC-0 to NC-0.75 led to changes in hydrophilicity. When the as-prepared carbon materials are used as catalysts for the oxygen reduction reaction, high catalytic activity values are obtained, sample NC-0.5 shows the best performance due to the porous structure and doping effect of N atoms. More importantly, it is concluded that producing N-doped carbon materials from soybean dregs in molten salt medium using NaNO₃ as etching agent could provide a promising approach for the synthesis of opened N-doped carbons of controlled porous structures and large specific surface areas based on biomass precursors.

1. Introduction

Porous carbon materials, especially those with targeted functionalities, *i.e.* the broad range of heteroatom-containing porous carbons possessing high specific surface areas (apparent surface area > 1000 m² g⁻¹), are one of the most competitive material choices in many applications such as catalysis and water treatment, when compared to other classes of porous materials such as zeolites, porous silica, MOFs and many others [1,2]. This is due to their “lightweight constructions” (with each “module” just weighting 12 mass units), but also due to the extraordinary chemical, mechanical and thermal stability of carbon materials and their wide abundance [3].

To produce such materials of adequate porosity, it is often necessary to use hard and soft templating techniques [4,5]. In the hard-templating strategy, porous materials such as zeolite or porous silica with definite-sized pores are often used as porogen to form the pores in the carbon

structure [6–9]. Although porous structures of high surface areas can be obtained, two crucial steps during the preparation are required; the first step, hard templating, involves the synthesis and removal of the crystalline template afterwards, making such a process barely scalable [10]. In the case of soft templating, a large number of surfactants or/and organic polymers such as organic polymers acting as the template to form the porous structure is used [11–15]. Most of these reagents are hazardous and costly chemicals. The soft templating method is not an economic and “green” method for the synthesis of porous carbon materials. Another way for the synthesis of carbon materials of desired porosity is the chemical activation method. In this chemical activation process, the pores are etched into the carbon material by the chemical reaction between the etching agents (*e.g.* an alkali hydroxide or a stream of CO₂) and carbon [16–18]. This method has been successfully employed to produce porous carbon materials at industrial scale owing to its simplicity. Nonetheless, improvement of the chemical activation

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technique for the rational pore design is still required, for example reducing the carbon mass loss and minimizing the chemical composition changes in regard to the dopants (e.g. structural nitrogen).

In the jewelry industry, NaNO_3 has been used as etching agent to mechano-chemically super-polish diamond surfaces as decomposed oxygen from NaNO_3 can chemisorb on the surface and react with carbon to form CO and CO_2 [19]. This observation implies that NaNO_3 could act as chemical active agent for producing porous carbon materials. Moreover, a few studies have reported that the use of nitrates such as LiNO_3 and $\text{Co}(\text{NO}_3)_2$ as chemical activation agents leads to the generation of the pores in the carbonaceous material structure [20]. Compared with LiNO_3 and $\text{Co}(\text{NO}_3)_2$, NaNO_3 is much cheaper and mild etching agent. Therefore, in this study, NaNO_3 was used with $\text{NaCl}/\text{ZnCl}_2$ to form eutectic molten salt during the carbonization process of SD, in the hope of using less salt to prepare porous nitrogen-doped (N-doped) carbon materials with tunable porous structures. Furthermore, the extent of the porosity development and corresponding pore size distribution of the obtained N-doped materials can be tuned by carefully controlling the amount of NaNO_3 in the process. The physical results showed that the presence of NaNO_3 had a substantial impact on the thickness of the carbon sheets, mesoporous structure and specific surface area of the N-doped carbon materials, in turns affecting their electrochemical performance. Compared with reported LiNO_3 method, NaNO_3 etching process resulted in more fluffy carbon network, of which the specific surface area and total pore volume are larger, when consuming the same quantity of etching agents [20]. In our investigation, it was found that these as-prepared materials exhibited large capacitance and acceptable ORR activity values (*on-par* with those obtained for commercial Pt/C materials).

2. Experimental

2.1. Preparation of SD-derived mesoporous N-doped carbons

The detailed procedure for preparing mesoporous N-doped carbons derived from soybean dregs (SD) 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 large particles. 1 g of dried SD was mixed with 10 g $\text{NaCl}/\text{ZnCl}_2$ (NaCl 80 mol%) mixture and x g of NaNO_3 (which is acted as oxidizing agent to publish the surface of obtained carbon materials at high temperature), then ball milled in a zircon jar at 600 rpm for 6 h. After that, the mixture was loaded into a ceramic crucible and then placed in an inert gas tube furnace. The temperature was increased to 900°C with a heating rate of $2.5^\circ\text{C min}^{-1}$ under nitrogen atmosphere, and kept at this temperature for 60 min. Subsequently, the temperature was cooled down to 50°C at a cooling rate of 5°C min^{-1} . The obtained product was immersed into 400 ml of H_2O (ultrapure) and magnetically stirred for 6 h, filtered out and then dried at 80°C in a vacuum oven for 12 h. Afterwards, the carbon material was immersed in 2 M HNO_3 solution for 24 h to remove inorganic insoluble components, if any. After acid washing, the sample was washed with ultrapure water until the pH of the filtered water reached neutrality, and then dried at 80°C in a vacuum oven for 12 h again. The final N-doped carbons were labeled as NC- x (x is the mass of NaNO_3 in the mixed salts). For comparison purposes, a sample made of SD mixed with 10 g of $\text{NaCl}/\text{ZnCl}_2$ mixed salts without NaNO_3 was also prepared by the same method for preparing NC- x . The final product was labeled as NC-0.

