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Naturally derived carbon nanofibers as sustainable electrocatalysts for microbial energy harvesting: A new application of spider silk

Lihua Zhou [a], Peng Fu [a], Xixi Cai [b], Shungui Zhou [b], Yong Yuan [b,*]

[a] Institute of Natural Medicine & Green Chemistry, School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China

[b] Guangdong Key Laboratory of Agricultural Environment Pollution Integrated Control, Guangdong Institute of Eco-Environmental and Soil Sciences, Guangzhou 510650, China

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ABSTRACT

Carbon nanofibers (CNFs) have drawn considerable attention as alternative catalysts for the oxygen reduction reaction (ORR). However, their facile, cheap, and environmentally friendly synthesis is still a great challenge. Herein, heteroatom-doped porous CNFs have been fabricated via a simple pyrolysis method using natural spider silk (SS) as a precursor. The prepared CNFs exhibit excellent ORR activity (half-wave potential of 0.85 V and on-set potential of 0.98 V vs RHE), superior to that of the Pt/C catalyst and most reported metal-free carbon catalysts in alkaline conditions. The catalytic proficiency is attributed to abundant electronegative N and S atoms within the carbon lattice, and a high surface area due to their nanofibrillar and porous structure. The prepared CNFs also exhibit excellent ORR activity in neutral solution (pH 7.0), showing potential application as cathode catalysts in microbial fuel cells (MFCs). An MFC equipped with the resulted CNF cathode presents a maximum power density of 1800 mW/m^2, 1.56 times higher than that with a Pt/C cathode. The performance of the resulting CNFs exceed that of other metal-free carbon catalysts in the current state of research on microbial energy harvesting.

1. Introduction

The oxygen reduction reaction (ORR) is one of the crucial reactions in fuel cells and other electrochemical devices, determining their efficiency and performance [1–3]. Electrocatalysts are necessary to accelerate the sluggish kinetics of the ORR. So far, the most efficient catalysts for the ORR are still platinum (Pt)-based materials. However, the widespread utilization of Pt-based catalysts is impractical due to their high costs, the scarcity of platinum and poisoning effects [4,5]. Recently, the incorporation of heteroatoms (i.e., nitrogen, sulfur, phosphorus, and boron) into carbon materials has been extensively investigated to provide alternatives to Pt-based catalysts due to their excellent catalytic activities, low costs, high tolerance to fuel poisoning and long-term stability [6,7]. Most of these studies focused on heteroatom-doped carbon nanotubes and graphene, some of which exhibited a comparable ORR performance to commercial Pt/C catalysts [8,9].

Carbon nanofibers (CNFs), another promising carbonaceous material with a cylindrical shape, have also drawn considerable attention as alternative catalysts for the ORR due to their unique textural and structural features. CNFs fabricated from temperate synthesis and electrospinning have been examined as potential electrocatalysts for the ORR [10,11]. The catalytic activity of CNFs can also be enhanced by heteroatom doping [12,13]. However, the need for relatively expensive, harmful precursors and tedious synthetic procedures are the major disadvantages to the large-scale production of these doped CNF materials. To mitigate these issues, an ideal solution is to achieve doped CNFs from widely available, accessible and recyclable biomass using cost-effective and eco-environmentally friendly methods. In this respect, Liang et al. reported a new type of N-doped CNF catalyst that is fabricated by the direct pyrolysis of bacterial cellulose, followed by N-doping by annealing in NH_3 [14]. However, the resulting N-doped CNFs still displayed lower activity for the ORR compared with the state-of-the-art Pt/C catalysts, and harmful NH_3 gas was needed for the activation.

Spider silk (SS), is a filamentous natural protein fiber (spidroins) made of repeated amino acid pattern that is known as one of the strongest natural materials [15]. Studies on the SS are gen-

* Corresponding author.
E-mail address: yuanyong@soil.gd.cn (Y. Yuan).

