



Nitrogen-doped ordered mesoporous carbon: synthesis and active sites for electrocatalysis of oxygen reduction reaction



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ABSTRACT

In the present work, a novel impregnation method, namely vaporization-capillary condensation method, is developed to synthesize nitrogen-doped ordered mesoporous carbon. This method allows for the preferential infiltration of the carbon precursor (like pyrrole) into the mesochannels other than into the texture pores or onto the outer wall, which outperforms the traditional methods like 'incipient wetness impregnation'. It is found that the synthesized carbon shows high specific surface area and activity towards the oxygen reduction reaction (ORR). Methanol fuel cell test thereafter reveals two times higher performance with such catalyst than Pt. Moreover, the electrocatalytic activity is correlated with the fraction of nitrogen-activated carbon atoms, indicating that in such catalysts the active sites are C–N groups. The obtained electrochemical results and surface analysis suggest that the transition metal might not be directly involved in the active sites.

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1. Introduction

Nitrogen-doped ordered mesoporous carbon (NOMC) features high specific surface area and unique pore structure, which make it very promising in the applications of catalysis, electrochemistry and energy-related fields [1–4].

Nanocasting method is a universal strategy to synthesize such materials, which generally involves the following steps [5]: (i) infiltration of the template with carbon precursors, (ii) carbonization and (iii) removal of the template. Mesoporous silica has been widely used as the hard template to synthesize these carbon materials [6–13]. Joo [6] investigated the effect of the template on the pore structure and surface area of the carbon catalysts. The best electrocatalytic activity was obtained by using SBA-15 as the template when FeTMPP-Cl and CoTMPP were simultaneously used as the precursor. Sevilla [7] synthesized nitrogen-doped mesoporous carbon with polypyrrole as the carbon source with the aid of SBA-15, which yielded a high specific surface area and thereby decent electrocatalytic activity to the oxygen reduction reaction (ORR). Asefa

[8] improved the synthesis route by pre-anchoring the oxidant onto the inner wall to avoid the polymerization of aniline onto the outer surface of the template.

It is acknowledged that the impregnation is the most critical step to determine the specific surface area and pore structure [5]. Ideally, the carbon precursor needs to be infiltrated into the mesopores rather than into the texture pores or coated onto the outer wall of the template. To achieve this goal, the incipient wetness impregnation (IWI) method is generally used to infiltrate the precursors. However, in practice, an excessive volume is required for the homogeneous impregnation, which inevitably produces less porous or even nonporous carbon. Most probably, this could be the reason for the discrepancies in the pore features, even for those carbon atoms synthesized under very similar conditions [7–10,14].

The questions about the intrinsic nature of the active site of the nitrogen-doped carbon catalyst for the oxygen reduction reaction (ORR) and about the precise role of the transition metal still remain open in terms of electrocatalysis.

In terms of electrocatalysis, it remains to be an open question on what is the intrinsic nature of the active site of the nitrogen-doped carbon catalyst for the oxygen reduction reaction (ORR), especially what about the precise role of transition metal.

It has been claimed that the transition metal could promote the formation of the catalytic active sites during pyrolysis, but not get

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involved in catalyzing the ORR [15–17]. This claim is mostly based on the absence of metal signal in the XPS spectra, but it is also confirmed by the absence of TM-N peak in either the Mossbauer or the EXAFS spectra [15–17]. In comparison, other research groups argued that the transition metal coordinated with nitrogen directly participates in the active sites [6,18–23]. Dodelet [24] suggested that the transition metal is involved in the active sites, which can be simply described as MeN_xC_y . Zelenay [19] found that apart from involving in the active centre, the transition metal ions promote the formation of specific type of nitrogen atoms. Bao [25] suggested that although the transition metal is not directly involved in the catalysis, the charge transfer from the underneath transition metal to carbon lowers the work function and facilitates the adsorption of oxygen.

In the present work, a novel vaporization-capillary condensation impregnation (VCCI) method is developed to infiltrate the monomer like pyrrole into the mesoporous template. This method allows for the preferential infiltration of the precursor inside the nanochannels, which avoids further production of less porous or even nonporous carbon. The resultant carbon shows high specific surface area and outperforms the Pt counterpart in promoting the ORR. Then, an extensive surface analysis was performed to probe the active sites and the result suggests that the transition metal might not be directly involved in the active sites. It is further noted that the electrocatalytic activity can be correlated with the fraction of nitrogen-activated carbon atoms, indicating that the active sites are mostly C–N groups in such catalysts.

2. Experimental

2.1. Preparation of SBA-15

SBA-15 was synthesized by using the tri-block copolymer, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (Pluronic P 123, BASF) and tetraethyl orthosilicate (TEOS, 99%) [26]. In a typical synthesis, 4.0 g of Pluronic P 123 was dissolved in 126 ml of deionized (DI) water and 20 ml of hydrochloric acid (37 wt%), and then 9.2 ml of TEOS was added and stirred for 20 h at 35 °C. The slurry was hydrothermally treated at 100 °C for 12 h. Finally, the product was filtered, dried and calcined at 550 °C for 6 h in air to remove the template.