2.2. Physical characterizations

X-ray diffraction (XRD) patterns were performed on a Shimadzu XD-3A with $\text{CuK}\alpha$ radiation. The scans were conducted between 5° and 80° with a rate 4° min^{-1} for 2θ values. The morphology of the carbon samples was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM images were

generated on a Carl Zeiss Ultra Plus. TEM images of the catalysts were conducted on a JEOL (JEM-2000 FX) microscope operating at 200 kV. Specific surface areas were determined by the nitrogen (N) adsorption region of relative pressures from 0.05 to 0.25, and the total pore volume was measured at 0.99. Furthermore, the pore size distribution was obtained using the density functional theory (DFT) method. X-ray photoelectron spectroscopy (XPS) spectra were generated with a PHI-5702 multifunctional X-ray photoelectron spectrometer (American). Binding energies were calibrated by referencing to the C 1s peak at 285.0 eV. Water contact angles were measured using an SL200KB apparatus at ambient temperature. For all measurements, the volume of water was $5\ \mu\text{L}$. Raman spectroscopy was recorded on a FT-Raman spectrometer (RFS 100, BRU-KER) with a 1064 nm excitation laser beam wavelength. The intensity of D and G peaks was gauged by the height from the top point of each band.

2.3. Electrochemical characterizations

The electrochemical activities were performed using a potentiostat/galvanostat CHI650D (CH Instruments). A rotating disc glass carbon (GC) electrode of diameter 5 mm was used as the working electrode, a Pt wire as the counter electrode and a Ag/AgCl (saturated KCl) as the reference electrode. The GC disc electrode was carefully polished and cleaned before and after each test. Each carbon suspension slurry was prepared by making 2 mg of activated carbon dispersed in 0.4 mL Nafion®/ethanol (0.25% Nafion®) solution. After ultrasonication (ultrasonic bath, 38 kHz) for 20 min, $10\ \mu\text{L}$ of the catalyst ink was applied onto the GC disc electrode, and then dried at room temperature. The geometric area of the working electrode was about $0.196\ \text{cm}^2$, and the mass loading of each carbon materials as well as commercial 20 wt.% Pt/C was about $0.255\ \text{mg cm}^{-2}$. Through careful calculation, the Pt-loading on the disc electrode was approximately $51\ \mu\text{g}_{\text{Pt}}\ \text{cm}^{-2}$.

3. Results and discussion

During the chemical activation process, the formation of pores is accompanied by a mass loss resulting from the reaction between the etching agent and carbon. The effect of NaNO_3 on the yield of the final carbon materials is shown in Fig. 1. It is clearly observed from the photographs that the yield of the final carbon materials decreases with increasing amount of NaNO_3 . When the NaNO_3 mass relative to the SD precursor increases from 0.25 to 0.75, the carbon material yields (relative to the precursor) decreases from 22.7% to 17.0%. This carbon mass loss can be explained as follows: during the carbonization process, high temperatures are used and the NaNO_3 etching agent decomposes

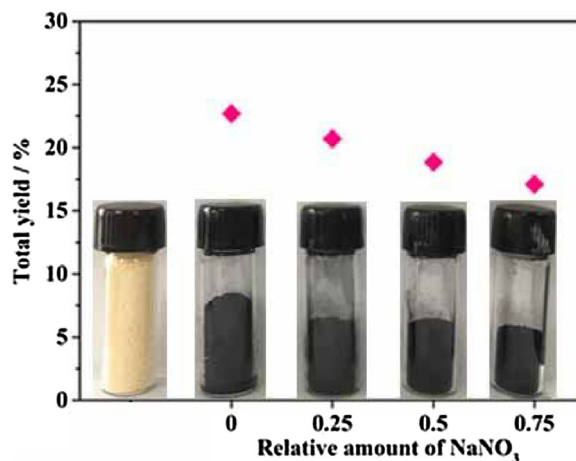


Fig. 1. From left to right, photographs of the SD precursor sample and the obtained carbon material samples, as well as the yield of final carbon materials vs. the amount of NaNO_3 relative to the SD precursor.

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