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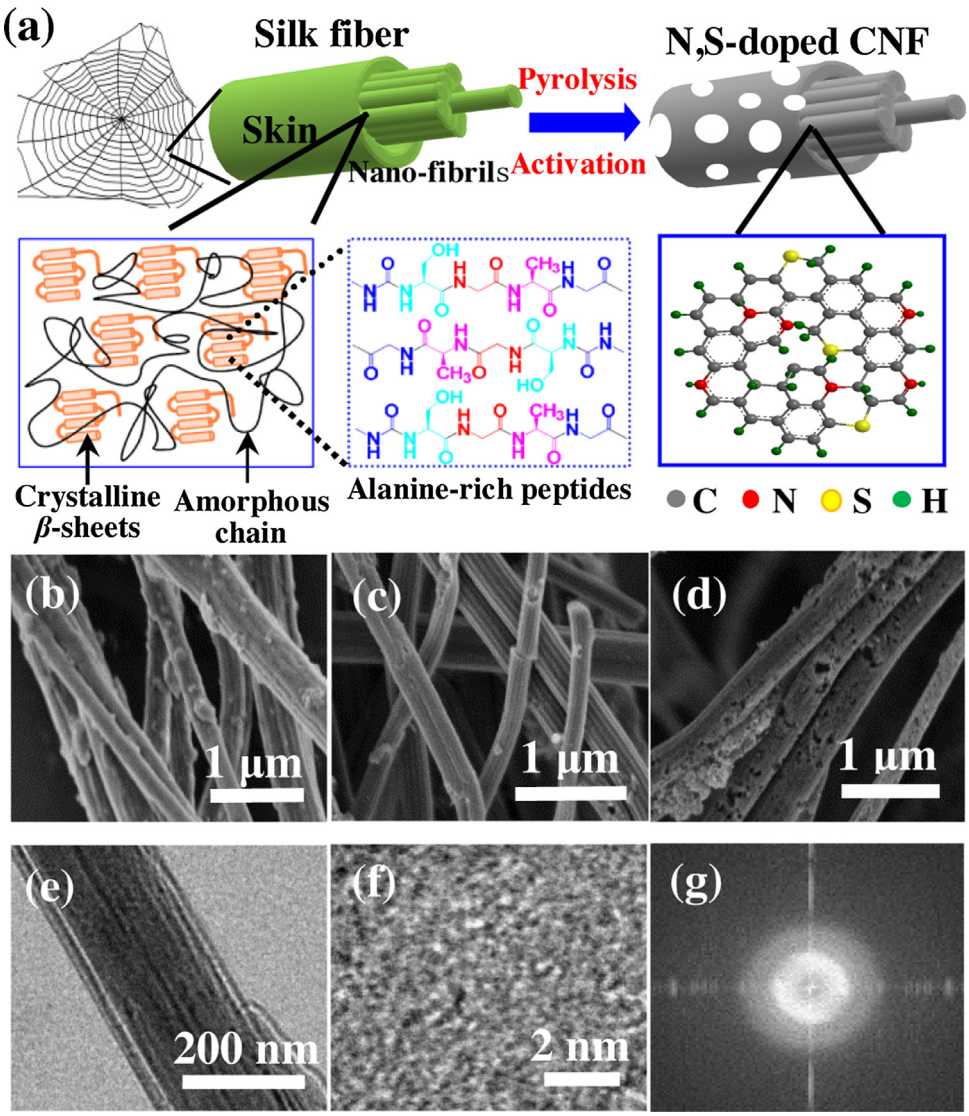

Fig. 1. (a) Schematic illustration of the procedures used for making SS-derived heteroatom-doped CNFs, the skin core structure of an individual dragline silk fiber, and compositions of a silk core fibril; SEM images of raw spider silks (b), S-CNF-900 (c) and SA-CNF-900 (d); TEM (e) and high-resolution TEM (f) images of SA-CNF-900; (g) SEAD pattern of SA-CNF-900.

erally focused on its applications in the biomedical and clinical fields due to its excellent biocompatibility and biodegradability [16]. Moreover, due to its sufficient flexibility and excellent mechanic properties, SS can serve as a versatile scaffold for functional nanomaterials used for fluorescent, magnetic and electronic applications [17–20]. However, it is worth mentioning that silk fibers are assemblies of highly oriented alanine-rich nanocrystals of antiparallel β-pleated sheets along the fiber axis and disordered glycine-rich peptide chains filled up the remaining fibrillar volume (Fig. 1a). The rich polypetites of the natural SS indicates the high contents of C, N, and O elements, which might provide great opportunity for converting it into naturally derived heteroatom-doped carbon catalysts (Fig. 1a). Herein, for the first time, we fully utilized the chemical composition and fibrous structure of SS to convert it into heteroatom-doped porous CNFs through simple pyrolysis, following activation by the less harmful $ZnCl_2$. The resulting activated CNFs showed excellent electrocatalytic activity for the ORR. By investigating the correlation between the structural variation and the ORR activity, we elucidated the ORR active sites of the CNFs. Finally, we also demonstrated that the SS-derived activated CNFs (SA-CNFs) exhibited remarkable electrocatalytic activity for the ORR in microbial fuel cells (MFCs).

2. Experimental methods

2.1. Preparation of activated SS-derived carbon nanofibers (CNFs)

Natural spider silk (SS) samples produced by *Pholcus opilionoides* were collected from the local area and converted into carbon materials as depicted by Fig. S1. In brief, the obtained SS samples were washed with distilled water and then treated with 1 M HCl in an ultrasonic bath for 2 h to remove adsorbed impurities [21]. This process was repeated twice to ensure the complete elimination of any impurities on the SS samples. Then, the SS samples were washed with distilled water to remove the acid and dried at 30 °C for 24 h. The cleaned SS samples were then heated in an alumina crucible at 250 °C under a N_2 atmosphere for 2 h. The solid product was first dispersed into a 0.1 mol/L $ZnCl_2$ solution and then evaporated to dryness at 100 °C. The resulting solid samples were finally heated in an alumina crucible at 700, 800, 900, or 1000 °C under a