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Refining cocoon to prepare (N, S, and Fe) ternary-doped porous carbon aerogel as efficient catalyst for the oxygen reduction reaction in alkaline medium

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HIGHLIGHTS

- Heteroatom (N, S, and Fe) ternary-doped, porous carbon aerogel (HDCA) catalyst is derived from the biomass of cocoon.
- HDCA-800 (obtained at 800 °C) displayed excellent catalytic activity that comparable to Pt/C.
- The porous structures of HDCA-800 contributed to the transportation and diffusion of oxygen molecules/electrolytes.
- The physical and chemical evaluation of all catalysts validated crucial role of N and S atom in determining ORR activity.

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ABSTRACT

Various advanced sulfur doped Fe-N-C non-noble metal catalysts of oxygen reduction reaction (ORR) have been recently designed and reported with excellent catalytic activity. Herein, we refined cocoon with several steps to form silk fibroin solution, treated with iron salt to prepare an easy available, heteroatom (N, S, and Fe) ternary-doped, porous carbon aerogel (HDCA). Heteroatom existed in organic compounds in silk fibroin endow active site for ORR of the resultant carbon frameworks. Moreover, the amino acids presented in silk fibroin acted as ligands, functioning with Fe ions to form FeN_x coordination compounds, which also served as active sites towards ORR. The synthesized HDCA electrocatalysts, especially HDCA-800 (obtained at 800 °C) displayed excellent catalytic activity with onsets, half-wave potential of 0.94 V, 0.79 V and higher limited current density of 3.80 mA cm^{-2} through a near four-electron reduction pathway with an average electron transferred number of 3.86, making them promising alternatives for state-of-the-art ORR electrocatalysts in fuel cell field. The porous structure with synergistic effect of N and S heteroatom doping has been proposed to play a key role in facilitating the desired ORR reaction.

1. Introduction

Cathode reaction generally referred as oxygen reduction reaction (ORR) is one of the significant component in designing fuel cell [1,2]. Pt and Pt based material usually used to overcome the sluggish kinetics of ORR, but their high cost, scarcity, poor stability, and feasibility to methanol and carbon monoxide crossover reactions greatly hinder the commercialization in fuel cells [3–6]. As a consequence, enormous efforts have been paid to explore efficient, durable, and economically feasible alternatives, such as metal carbides [7], nitrides [8], transition-metal doping carbon materials [9–11], and various heteroatom-doped composite carbon materials, to reduce the reliance on such limited resources [12,13]. Among them, heteroatom-doped composite carbon materials, have received considerable concern because of their low cost, easy synthesized property and more importantly, their superior catalytic activities, which originates from the hybridization of doped heteroatoms into the carbon frameworks [14–18]. Despite great progress and efforts made in producing large scale multi-element-doped electrocatalysts and the enhancement of ORR performance [19,20], finding sustainable routes to prepare high-performance catalysts using renewable precursor still remains challenging for scalable commercialization of fuel cells.

Recently, the conversion of biomass into high-efficiency and easily available electrocatalysts toward ORR has been actively perused owing to continual demand for conversion and storage of renewable energy [21]. A variety of biomass have been used for the synthesis of ORR catalysts, including pomelo peels [22], egg [23], coir [24], and seaweed [25]. Specially, natural materials contain diverse compounds are good

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sources of carbon, nitrogen, oxygen, sulfur, and phosphorus etc., they can serve as suitable precursors for the carbon frameworks and adopt as the heteroatom dopants that assigned as main factor for the improvement of catalytic activity toward ORR [12,26]. Also, the obtained heteroatom-doped carbon materials retain abundant active sites homogeneously distributed throughout the whole carbon framework owing to the uniform distribution of precursor elements in natural materials [27]. Within this context, Dai et al. developed a N, P, and Fe ternary-doped, hierarchically porous carbon material with micro-, meso-, and macropores by pyrolyzing tea leaves soaked with iron salt, in this case the superior electrocatalytic activity is associated with the synergistic effect between the heteroatom dopant of C, O, N, and P element as well as good electrical conductivity in carbon framework [28]. Besides, Borghei et al. used coconut shell residues as the precursor to prepare heteroatom-doped carbon materials with excellent catalytic performance, long durability, and good methanol tolerance for ORR [29]. Interestingly, Wang et al. transformed coke wastewater sludge flocs into N, S dual-doped graphene-like carbon, which exhibited ultrahigh capacitance and oxygen reduction performance [30]. Remarkably, further studies validate a strong synergistic effect between N and S into graphitic structure has a favorable oxygen adsorption capability, which contributed to the enhancement of ORR activity [31–34]. The commonly adopted route to prepare such heteroatom-doped carbon materials is pyrolysis or chemical vapor deposition of carbon-containing precursors including organic monomers or polymeric molecules (PVP, melamine, dopamine, urea and thiourea etc.) that are rich in N and S elements [31–33]. These precursors are expensive and non-environmentally friendly, and some are even toxic to human beings. Apparently, combining with their distinctive properties, such as easy availability, abundance, and environmental friendliness, a variety of natural resources can be employed as promising precursors to synthesize various functional carbon materials with widely potential applications in both fuel cells and biosensors [21,35].

