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Nitrogen-Doped Porous Carbon Derived from Malachium Aquaticum Biomass as a Highly Efficient Electrocatalyst for Oxygen Reduction Reaction

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ABSTRACT

In this work, N-doped porous carbon materials are synthesized from natural biomass (malachium aquaticum). The as-prepared sample with high Brunauer-Emmett-Teller surface area (851.41 $m^2 g^{-1}$) possesses excellent oxygen reduction reaction (ORR) performance. Its onset potential is higher (about 10 mV) than that of Pt/C, and more interestingly, the current density is almost double that of Pt/C. Besides, the tolerance to methanol and stability of the as-prepared sample is also superior to those of Pt/C. The excellent performance is probably due to the balance of 3D structure, rich active sites, superior electrical conductivity, especially the superhydrophilicity, which originates from the roughness and hydrophilic functional groups on the surface and facilitates the deep wetting by the electrolyte into the micro/nano-scale pores, and enables more oxygen have the opportunity to contact the catalyst. Our study further rationalizes such method to prepare functional carbon materials using environmental biomass waste as precursors with practical applications in electrochemistry.

1. Introduction

Due to the world energy crisis and environmental problems, fuel cells have drawn increasing interest for their high power density and low emission of pollutants. However, the performance of fuel cells is being hampered by the high oxygen reduction reaction (ORR) overpotential in cathode. Generally speaking, Pt and Pt-based electrocatalysts for the four-electron ORR in alkaline fuel cells are regarded as the best catalysts since 1960s because of their relatively low overpotential, excellent stability, and high current density [1]. Apart from the high cost of Pt, the large-scale production and commercial operation of fuel cells still suffer from CO poisoning and low tolerance to methanol of the Pt and Pt-based materials [2,3]. Consequently, considerable efforts have been made to explore cost-effective catalysts to replace the scarce and expensive Pt and Pt-based electrocatalysts for ORR.

In the 1960s it was found that Co-phthalocyanines exhibits eminent performance for ORR [4]. Since then non-noble metal and metallic compound as efficient ORR catalysts were developed, but they still suffer from insufficient activity, which possibly comes from the strong bond between the metal active sites and intermediate product (OOH^*/OH^*), along with the hampered performance by the poor electronic conductivity [5,6]. After Dai's report portraying nitrogen-containing carbon nanotubes as oxygen reduction catalyst [7], carbon materials doped by nitrogen, sulfur, boron, or phosphorus etc. have attracted intensive research as promising metal-free ORR electrocatalysts [8–11]. As a result, thiourea, dicyandiamide, urea and phytic acid etc have been used as precursors to synthesize heteroatom-doped (especially N-doped) carbon nanomaterials [12–15]. However, the complex synthesis procedure and toxic raw materials seriously hinder the large-scale production. Therefore, it is eagerly expected to develop highly cost-effective N-doped carbon catalysts with excellent ORR properties by using non-toxic and simpler procedures. Keep this in mind, we focus on the nature which supplies a nearly limitless resource for the preparation of new materials with excellent properties and novel structures [16,17]. Malachium aquaticum is widely distributed in the northern and southern China, which has the effect on hypertension and pneumonia as chinese medicine. In most cases, malachium aquaticum is known as malignant weed in the field, most of them are thrown away as cast off during processing, and only a small minority are used as fodder owing to that each hectogram wet sample contains 3.6 g of protein and 1.2 g of cellulose. Herein we chose malachium aquaticum as precursor to

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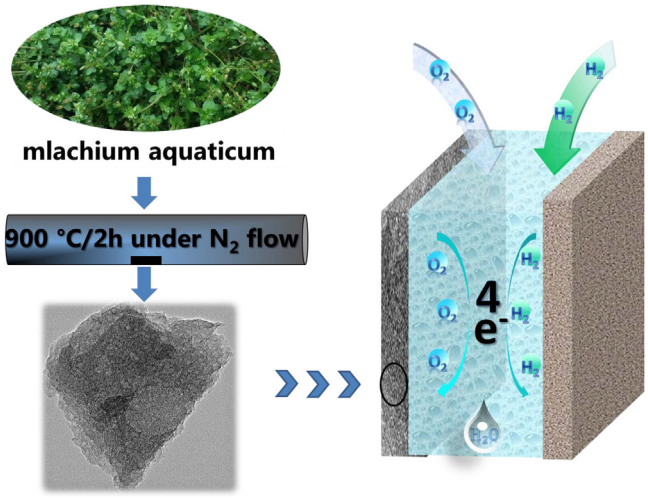
synthesize efficient N-doped electrocatalyst for ORR because of its high protein/cellulose mass ratio and high molar weight of protein and cellulose, which will prevent carbon frame vaporization at high temperatures. On the other hand, the use of biowaste (malachium aquaticum) as a cheap raw material to synthesize ORR catalysts makes large-scale commercialized production possible.

