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Functional materials from nature: honeycomb-like carbon nanosheets derived from silk cocoon as excellent electrocatalysts for hydrogen evolution reaction

Xinrong Liu[a], Ming Zhang[a,b,*], Danni Yu[a], Tao Li[a], Meng Wan[a], Han Zhu[a,b], Mingliang Du[a,b], Juming Yao[a,b]

[a] College of Materials and Textiles, Zhejiang Sci-Tech University, Hangzhou 310018, PR China
[b] Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Zhejiang Sci-Tech University, Ministry of Education, Hangzhou 310018, PR China

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ABSTRACT

We developed a facile method to synthesize porous and N-rich carbon materials derived from *Bombyx mori* silk cocoons with an activation and thermal carbonization process. The silk-derived nanosheets carbon fibers consist of a porous and multilayer structure, endowing the materials with high surface area of 349.3 $m^2 g^{-1}$ and much exposed active sites. The synthesized N-rich (4.7%) carbon materials are employed as electrocatalysts for hydrogen evolution reaction (HER) and exhibit incredible catalytic performance as well as promising electrochemical durability, which are mainly attributed to the large amount of exposed active sites, high graphitization degree and the rich nitrogen elements, especially pyridine-N and graphitic-N. Typically, the silk-derived nanosheets carbon fibers activated by KCl afford a low onset potential of −63 mV (vs. RHE), a low overpotential of 137 mV at 10 mA cm^{-2} and a Tafel slope of 132 mV dec^{-1}. The results may offer a novel and promising method for the preparation of non-metal HER catalysts derived from abundant biomass.

1. Introduction

Subject to energy crisis and environment problems, continuous and great attentions are paid to develop clean and sustainable energy. Hydrogen is generally considered as the most ideal candidate for the fuel due to its free-pollution and high combustion value. Producing hydrogen by electrocatalytic water splitting requires the effective electrocatalysts with high activity and low potential during the hydrogen evolution reaction (HER) process [1]. As is well known, the Pt-group metals are considered as the best catalysts for the HER, however, the rarity and high cost limit their widely application [2]. Therefore, it is high time to develop sustainable, cost-effective and earth-abundant HER catalysts.

Recently, some non-precious electrochemical catalysts have been reported, such as transition metal sulfides [3–15], transition metal selenium [16,17] and biomass-derived carbon materials [18]. Especially, as non-metal catalysts, N-doped carbon nanomaterials exhibit relative high catalytic activity in oxygen reduction (ORR) and oxygen evolution reaction (OER). As is reported, the N-doped carbon nanostructures show n-type behavior, increasing the metallic behavior, which are expected to have greater electron mobility than their corresponding un-doped nanostructure. Nowadays, plenty of work focuses on the N-doped carbon nanomaterials used as electrocatalysts for ORR [19–21] and OER [22]. Experimentally, Mater et al. concluded that pyridinic nitrogen is the only active site [19], while Subramanian reported that both pyridinic and graphitic nitrogen can activate the ORR process [20]. *Wong* et al. examined the nitrogen-doped graphene also had high catalytic activity toward OER [21]. However, N-doped carbon materials used as HER catalyst are not widely investigated so far. *Liu* et al. presented N-doping carbon materials prepared by vapor deposition offering a novel and effective methodology for HER [23]. For the preparation of N-doped carbon materials, there are two main approaches: hydrothermal reaction and thermolysis [24–28]. In these methods, the nitrogen content of the carbon substrate is poor, and they usually introduce an extra N resource into their precursor to improve the catalytic performance. Due to

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* Corresponding author at: College of Materials and Textiles, Zhejiang Sci-Tech University, Hangzhou 310018, PR China. Tel.: +86 571 86843763; fax: +86 571 86843255.
E-mail address: zhangming@zstu.edu.cn (M. Zhang).

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the rich N element, some biomass such as silk are expected to be the idea precursor of the porous N-doped carbon materials [29,30], which usually exhibit impressive catalytic performance toward ORR.

