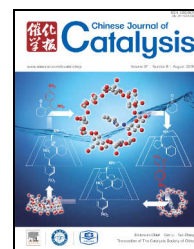


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Article

Preparation of nitrogen-doped carbon nanoblocks with high electrocatalytic activity for oxygen reduction reaction in alkaline solution



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ABSTRACT

The oxygen reduction reaction (ORR) is traditionally performed using noble-metals catalysts, e.g. Pt. However, these metal-based catalysts have the drawbacks of high costs, low selectivity, poor stabilities, and detrimental environmental effects. Here, we describe metal-free nitrogen-doped carbon nanoblocks (NCNBs) with high nitrogen contents (4.11%), which have good electrocatalytic properties for ORRs. This material was fabricated using a scalable, one-step process involving the pyrolysis of tris(hydroxymethyl)aminomethane (Tris) at 800 °C. Rotating ring disk electrode measurements show that the NCNBs give a high electrocatalytic performance and have good stability in ORRs. The onset potential of the catalyst for the ORR is -0.05 V (vs Ag/AgCl), the ORR reduction peak potential is -0.20 V (vs Ag/AgCl), and the electron transfer number is 3.4. The NCNBs showed pronounced electrocatalytic activity, improved long-term stability, and better tolerance of the methanol crossover effect compared with a commercial 20 wt% Pt/C catalyst. The composition and structure of, and nitrogen species in, the NCNBs were investigated using Fourier-transform infrared spectroscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, and X-ray diffraction. The pyrolysis of Tris at high temperature increases the number of active nitrogen sites, especially pyridinic nitrogen, which creates a net positive charge on adjacent carbon atoms, and the high positive charge promotes oxygen adsorption and reduction. The results show that NCNBs prepared by pyrolysis of Tris as nitrogen and carbon sources are a promising ORR catalyst for fuel cells.

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1. Introduction

Fuel cells are highly promising energy conversion devices because they are renewable and have low emissions and high efficiencies. The oxygen reduction reaction (ORR) significantly affects the cathode performance in fuel cells, and efficient ORR electrocatalysts are necessary for practical applications of fuel cells [1–5]. The main products of the ORR are OH^- and HO_2^- ,

and are determined by the major component of the electrode material, electrode potential, and electrolyte [6–8]. Pt and its alloys are currently regarded as the best catalysts for the ORR [9,10]. However, the limited reserves of Pt, high cost, activity deterioration with time, and poor durability severely hinder large-scale use of Pt in ORRs [11–13]. The development of nonprecious-metal and Pt-free catalysts for fuel cells is therefore important [14–18].

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Carbon materials have many advantages such as excellent catalytic activity, low costs, long-term stability, and good tolerance of the methanol crossover effect [19–21]. Carbon materials for use in the ORR as alternatives to Pt-based catalysts have therefore attracted enormous interest. It was recently reported that nitrogen-doped carbon materials show excellent ORR electrocatalytic activity because of their unique electronic properties derived from conjugation between nitrogen lone-pair electrons and the graphene system, i.e., nitrogen doping can improve the electron-donor properties, improving interactions between carbon and oxygen molecules to create metal-like conductivity [22–25]. Dai's group [26] used chemical vapor deposition to produce a nitrogen-doped graphene (NG) that showed better ORR catalytic activity than Pt in alkaline fuel cells. They also developed nitrogen-doped carbon nanotube arrays that showed better electrocatalytic activity, long-term operational stability, and tolerance to the methanol effect than did Pt in oxygen reduction in alkaline fuel cells [27]. Shen's group [28] prepared an ORR catalyst consisting of nitrogen-doped porous carbon particles with a high proportion of pyridinic nitrogen atoms using a combination of the Maillard reaction and thermal annealing in an NH_3 atmosphere. Xian's group [29] synthesized a non-precious-metal oxygen electrode electrocatalyst consisting of MoS_2/NG by physically mixing MoS_2 sheets with NG; the catalyst showed improved electrocatalytic activity in the ORR based on a four-electron pathway in alkaline solutions.

