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High content of pyridinic- and pyrrolic-nitrogen-modified carbon nanotubes derived from blood biomass for the electrocatalysis of oxygen reduction reaction in alkaline medium

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ABSTRACT

Here we present a facile synthetic route to design nitrogen-doped nanostructured carbon-based electrocatalyst for oxygen reduction reaction (ORR) by the copyrolysis of blood biomass from pig and carbon nanotubes (CNTs) at high temperatures. The nitrogen-doped CNTs obtained at 800 °C not only results in excellent ORR activity with four-electron transfer selectivity in alkaline medium, but also exhibits superior methanol-tolerant property and long-term stability. It is confirmed that high-temperature pyrolysis processes can facilitate to produce higher contents of pyridinic- and pyrrolic-N binding groups in electrocatalysts, contributing to the enhancement of ORR performance in terms of onset potential, half-wave potential, and limited current density. We also propose that the planar-N configuration may be the active site that is responsible for the improved ORR electrocatalytic performance. The straight-forward and cheap synthesis of the active and stable electrocatalyst makes it a promising candidate for electrochemical power sources such as fuel cells or metal-air batteries.

1. Introduction

In light of increasing challenges in energy and climate change, the pursuit of "green" energy sources becomes ever more urgent. Possibly the optimal choice among alternative energy sources is the fuel cell, which converts chemical energy directly into electrical energy with the advantages of high efficiency and low emission of pollutants [1]. The types of fuel cells under development include metal-air batteries (MABs), alkaline fuel cells (AFCs), phosphoric-acid fuel cells (PAFCs), polymeric-electrolyte-membrane fuel cells (PEMFCs) and so on [2]. General performance of these fuel cells is directly controlled by ORR at the cathode side. Core to solve this problem is to effectively accelerate the ORR rate. In the past decades, various electrode materials have been used as cathodic ORR electrocatalysts in acidic and alkaline environments. In addition to traditional platinum/carbon catalysts, many nitrogen-doped carbon materials have received tremendous attention, which exhibited reasonable ORR electrocatalytic activity and long-term stability, in particular nitrogen-doped graphenes(N-GP) and nitrogen-doped carbon nanotubes (N-CNTs) [3–7]. Interestingly, the synthesis of these materials can be derived from several biological proteins, such as peptides [8], hemoglobin [9] and collagen [10]. In recent years, approaches have included the study of oxygen reduction reaction behavior in many nitrogen-doped electrocatalysts utilizing N-enriched amino acids as the N sources or metal macrocyclic complexes contained

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inside hemin biomaterials as effective precursors [11–15]. Although they have superior ORR performance, their stability still can't meet the requirements for practical application in renewable energy. It is also reported that Me-N active sites inside the carbon structure plays a key role in catalytic properties [16]. However, the elusive configuration, toxic and corrosive nature, complex procedures and expensive equipment restrict the application of N-doped carbon materials [5]. Exploration of new method for the synthesis of nitrogen-doped electrocatalysts for replacing traditional Pt-based catalysts has remained vital.

Animal blood biomass which contains large amounts of various biological proteins (e.g, hemoglobin and myoglobin) and N-rich amino acids, is an abundant, cheap and renewable source of energy. However, utilizing it in a cost-effective way still remains a difficult challenge. Pyrolysis of biomass is recognized as a feasible and efficient process to selectively produce novel nitrogen-doped electrocatalyst. Several previous researches have proved the superiority in direct fabrication of non-precious-metal catalysts [17–22]. Notably, blood protein contained from animals in meat industry has raised concern in recent years. Blood protein is the major constituent of boiled pig blood except water, which is normally discarded as waste. It is known that blood protein includes an abundance of hemoglobin and various amino acids. Hemoglobin has been reported to successfully produce active electrocatalysts for ORR in acidic and alkaline environments in previous research [23]. Thus, BP material could be a certainly promising precursor and nitrogen source for preparing highly active electrocatalysts for ORR.

However, there is no systematic method on the pyrolysis of blood proteins instantly. Maruyama et al. [24] reported the two-step carbonization process of hemoglobin from bovine blood in 2008. The substance prepared in the first heat-treatment step was designated as a precursor for the catalyst. Recently, it has been recognized that the substance obtained by thermal treatment of a polymer material at certain temperature is an intermediate between the polymer and carbon material because of its incomplete carbonaceous phase generation and could be called a pyropolymer [24]. Several investigations have been done to exploit the characteristics of the pyropolymer [25,26]. Blood pyropolymer is confirmed to be an effective precursor of ORR catalyst in alkaline solution [26]. Furthermore, the active centers inside the pyropolymer could be promoted by an increase in the pyrolysis temperature, resulting in the enhancement of the ORR activity. In addition, the internal carbon structure of pyropolymers is independent of the phase change, reported in our previous research [26]. Herein, we named the pyropolymer obtained from blood powder (BP) by carbonization process at 350 °C as BP350 for convenience. BP350 is an intermediate between the polymer and carbon material because of its incomplete carbonaceous phase generation. Its effective electrochemical property was further studied via a series of electrochemical measurements.

