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Nitrogen-doped micropore-dominant carbon derived from waste pine cone as a promising metal-free electrocatalyst for aqueous zinc/air batteries

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HIGHLIGHTS

- A microporous and effective catalyst was synthesized based on waste biomass.
- The as-prepared N-PPC-900 possesses higher onset potential over Pt/C.
- The N-PPC-900 exhibit excellent performance in ORR and zinc/air batteries.

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ABSTRACT

The exploitation for highly effective and low-cost metal-free catalysts with facile and environmental friendly method for oxygen reduction reaction is still a great challenge. To find an effective method for catalyst synthesis, in this manuscript, waste biomass pine cone is employed as raw material and nitrogen-doped micropore-dominant carbon material with excellent ORR catalytic activity is successfully synthesized. The as-prepared N-doped micropore-dominant carbon possesses a high surface area of 1556 $m^2 g^{-1}$. In addition, this carbon electrocatalyst loaded electrode exhibits a high discharge voltage 1.07 V at the current density of 50 mA cm^{-2}, which can be ascribed to the rich micropores and high content of pyridinic N of the prepared carbon, indicative of great potential in the application of zinc/air batteries.

1. Introduction

Developing high-power density, safe and environmentally friendly energy storage devices has attracted a keen interest of researchers due to the increasingly serious environmental pollution and the limited reserves of fossil fuels [1,2]. Aqueous metal/air batteries, as highly efficient and clean energy storage devices, are of great significance to meet the challenge of future energy shortage [3,4]. The sluggish rate of oxygen reduction reaction (ORR) happening on the cathode of fuel cells and metal/air batteries becomes one of the key factors to limit the application of these two kinds of batteries [5]. Due to the high cost and low reserves of precious metal, developing a non-precious electrocatalyst as candidate of Pt-based electrocatalysts is in urgent demand. The relatively high cost and underlying environmental problems restrict the progress of metal-based electrocatalysts [6]. Carbon material, as a kind of metal-free catalyst, comes to be an ideal catalyst because of its good stability, high conductivity and environmental friendliness [7]. In the previous reports, carbon materials which are totally free of metals are developed. Most of them are nitrogen-doped carbon such as N-doped nanocarbon materials (carbon nanotube [8], graphene [9] and hierarchical porous carbon materials [10]). To date, it is in urgent demand but still a great challenge to exploit metal-free carbon catalysts with low cost, nontoxicity and especially highly efficient electrocatalytic activity.

Generally, carbon materials with abundant active sites were

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called for highly effective electrocatalyst. In order to enrich the active sites of carbon, several aspects should be noticed: (1) large surface area is required; (2) high conductivity is in demand. Moreover, porous structure with ample nanopores is considered to be efficient in accelerating the oxygen transfer process and facilitating the formation of active sites. In previous research, the fabrications of nanopores in carbon matrix were often achieved by various templates and some pore formers. The addition of templates and pore formers usually need acid-etching to remove the impurities for the carbon material. This makes the synthetic process time-consuming and high-cost. In order to find effective and low-cost method to synthesize nanoporous carbon, several efforts have been made. Waste biomass is optimal as carbon precursor to fabricate nanopores due to its special structure to transport water and nutrition. Therefore, the nanoporous carbon materials can be acquired by using waste biomass as raw material.

Recently, heteroatoms-doping is effective in improving the active sites of carbon materials. Typically, nitrogen-doped carbon materials have been proved to be potential candidate for Pt-based catalysts because of its high catalytic activity and good stability [11]. Carbon material derived from waste biomass attracts enormous attention from researchers due to the sustainable resources and its capability of high-scale production. Based on this, biomass-induced N-doped porous carbon materials come to be a prior choice for superior electrocatalyst. There exist some progresses made by researchers which employ amaranthus [12], coconut shell [13] and typha orientalis [14] and pomelo peel [15] as raw materials to prepare active catalysts for ORR. The original structure of biomasses contain abundant hydrophilic oxygen-rich functional groups and nutrient transport channel which may lead to effect N doping and rich pores. Therefore, the different results with different sources of biomass are often based on the contents and structures of various biomasses, which may lead to different N doping efficiency and pore structures. And the highly effective N doping, high surface area and suitable pore structures are often called for highly active electrocatalysts. As a result, these studies further highlight the considerable significance of waste biomass in the exploitation of metal-free carbon catalysts. These waste biomass-derived carbon materials exhibited comparable electrocatalytic activity as with Pt/C. To further improve the electrocatalytic activity of these biomass-based carbons, maybe the synthesis process need to be optimized. However, the application in aqueous metal/air batteries of these materials has not been investigated.