Silkworm silk from cocoon, a natural protein fiber produced by Bombyx mori, has been extensively used in the textile industry since 5000 years ago [36]. The cocoon with inherently large levels of nitrogen and sulfur atoms can be refined to prepare organic-rich silk fibroin containing abundant glycine, alanine, serine and other amino acids. Such organic-rich property makes the silk fibroin can be served as unparalleled heteroatom dopant material compared with other biomass [37,38]. Moreover, excellent biocompatibility of silk fibroin enables it promising application in bioscience, including serving as sutures, drug delivery carriers and tissue engineering scaffolds [39,40]. It is speculated that the unique properties of silk fibroin make them promising for the preparation of carbon nanomaterials with heteroatom doped carbon active sites to would considerably enhance the ORR performances in electrocatalytic field.

Based on the above discussions, we designed a novel ORR catalyst using cocoon as precursor to synthesize heteroatom (N, S, and Fe) ternary doped porous carbons aerogel, which possesses diverse active sites including Fe_3C, FeN_x and various N species. Remarkably, the as-obtained heteroatom (N, S, and Fe) ternary-doped, porous carbon aerogel (denoted as HDCA-X, where X represents the pyrolysis temperature) catalysts, especially HDCA-800, which possesses a large specific surface area of 714.4 $m^2 g^{-1}$ and displays excellent electrocatalytic activity, including positive onset and half-wave potential of 0.94 V, 0.79 V (vs. RHE) as well as higher limited current density of 3.80 mA cm^{-2} through an near four-electron reduction pathway, closing to that of commercial Pt/C catalysts in alkaline media. In a word, we anticipate that the incorporation of organic-rich biomass (silk fibroin) into synthesizing HDCA catalysts will provide an attractive way to develop non-noble-metal ORR catalysts with high efficiency and good stability.

2. Experimental

2.1. Materials

The cocoon was purchased from a local village of Dongying city, Shandong province, China. Other commercially-available chemicals (analytical grade) were bought from Sigma-Aldrich and used without further purification. Dialysis membrane (MWCO 8-14 kDa) was purchased from the Beijing Solarbio science & Technology Co., Ltd. Nafion (Sigma-Aldrich, 5 wt%) was diluted to 0.05 wt% with ethanol. 20 wt% Pt/C catalyst was purchased from Alladin. A Milli-Q plus water purification system (18MΩ, Milli-pore Co., Ltd, USA) was used to obtain ultra-pure water and used in all part that related to the aqueous environment.

2.2. Synthesis of HDCA-X electrocatalysts

Cocoons were obtained by cutting it into small pieces, then degummed it by heating twice at temperature of 98 °C, 30 min for each heating process, in an aqueous solution containing 0.5 wt% Na_2CO_3 to remove silk sericin. Washing the degummed silk with distilled water thoroughly and dried it briefly at 37 °C. The dried silk fibers with bath ratio of 1:25 were dissolved in 50 wt% $CaCl_2$ solution at 98 °C for 10 min followed by centrifuged at 12000 rpm for 3 min to remove impurities and precipitated matter. After that, the protein solution was dialysated against frequent renew of distilled water at room temperature for three days using cellulose dialysis membrane (MWCO 8-14 kDa). The final obtained silk fibroin aqueous solution was mixed with $FeCl_3$ at the mass weight ratio of 20:1 (i.e. 1 g $FeCl_3$ was added into 20 g silk fibroin solution) to form a homogeneous solution, which was then placed in the freezer compartment of refrigerator for several hours to form totally solid phase. After all above procedures, the solids were put in vacuum freeze-drying machine to obtain yellow moisture-free porous material. Lately, yellow porous material was transferred into a quartz-tube reactor and pyrolyzed at 700 °C, 800 °C, 900 °C, in N_2 atmosphere for 2 h with a heating rate of 3 °C min^{-1} to prepare different HDCA-X catalyst, denoted as HDCA-700, HDCA-800, HDCA-900, respectively. Pyrolyzed silk fibroin was synthesized under 800 °C through above method just not involving the addition of $FeCl_3$, denoted as N-S-C-800. After the above steps, the ideal HDCA-X and N-S-C-800 catalysts were obtained successfully.

2.3. Structure characterization

SEM images and EDX mapping were obtained by environmental scanning electron microscopy (ESEM Quanta 650 FEG). TEM and HRTEM images were obtained using a JEM-2100F Transmission Electron Microscopy (Japan) operated at 200 kV. The BET surface area and pore size distribution of HDCA-X catalysts were characterized with a belsorpmax surface area detecting instrument (Tristar3000) by N_2 physisorption at 77 K. XPS measurements were performed on a VG Micro-tech ESCA 2000 using a monochromic 15 Al Kα X-ray source. Raman spectrum was carried out in Raman spectroscopy (Renishaw invia, 514 nm excitation laser). X-ray powder diffraction (XRD) was carried out on a MSAL XD-3 advance power diffract meter with Cu Kα radiation ($\lambda = 1.5406$ Å).

2.4. Electrochemical measurements

The preparation of working electrode was as following: the glassy carbon (GC) working electrode was polished with 1.0 and 0.05 μm alumina slurry prior to each use, followed by rinsing it thoroughly and sonicated with deionized water and ethanol to obtain a mirror-like surface. Dispersing 6 mg catalyst into 1 mL N-N-dimethlformamide (DMF) by sonication for 5 min to obtain 6 mg mL^{-1} catalysts ink. Then, 4.2 μL of the dispersion was dropped onto a glassy carbon electrode