We prepare nitrogen doped electrocatalysts for oxygen reduction from the co-pyrolysis of BP350 and carbon nanotubes at high temperatures. It showed that catalyst with a higher percentage of planar-N substantially enhances the ORR activity, implying the active role planar-N acts in ORR electrocatalysis. Our study can encourage researchers to exploit new N-doped materials for ORR catalysis by using animal biomass as the nitrogen source of active center structures.

2. Experiments

2.1. Materials

Blood powder from pig was supplied by the Food Testing Center of Chongqing Bureau of Quality and Technology Supervision. Single-walled carbon nanotubes (CNTs) were purchased from Beijing DK nano technology Co.Ltd. China.

2.2. Preparation of N-doped CNTs

First, 0.5 g of BP was decomposed in flowing N_2 at 350 °C for 5 h. The produced BP350 pyropolymer as nitrogen precursor was mixed with CNTs (mass ratio of 1:1) by the ball-milling method. The obtained sample was further pyrolyzed in flowing N_2 at 800 °C for 2 h to form N-doped CNTs, which is hereafter called N-CNT(800). As a control, the pyrolysis of the sample was conducted at 700 °C, 900 °C, and 1000 °C for 2 h and the resulting samples were named N-CNT(700), N-CNT(900), and N-CNT (1000), respectively.

2.3. Physical characterization

X-ray photoelectron spectroscopy (XPS) analysis was carried out using a VG Scientific ESCALAB 220 iXL spectrometer with an Al Kα ($h\nu = 1486.69$ eV) X-ray source. The Raman spectra were recorded with a Renishaw inVia unit using the Ar ion laser with an excitation wavelength of 514.5 nm.

2.4. Electrochemical measurements

Electrochemical experiments were conducted on a CHI 600A electrochemical workstation (CH instruments, USA). An Hg/HgO/1 mol l^{-1} KOH electrode and a platinum wire were used as the reference and counter electrode, respectively. A rotation disk electrode (RDE) with a glassy carbon (GC) electrode (5-mm diameter, LKXZ-1, Tianjing Lanlike Electrochemical Instruments, China) was used as the working electrode. The modified-GC working electrode was prepared by coating it with catalyst ink. Typically, 10 μl of catalyst ink, well-disperse of 0.5 wt.% Nafion solution, was dropped onto the GCE surface and then dried at room temperature. The mass loading of all samples is equal to ca.50 $\mu g\, cm^{-2}$. All voltammetric experiments for ORR were performed over the potential range of 1.17 V to 0.17 V at a scan rate of 5 mV s^{-1} in O_2-saturated 0.1 mol l^{-1} KOH solution. The onset potentials (the potential at which a current density of $-50\ \mu A\, cm^{-2}$ is recorded) were taken from the ORR polarization curves. The stability of N-CNT(800) was evaluated using an accelerated aging test (AAT), which used 10000 continuous potential cycles performed by cyclic scanning between 1.17 V and 0.17 V at a scan rate of 5 mV s^{-1} in 0.1 mol l^{-1} KOH solution purged with O_2. Besides, the methanol-tolerant property of N-CNT(800) was measured in 0.1 mol l^{-1} KOH solution containing 5 mol l^{-1} methanol. All the electrode potentials in this work are quoted *versus* a reversible hydrogen electrode (RHE).

3. Results and discussion

3.1. Structural and surface characteristics

Fig. 1a shows the XP spectra of four N-CNTs. The presence of N1s peak has been clearly observed, suggesting N atoms were incorporated into the graphite structure of the prepared samples, which was adequately confirmed by analyzing the C1s peak of the samples.

Fig. 1b displays the XP spectrum for the C1s region for N-CNT (800). The C1s peak at 284.6, 285.9, 287.5 and 290.5 eV could be assigned to graphitic carbon (sp^2 C=C), amorphous carbon (sp^3 C—C), sp^2 carbon atoms bonded to nitrogen (C—N) and sp^2 carbon atoms bonded to oxygen (O—C=O), with relative proportions of 77.9%, 10.2%, 7.2% and 4.7%, respectively. The percentage of C—N binding in N-CNT(800) is higher than that of C—N binding in other