2.2. Incipient wetness impregnation (IWI) of precursor

2.5 ml of newly distilled pyrrole or aniline (99%, Xiya Reagent) was added into 1.0 g of SBA-15 by vacuum impregnation for 24 h at 25 °C [10].

2.3. Vaporization-capillary condensation impregnation (VCCI) of the precursor

0.90 ml of newly distilled pyrrole (99%, Xiya Reagent), together with 1.0 g of SBA-15, was added into a vacuum container, which was then held in an oven at 133 °C for 2 h. After that, the container cooled to the room temperature, and the light-yellow powders were finally obtained. The same procedure was used for the impregnation of aniline except the oven temperature was set to 183 °C. The temperature used here ensures the complete evaporation of the liquid monomer outside the mesopores. The cooling process is well controlled at a slow rate, which allows for the controllable vapour capillary condensation, liquid spreading and filling into the mesopores of the template. The vacuum avoids the oxidation-polymerization of monomer during the impregnation process.

2.4. Preparation of nitrogen-doped ordered mesoporous carbon (NOMC)

The powders were added into 40 ml of 2.0 mol l^{-1} FeCl_3 aqueous solution, which was then vigorously stirred for 24 h at room temperature for polymerization [10]. The product was filtrated and thoroughly washed with DI water to remove metal salt. After dried, the black-coloured powders were pyrolysed at high temperatures for 3 h in argon (99.999%). Finally, the silica template was removed in 10 M NaOH at 120 °C for 24 h, followed by washing with DI water. The samples were referred to as C-PY-X for polypyrrole and C-PA-X for polyaniline, respectively. Here, X refers to the heat treat temperature, viz. 600, 800, 900 and 1000.

2.5. Physicochemical characterization

X-ray diffraction (XRD) measurements were carried out by using a TD-3500 X (Tongda Technology) diffractometer with a $\text{Cu K}\alpha$ radiation source operated at 40 keV and at a scan rate of 0.05 s^{-1} . Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was performed on Model PHI 7200. The analysis was carried out with a 25 keV Bi^{3+} beam and the scanned area was $200 \mu\text{m}^2$. Thermogravimetric analyses (TGA) were made using a TA Instrument SDT 2960. The experiment was performed at $10 \text{ }^\circ\text{C min}^{-1}$ from room temperature to 1000 °C in air at a flow rate of 20 mL min^{-1} . X-ray photoelectron spectroscopy (XPS) measurement was carried out with a Physical Electronics PHI 5600 multi-technique system using an Al monochromatic X-ray at a power of 350 W. Nitrogen adsorption/desorption isotherms were measured at 77 K using Micromeritics TriStar II 3020 analyzer. Before adsorption measurements, each sample was outgassed under vacuum for 3 h at 200 °C. The total surface area was analyzed with the well-established BET method, the microporous surface area was obtained with the MP method (*t*-plot method) and the pore size distribution was analyzed by the Barrett–Joyner–Halenda method.

2.6. Electrochemical characterization

The electrochemical behaviour of the catalyst was characterized by the cyclic voltammetry (CV) and linear sweeping voltammetry (LSV) using a three-electrode cell with an electrochemical workstation Zennium (Zahner) at room temperature (25 °C). A platinum wire and a double junction Ag/AgCl reference electrode (PINE) were used as the counter and reference electrodes, respectively. The working electrode was a glassy carbon disk (5.0 mm in diameter, PINE) covered with a thin layer of Nafion-impregnated catalyst. Typically, the thin-film electrode was prepared as follows. 10 mg of the catalyst was dispersed in 1 ml Nafion/ethanol (0.84 wt% Nafion) by sonication for 120 min. Then, 10 μl of the dispersion was transferred onto the glassy carbon disk by using a pipette, yielding the catalyst loading of 0.50 mg cm^{-2} . For comparison reasons, we also measured the electrocatalytic activity for ORR of the commercial 40 wt% Pt/C catalyst (HiSPEC4000, Johnson Matthey) with the metal loading of $20 \mu\text{g cm}^{-2}$.

The electrolyte solution, 0.10 M KOH, was first bubbled with argon for 60 min. Then, CV test was conducted at 20 mV s^{-1} in the potential range between 0 and 1.2 V (vs. RHE) for 20 cycles. LSV was collected by scanning the potential from 1.2 down to 0 V at 5 mV s^{-1} in the oxygen-saturated electrolyte solution under 1600 rpm, from which the ORR polarization curve was extracted by subtracting the capacitive current.

2.7. Fabrication of electrode and single-fuel-cell test

The anode is fabricated as follows. Anode catalyst 30 wt% Pd/C catalyst (Sigma), together with Nafion resin, was dispersed in

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