Transforming biomass into carbon materials with suitable nanopores turns to be a great challenge to satisfy the demand of electrocatalyst for ORR. *Pine tree* is one of the most important economic tree species because of their wood all over the world. Pine trees are widely distributed in most areas in China, and a large amount of pine cone is collected as waste biomass. Compared with other biomass, pincone possesses many advantages such as high content of lignin, special structure and low cost [16] which make it become an ideal precursor for high-performance metal-free carbon catalyst.

Here, a low-cost and micropore-rich N-doped carbon material was obtained from pine cone by a readily scalable approach combined with low-temperature precarbonization and post-treatment in ammonia gas (NH_3). This pinecone derived N-doped carbon material with large surface area, plentiful and uniform micropores exhibits excellent electrocatalytic activity, relatively much better stability and a much higher catalytic selectivity resisting the methanol electrooxidation over Pt/C, which proposed much better performance compared with other biomass-derived carbon catalysts. While the pine cone is a kind of waste biomass with rich lignin, similar with coconut shell, after the reported approach method in this manuscript, the as-prepared N-PPC-900 exhibits satisfactory ORR activity. This fact further shows the priority of this synthesis method for carbon catalyst. When it is employed as cathode catalyst for aqueous zinc/air batteries, the N-PPC-900 loaded zinc/air batteries also possess commendable performance.

2. Experimental section

2.1. Materials preparation

2.1.1. Preparation of PPC

Pine cones were collected and cut up into small pieces. Then these pine cone pieces were dried at 80 °C for 12 h. After that, the dried pine cone pieces were pre-carbonized at 400 °C in Ar atmosphere for 2 h with a heating rate of 5 °C min^{-1} to form initial pine cone carbon (IPPC). To further reduce the size of IPPC, the ball milling treatment with a milling rate of 400 rpm was carried out and maintained for about an hour.

To obtain the pinecone-derived porous carbon (PPC), the resultant pre-carbonized pinecone carbon was washed with 5 M HCl, and the washed carbon sample was followed by freeze-drying.

2.1.2. Preparation of N-PPC

The PPC sample was further modified by heating under NH_3 atmosphere for 2 h at 800, 900, 1000 °C with a heating rate of 5 °C min^{-1}, which can be labeled as N-PPC-800, N-PPC-900 and N-PPC-1000. The undoped sample PPC-900 was synthesized as comparison at 900 °C under Ar atmosphere.

2.2. Physicochemical characterization of materials

The microstructure of the carbon product was detected using a scanning electron microscopy (SEM, JSM-6360LV) and transmission electronmicroscopy (TEM, Tecnai G2 20ST). N_2 adsorption/desorption measurements were carried out using a Quantachrome instrument (Quabrasorb SI-3MP). In order to obtain the porous structure of the as-prepared carbon, the Brunauere Emmette Teller (BET) method was adopted to estimate the surface area and the pore size was summarized by the desorption branch using the Barrette Joynere Halenda (BJH) method. Raman spectra were executed using a laser Raman spectrometer (LabRAM HR800, JY) to get the carbon structure. The chemical states of the elements in carbon material were characterized by X-ray photoelectron spectroscopy (XPS, ESCA LAB 250Xi).

2.3. Electrochemical characterization of materials

For purpose of evaluating the electrocatalytic activity of the as-prepared carbon materials, the catalyst ink was firstly obtained by dispersing 8 mg carbon product into 2 mL ethanol/deionized water (vol:1/1) mixed solvent. The catalyst-loaded work electrode was fabricated by coating 5 μL catalyst ink was coated on the surface of glassy carbon rotating disk electrode (RDE). The Ag/AgCl electrode was employed as reference electrode and Pt spiral electrode was used as counter electrode. All these electrocatalytic properties were measured in 0.1 M KOH solution. In Fig. S1, the experiment employing Hg/HgO as reference electrode was also conducted, whose result shows nearly no difference compared with that of Ag/AgCl. So it is noted that, these results prove that Ag/AgCl electrode is also appropriate in 0.1 M KOH solution. So the measured results are reliable. The linear sweep voltammetry (LSV) curves were obtained in the scan range of 0.2 V to −1.0 V with a scan rate of 5 mV s^{-1}. And the cyclic voltammetry data were collected in the same range with LSV measurements while using a scan rate of 50 mV s^{-1}.