In this report, malachium aquaticum was used to prepare N-doped porous carbon named as MA-900 by air-drying and pyrolysis at 900 °C in nitrogen (Scheme 1). The as-prepared N-doped porous carbon materials possess 3D porous structure and high Brunauer-Emmett-Teller (BET) surface area (851.41 $m^2 g^{-1}$). The MA-900 shows decent electrocatalytic activity for ORR, and the overpotential is just 10 mV negative compared with that of Pt/C, the current density is 1.30 mA cm^{-2}, almost double that of Pt/C, 0.69 mA cm^{-2}. In addition, the tolerance to methanol crossover and durability of MA-900 are superior to those of Pt/C. Its performance should be attributed to the balance of superhydrophilicity, 3D structure, type of active sites, and superior electrical conductivity of the as-prepared sample. Especially the superhydrophilicity caused by the roughness and functional groups on the surface of MA-900 plays a significant impact on ORR performance, because superhydrophilicity can promote deep wetting by the electrolyte into the micro-scale pores, which enables more oxygen have the opportunity to contact the catalyst. At the same time, oxygen-containing functional groups on the surface have a significant impact on the adsorption of O_2, while the doped N atoms could change the charge density on the electrocatalyst and decrease the O-O dissociation energy barrier to improve the ORR performance [18], which is regarded as the rate-limiting step during the oxygen reduction [19].

2. Experimental sections

2.1. Materials

The malachium aquaticum was gathered from experimental field in Henan Normal University and used as precursor. Potassium hydroxide (KOH) was purchased from Tianli Chemical Reagent Co., Ltd. Hydrochloric acid (HCl) was purchased from Shuangshuang Chemical Co., Ltd. Deionized water was used throughout the experiments and all chemicals were of analytical grade and used as received.



Scheme 1. Schematic illustration for the fabrication of N-doped porous carbon from malachium aquaticum.

2.2. Materials synthesis

To synthesize the catalysts, the biomass mlachium aquaticum was washed with distilled water several times and then dried at 40 °C overnight. The dried biomass, which was cut into small pieces, was pyrolyzed in a tubular furnace at 900 °C for 2 h in N_2 atmosphere. Then, the carbonized material was washed by 2 mol L^{-1} HCl at 40 °C for 24 h to remove metal residue and inactive species, followed by thoroughly washing with distilled water until pH = 7. The final product was dried at 40 °C for 24 h under vacuum and named as MA-900. The other samples were pyrolyzed at 700 °C, 800 °C and 1000 °C and named as MA-700, MA-800, MA-1000.

2.3. Structural characterization

The morphologies of the samples were examined using high resolution transmission electron microscope (HRTEM), and field-emission scanning electron microscopy (FESEM, Zeiss Supra 40, 5 KV). The surface elemental analysis of the samples was performed by X-ray photoelectron spectroscopy (XPS) with monochromatic Al-Kα radiation (300.0 eV). X-ray diffraction (XRD) patterns were recorded on a XRD diffractometer (Bruker D8) with Cu-Kα radiation (λ = 0.154 nm). Raman spectrum was collected on a Raman spectroscopy (Renishaw, 514 nm excitation laser). The nitrogen adsorption/desorption was performed at liquid nitrogen temperature (−196.15 °C) using a Micromeritics ASAP-2020. Before measurements, the samples were outgassed at 350 °C for 3 h. The specific surface areas of all samples were obtained by employing BET, whereas pore-size distribution was derived by using the Barrett-Joyner-Halenda (BJH) method according to the adsorption branch. Fourier transform infrared (FTIR) spectra were collected in the wavenumber range of 400–4000 cm^{-1} on a FTS NEXUS (Thermo Nicolet Co., USA). To measure the wettabilities, a drop of the sample suspension in distilled water was placed on a cleaned slide glass and dried at room temperature to form film. The contact angles (CAs) were obtained with a contact angle meter (KRüSS DSA25) by averaging five measured values on different areas.

2.4. Preparation of working electrodes

Glassy carbon electrodes (GCEs) with diameters of 3 mm and 4 mm, respectively, were polished to a mirror with alpha alumina powder (0.05 and 0.3 μm), followed by sonicating in ultrapure water several times and dried under a gentle N_2 stream. To prepare working electrode, the catalyst ink is formed by sonicating the mixture of catalysts (1 mg), 20 μL of 5% Nafion and 100 μL ultrapure water for 30 min, and then 5 and 10 μL of the well-distributed catalyst suspension were dropped onto the mirror-like GCEs with diameters of 3 mm and 4 mm respectively and dried at room temperature for the following electrochemical measurements. Pt/C (20% Johnson Matthey) catalyst was prepared using the same method for comparison.

2.5. ORR test

ORR activity was tested on CHI 660E electrochemical workstation (CHI Instruments, Shanghai) in a three-electrode system with an Hg/HgO and a piece of Pt foil as reference and counter electrodes respectively, and the modified GCE was used as working electrode. Both cyclic voltammetry (CV) and rotating disk electrode (RDE) were tested in 0.1 mol L^{-1} KOH saturated with O_2 or N_2 at room temperature. The linear sweep voltammograms were recorded under various rotating speeds from 400 to 2025 rpm. Koutechy-