Different preparation conditions can change the structural properties of material such as the specific surface area, electronic conductivity, doping content, and doping state, and these significantly affect the ORR electrocatalytic performance of nitrogen-doped carbon materials. Various direct synthetic methods such as spray pyrolysis, chemical vapor deposition, and solvothermal reactions are effective for preparing nitrogen-doped carbon materials, but high costs, low yields, and complicated processes make these methods unsatisfactory [30–32]. Despite much effort using various synthetic methods, the development of cheap, efficient, and simple methods for the production of nitrogen-doped nanocarbons with excellent catalytic performance in ORRs is still a challenge [33–36].

In this study, we developed an improved approach based on direct one-step pyrolysis for preparing nitrogen-doped carbon nanoblocks (NCNBs) with high nitrogen contents (4.11%). We used tris(hydroxymethyl)aminomethane (Tris) as the carbon and nitrogen sources because it is a cheap and readily available small molecule containing hydroxyl and amino groups. The NCNBs obtained by pyrolysis below 800 °C had diameters of approximately 60 nm and gave a good catalytic performance in the ORR. This can be ascribed to the electron-accepting ability of the nitrogen atoms resulting in creation of net positive charges on adjacent carbon atoms, and these readily attract electrons. The morphology of the prepared NCNBs was studied using scanning electron microscopy (SEM). X-ray photoelectron spectroscopy (XPS) was used to identify the surface nitrogen groups. The electrochemical performance of the NCNBs in the ORR was evaluated in detail.

2. Experimental

2.1. Chemicals

Tris was purchased from Sigma. A saturated solution of Tris was prepared using double-distilled water. A 20% Pt/C catalyst was purchased from Aladdin. All other chemicals (analytical grade) were purchased from the Beijing Chemical Reagent Company (Beijing, China) and used without further purification. Ultra-pure water was obtained using a Milli-Q plus water purification system (18 MW, Milli-pore Co., Ltd., USA).

2.2. Apparatus

SEM images were obtained using a Hitachi S-2600N instrument. Elemental analysis was performed using a Flash EA 1112 instrument. XPS was performed using a VG Micro-tech ESCA 2000 instrument with a monochromatic 15 Al X-ray source. Fourier-transform infrared (FTIR) spectroscopy was performed using an EQUINOX 55 instrument (Bruker, Germany). Electrochemical measurements were performed using a computer-controlled electrochemical analyzer (CHI600E, Chenhua, China) in a two-compartment electrochemical cell with a bare or modified glassy carbon electrode (GCE, diameter 3 mm) and a rotating ring disk electrode (RRDE; PINE) of diameter 4 mm as the working electrode. The geometric area of the RRDE was 0.1256 cm^2 . Pt wire was used as the counter electrode, and the reference electrode was Ag/AgCl (3 mol/L-KCl).

2.3. NCNB preparation

A saturated solution of Tris was placed in a quartz-tube reactor and dried overnight at 70 °C. The quartz-tube reactor was transferred to a tube furnace and pyrolyzed in a vacuum at 700, 800, or 900 °C for 2 h, to prepare different NCNBs, denoted by NCNBs-700, NCNBs-800, and NCNBs-900, respectively.

2.4. Electrochemical characteristics

A GCE of diameter 3 mm and geometric area 0.07065 cm^2 was used as the working electrode. The GCE was polished with 1.0, 0.3, and 0.05 μm alumina slurries, and then washed with ultraclean water and ethanol, respectively, to form a mirror-like surface. NCNBs (6 mg) were ultrasonically dispersed in dimethylformamide (DMF, 1 mL). The prepared ink solution (5 μL) was dropped onto the GCE. The working electrode was prepared as follows. The NCNB suspension (5 μL , 6 mg/mL in DMF) was dropped onto the GCE surface, and exposed to air to evaporate the solvent. The electrode surface was covered with Nafion solution (5 μL , 0.5%, 5 diluted 10 times with deionized water) and dried to form a modified working electrode. The electrode was rinsed thoroughly with deionized water to remove physically adsorbed materials to give an NCNBs/GCE. The modified working electrodes were used to study ORR activity.

All electrochemical experiments were performed at room temperature. The NCNBs/GCE was pretreated by electrochem-

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