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RAPID COMMUNICATION

Bacterial cellulose derived nitrogen-doped carbon nanofiber aerogel: An efficient metal-free oxygen reduction electrocatalyst for zinc-air battery

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Abstract
The prohibitive cost and scarcity of the platinum-based eletrocatalysts for oxygen reduction reaction (ORR) in fuel cells and metal-air batteries hamper dramatically the commercialization of theses clean-energy technologies. Here, we develop a highly active nitrogen-doped carbon nanofiber (N-CNF) aerogel metal-free ORR electrocatalyst, prepared by direct pyrolysis of a cheap, green, and mass-producible biomass, i.e., bacterial cellulose, followed by NH_3 activation. The N-CNF aerogel inherits the three-dimensional nanofibrous network of bacterial cellulose and meanwhile possess high density of N-containing active sites (5.8 at%) and high BET surface area (916 m^2/g). Such N-CNF aerogel shows superior ORR activity (half-wave potential of 0.80 V versus reversible hydrogen electrode) and high selectivity (electron-transfer number of 3.97 at 0.8 V), and excellent electrochemical stability (only 20 mV negative shift of half-wave potential after 10,000 potential cycles) in alkaline media. The ORR activity of N-CNF aerogel exceeds that of NH_3-treated carbon blacks, carbon nanotubes as well as reduced graphene oxide aerogels, and that of most reported metal-free catalysts. Importantly, when used as a cathode catalyst for constructing the air electrode of Zn-air battery, the N-CNF aerogel exhibits high voltages of 1.34 and 1.25 V at the discharge current densities of 1.0 and 10 mA cm^{-2}, respectively, which are highly comparable with the state-of-the art Pt/C catalyst

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(20 wt% Pt, BASF), indicating the great potential of this metal-free catalyst as a promising alternative to the Pt/C for alkaline fuel cells and metal-air batteries.

Introduction

Electrochemical reduction of oxygen is an important process for many energy conversion and storage technologies, including fuel cells, metal-air batteries, and electrolyzers. Due to the high overpotential caused by the sluggish nature of oxygen reduction reaction (ORR), development of efficient ORR electrocatalysts is crucial for practical applications of these electrochemical devices. Although Pt and Pt-based alloys, up to now, are known as the most efficient catalysts for ORR, the high costs and scarce reserves of Pt significantly hinder its large-scale applications [1,2]. Additional problem associated with Pt is its poor durability during long-term electrochemical process, as Pt-based catalysts suffer from nanoparticle migration, coalescence, and even detaching from support materials in both acidic and alkaline electrolytes [3-5].

Accordingly, substantial efforts have been dedicated to searching for alternative ORR catalysts with low cost, high activity, and long-term durability [6-14]. In particular, recent experimental observations and theoretical calculations both revealed that heteroatoms (e.g., nitrogen or/and phosphorus, boron)-doped carbon materials could serve as efficient metal-free electrocatalysts for ORR as the result of their unique electronic properties, which are derived from the heteroatom-induced charge transfer and delocalization [15-20]. In order to achieve a high ORR performance, it is essential to fabricate carbon-based materials with rationally nanostructural design that would offer a desirable combination of high internal reactive surface area and straightforward transport path leading to such a surface. In this respect, heteroatoms-doped carbon nanotubes [15,21], mesoporous carbon [16-18], and grapheme [22-26] have been developed, some of which exhibited comparable ORR performance with that of commercial Pt/C catalysts in alkaline media [15,17]. Of particular interest, Dai et al. reported vertically aligned nitrogen-doped carbon nanotubes (VA-NCNTs) as ORR electrocatalysts [15]. Besides the electronic effect induced by nitrogen doping, the authors believed that the well-defined geometric features of aligned CNTs provide additional structural benefits in achieving high electrocatalytic performance [15]. Although certainly promising, considering the complex fabrication methods, it remains a question to what extent these materials will affect a real cost reduction when compared to Pt-based catalysts. An inexpensive, green and scalable process is quite desirable to lower the fabrication cost of carbon-based metal-free catalysts for industrial applications.

Herein, we report a new type of metal-free ORR catalysts based on nitrogen-doped carbon nanofiber (N-CNF) aerogels, which are fabricated from bacterial cellulose (BC), a cheap and green biomass that has long been known as the raw material of an indigenous dessert food (*nata-de-coco*) of the South-East Asia. Our recent studies revealed that BC was an excellent precursor for producing highly conductive carbon nanofiber (CNF) aerogels by direct pyrolysis of lyophilized BC under an inert atmosphere [27-29], and heteroatom-doped CNFs for energy storage and conversion [30-32]. In the present study, we demonstrate that the BC-derived CNF aerogels, following nitrogen-doping by annealing them in NH_3, can act as efficient electrocatalysts for ORR. The as-prepared N-CNF aerogels possess a high level of nitrogen doping (N content, 5.8 at%) and high Brunauer-Emmett-Teller surface area (S_{BET} up to 916 m^2/g). It is believed that the three-dimensional (3D) nanofibrous structures of N-CNF aerogels would be favorable for easy molecular/ionic diffusion throughout the highly porous architecture to the reactive surface and facilitate the rapid transport of electrons along the interconnected carbon fibrous networks during electrocatalysis. As a consequence, the ORR activity of the N-CNF aerogels is much higher than that of NH_3-treated carbon blacks, carbon nanotubes, and reduced graphene oxide aerogels. More importantly, as a cathode electrocatalyst for the Zn-air battery, the N-CNF aerogel exhibits highly comparable performance with the state-of-the-art Pt/C catalyst (20 wt%, BASF).

Experimental section

Synthesis of N-CNF aerogels electrocatalysts

Purified BC pellicles with fiber content of ~1% (vol/vol) were kindly provided by Ms CY Zhong (Hainan Yeguo Foods Co., Ltd., Hainan, China). They were produced in an industry-scale by the bacterial strain *Acetobacter xylinum* using a culture of coconut milk and sucrose [33]. The wet BC pellicles were first cut into rectangular shapes with a sharp blade, frozen in liquid nitrogen (-196 °C) and then freeze-dried in a bulk tray dryer (Labconco Corporation, Kansas City, MO, USA) at a sublimating temperature of -50 °C and a pressure of 0.04 mbar. The dried BC aerogels were then pyrolyzed under flowing N_2 at 800 °C to generate black CNF aerogels. Finally, N-CNF aerogel catalysts were obtained by a second heat-treatment of CNF aerogels under an NH_3 atmosphere at 700-900 °C. NH_3 heat-treatment was performed by placing CNF aerogels in a quartz tube under flowing NH_3 with a heating ramp rate of 5 °C/min to desired temperatures and the temperature was kept for 1 h. The heating and cooling steps were performed in a N_2 atmosphere. For comparison, four reference carbon materials, including Vulcan XC-72R (S_{BET}, ca. 240 m^2/g), Ketjenblack EC-300J (S_{BET}, ca. 800 m^2/g), CNTs, and reduced graphene oxide (RGO) aerogels, were also doped with nitrogen by the same NH_3 treatment process. RGO aerogels were prepared by hydrothermal treatment of GO solution (2 mg/mL) at 180 °C for 2 h [34].