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A biomass derived nitrogen doped carbon fibers as efficient catalysts for the oxygen reduction reaction

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A B S T R A C T

Nitrogen doped carbon nanomaterials are excellent electrode materials and catalysts due to their extraordinary conductivity, prolific structures, and abundant active sites. Herein, two kinds of waste biomass, catkins and Okara were used as precursors for the preparation of novel nitrogen doped carbon fibers via hydrothermal and pyrolysis process. The blend of nitrogen-rich Okara with catkins effectively enhanced the content of doped nitrogen in the product. The as-prepared sample (denoted as NCF900) exhibited a hollow fiber like structure with a diameter of 2 to 5 μm and had abundant highly active sites of pyridinic N and graphitic N, thereby improving its electrocatalytic activity in oxygen reduction reaction (ORR). The typical rotating disk electrode test proved that the NCF900 exhibited a high onset potential (0.82 V vs RHE) and a nearly four-electron pathway for ORR in alkaline solution as well as stronger methanol tolerance and better long-term durability than commercial Pt/C. The green, low cost synthetic method and the excellent ORR catalytic efficiency of NCF900 made it a promising electrocatalytic material for the ORR in fuel cells.

1. Introduction

The high use of the traditional fossil-fuel energy accelerates the development of global warming and many environmental problems [1]. With the development of the renewable energy, proton exchange membrane fuel cells (PEMFCs) are considered as a promising energy conversion technology [2]. For PEMFCs, efficient electrocatalysts have been extensively explored and are still highly desired owing to the inherent sluggish kinetics and high overpotential of the oxygen reduction reaction (ORR) at the cathode [3,4]. Nowadays, the platinum-based catalysts have been commercially applied as candidates for ORR, but they suffer from high cost, low reserves, and methanol intolerance [5,6]. Metal-free carbon materials doped with some heteroatoms (such as N, B, P, S, and I) have been considered as the most promising ORR catalyst in replacement of Pt-based catalysts [7–15]. Among these materials, N-doped carbon materials have been demonstrated to have a high ORR activity in alkaline media, comparable to Pt-based catalysts [16]. Moreover, the ideal carbon nanoarchitectures for the ORR are supposed to possess the features of abundant surface active sites, high conductivity, and fast mass transport channels. Recently, carbon fibers have been widely reported because of their unique chemical, electrical, magnetic, and mechanical properties [17–19]. Hollow carbon fibers with porous structures and larger specific surfaces are promising for structuring efficient ORR electrochemical catalysts [20].

The sustainable conversion of biomass into highly valuable carbon materials has recently attracted increasing attention [21]. Carbon materials derived from biomass have been explored for preparing none metal based ORR catalysts, such as bamboo fungus [22], cellulose fibers [23], pomelo peel [24] and *Typha orientalis* [25]. These biomass materials are extensively available, accessible and recyclable. Moreover, these products after simple pyrolysis could possess considerable electrocatalytic activities for the ORR. As seeds of willows and poplars, large quantities of catkins could be produced by willows in spring, which are available free of cost and even considered to be environmental pollutants in many areas. Catkins consist of a slender axis with many unisexual apetalous flowers along its sides. The white villiform flowers of catkins are natural nanotubes with the main component of cellulose [26]. Owing to their component and natural nanostructure, catkins may directly serve as the precursor to prepare hollow carbon fibers just by the simple carbonization procedure without using any template. Thus, our interest focused at developing N doped carbon fibers with high N active site density and excellent ORR electro-catalytic

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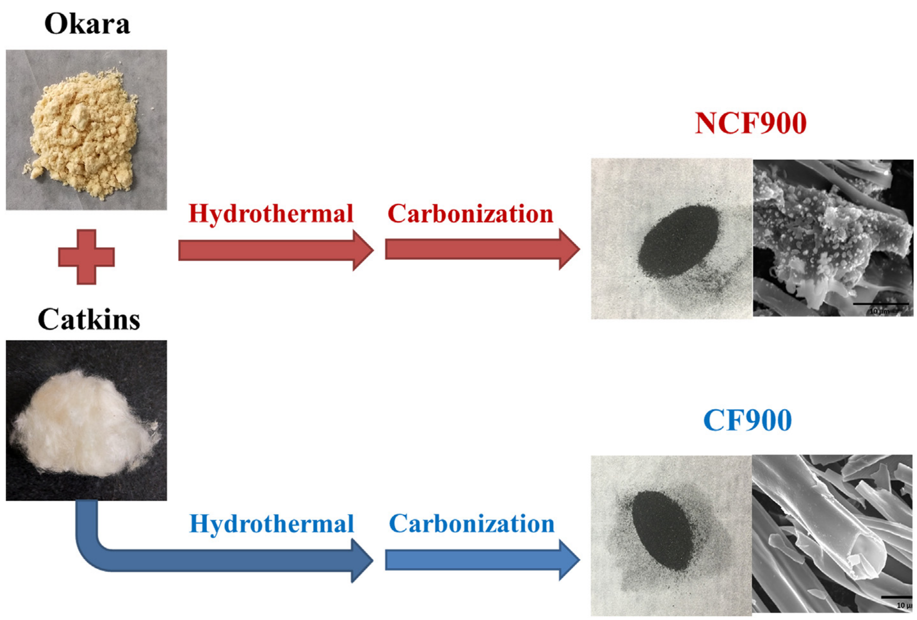

Scheme 1. Illustration of the preparation procedures for the NCF900 samples.

activity from the abundant catkins. Since nitrogen content of catkins is in relatively low level, another nitrogen-rich biomass need to be introduced as nitrogen source. Okara is the byproduct from the production process of the soybean oil and soy milk. Billions tons of Okara waste have been produced every year and most of them were incinerated directly, which resulted in increasing environmental problems. Dried Okara is rich in nitrogen content, whose major composition is crude protein (34.3%), crude fat (11.8%), crude fiber (6.7%), and total ash (3.6%) [27]. Okara is a promising candidate as nitrogen source for the synthesis of N-doped carbon nanomaterials [28].

Herein, we report a simple and low-cost approach to synthesize nitrogen doped hollow carbon fibers (denoted as NCF900) derived from plant biomass. Catkins and Okara were used as precursors and treated with a hydrothermal process followed by a pyrolysis, which is shown in Scheme 1. During the synthesis process, renewable catkins were used as carbon source and self-template, while N-rich Okara were used as nitrogen source. The as-prepared carbon nanomaterials possessed a hollow tube-like structure with large amounts of nitrogen active sites which was benefit to the promotion of the ORR catalytic performance. This work would open up a sustainable avenue to produce promising ORR electrocatalysts by using biomass.

2. Experiment section

2.1. Chemicals and materials

The catkins were collected in Nanjing, China. The soybean was brought from the Beidahuang Co., Ltd. through the JD.com. Ultrapure Water (18.2 MΩ cm) was acquired from a Smart2 water purification system (Thermal, USA). Unless otherwise specified, all chemicals and solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. or Aladdin Chemistry Co., Ltd. and were of analytical reagents and used without further purification.

2.2. Apparatus

The morphologies of the as-prepared materials were studied by using a field-emission scanning electron microscope (SEM, Nova NanoSEM 450, FEI, USA). Energy dispersive X-ray spectra (EDS) were taken on a field-emission scanning electron microscope (SEM, Nova NanoSEM 450, FEI, USA). Transmission electron microscopy (TEM) was recorded on JEM-2100 transmission electron microscopy (JEOL, Japan). X-ray photoelectron spectroscopy (XPS) were performed by a PHI5000 VersaProbe (Ulvac-Phi, Japan) system with a monochromic Mg-Ka radiation. X-ray diffraction (XRD) were performed on a D8 (Advance, Bruker, Germany) and the data were collected in the 2θ range of 10–70° at a step size of 0.02°. Raman spectra were carried out on an XploRA PLUS laser Raman microscope (λ = 532 nm, HORIBA JOBIN YVON, France). Thermogravimetric analysis (TGA) was performed on the TG209 F3 thermal analyser (Netzsch, Germany) in a N_2 atmosphere at a heating rate of 20 °C min^{-1} with temperature ranging from 35 to 1000 °C. The surface area was calculated by Brunauer-Emmett-Teller (BET) method according to nitrogen adsorption-desorption isotherms conducted on a NoveWin 1000e instrument (Quantachrome, USA).

2.3. Preparation of N-doped carbon fibers from catkins and Okara

The catkins were successively washed by distilled water, hydrochloric acid (1 mol L^{-1}) and distilled water. Then they were dried at 80 °C for 3 days. The Okara were ground to powder and dried at 80 °C for 3 days. The thoroughly dried catkins (0.5 g), Okara (0.5 g) and distilled water were added into a Telfon lined stainless autoclave. The autoclave was kept at 120 °C for 5 h and cooled to room temperature naturally. Then, the product was annealed in a quartz tube under the protection of nitrogen atmosphere at a heating rate of 1 °C min^{-1} to different carbonization temperature of 700 °C, 800 °C and 900 °C for 3 h, respectively. The collected products were denoted as NCF700, NCF800 and NCF900.

As controls, catkin derived carbon fiber samples without Okara as nitrogen source at the annealing temperature of 900 °C were prepared in a similar way. The obtained sample was named as CF900. Okara derived Nitrogen doped carbon nanosheets with only Okara as precursor at the annealing temperature of 900 °C were also prepared in a similar way. The obtained sample was denoted as NCNS900.

2.4. Electrochemical characterization

All of the electrochemical measurements for ORR tests were performed on a standard three-electrode system on CHI700E workstation (CH Instruments, USA). Pt wire was used as the counter electrode and commercially Ag/AgCl (saturated KCl, E(RHE) = 0.196 + E(Ag/