So far, silk-derived carbon materials have been used in energy storage such as lithium battery [31] and supercapacitor [32,33]. However, the investigations in electrocatalytic, especially HER, are seldom reported. In this paper, we developed a facile and low-cost method to synthesize porous and N-rich porous carbon materials derived from *Bombyx mori* silk cocoons through a thermal carbonization process at controlled temperature with KCl as the activation reagent. As for KCl, it belongs to alkaline metal chlorides and the effect on porous formation is likely to be similar with KOH without degumming of silk. After the soak of KCl, the surface of silk fibers was full of KCl and K ions reacted with C and O of silk during high temperature carbonization, generating K_2CO_3 which would pyrolyze into K_2O and CO_2 further. When the CO_2 escaped, the porous formation was left. The produced N-doped carbon materials exhibit several advantages: 1) carbon resource derived from silk cocoons is naturally sustainable biomass which is rich in the content of nitrogen; 2) silk-derived carbon materials show a hierarchical porous and multilayer structure, a large specific surface area, and uniform nitrogen doping, especially high contents of nitrogen; 3) the synthesis procedure is facile without the use of templates and the activation reagent is easy to remove. The carbon materials are employed as water splitting catalysts and exhibit extraordinary high electrocatalytic activity for HER in acid media as well as outstanding stability and durability to acid corrosion medium. Those results may not only drive to facilitate the activity of non-precious-metal catalysts for HER but also accelerate the development of biomass-derived carbon material catalysts for electrocatalytic reactions.

2. Experiments

2.1. Materials synthesis and method

In a typical synthesis procedure, the *Bombyx mori* silk cocoons were firstly washed by deionized water for three times. Then, the washed silk cocoons were cut into $1 \times 1\,cm^2$ pieces and immersed into saturated KCl solution for 24 h at room temperature. After that, the silk cocoons were dried in a vacuum oven at 40 °C. Subsequently, the silk cocoons were placed into a home-built tubular furnace for carbonization at a certain temperature (400, 600, 700, 800, 900 °C) for 4 h under argon atmosphere with a heating rate of 5 °C/min. The silk-derived carbon materials activated by KCl were washed with deionized water and dried at 50 °C for 24 h in a vacuum oven. The obtained products were denoted as KCl-T, where T denoted the carbonization temperature (400, 600, 700, 800, 900 °C). As a control, the silk cocoons without KCl activation were synthesized in the same procedure, denoted as CS-900.

2.2. Material Characterizations

The Field emission transmission electron microscope (FE-SEM, JEOL, Japan) at an acceleration voltage of 3 kV was used to observe the morphologies of all the samples. Transmission electron microscopy (TEM) images were obtained by a JSM-2100 transmission electron microscopy (JEOL, Japan) at an acceleration voltage of 200 kV. XRD patterns of the samples characterized with a SIEMENS Diffraktometer at 35 kV ($\lambda = 1.5406\,Å$), with a scan rate of 0.02 in the 2θ range of $10-80°$. X-ray photoelectron spectra of all the samples were recorded using an X-ray Photoelectron Spectrometer (Kratos Axis Ultra DLD) with an aluminum (mono) $K\alpha$ source (1486.6 Ev). The aluminum $K\alpha$ source was operated at 15 kV and 10 Ma.

2.3. Electrochemical Measurements

All electrochemical tests were performed at room temperature in a standard three electrode system controlled by a CHI 660E electrochemistry workstation. Carbon rod and saturated calomel electrode (E(RHE) = E(SCE) + 0.244 V) were used as counter and reference, respectively. In all measurements, the SCE reference electrode was calibrated with respect to reversible hydrogen electrode (RHE). For preparation of working electrode, all samples were fixed in a Teflon electrode clamp, put into 0.5 M H_2SO_4 (aq.) electrolyte saturated with Ar. Cyclic voltammograms (CVs) were obtained to stabilize the catalysts. The performance of the catalysis was recorded by linear sweep voltammetry (LSV) at a scan rate of 2 mV/s. Electrochemical impedance spectroscopy (EIS) was carried out at -0.121 V vs RHE, with the frequency from 10^{-2} to 10^{6} Hz. All the electrochemical measurements were tested without IR compensation.

3. Results and discussion

A *Bombyx mori* silk cocoon consists of hundreds of individual fibers with a diameter in the range of 10–20 μm and the fibers are typical twin fibers composed of two type proteins: fibroin and sericin seen in Fig. S1. As shown in Fig. 1a, after carbonization at 900 °C under Ar/NH_3 atmosphere, the carbonized silk fibers (CS-900) indicate a few of micropores on the surface. However, after the treatment by KCl solution, the surfaces of the carbonized silk fibers (KCl-900) exhibit honeycomb-like and porous surfaces. And the nanosheets are thin and transparent, which look like graphene-like nanosheets, randomly distributed on the surface (see Fig. 1b), forming a rougher surfaces than the CS-900. The insets in Fig. 1c and d depict typical transmission electron microscopy (TEM) image of the two products and further demonstrate the difference of their structures.

There are no pores observed in CS-900 shown in Fig. 1d, however, many nanopores can be clearly found in KCl-900, and the thickness of the nanosheets can be estimated in several nanometers. Furthermore, the HRTEM image of CS-900 shows that the carbon nanosheets have no obvious lattice fringe (see Fig. 1e), while the nanosheets of KCl-900 display clear well-defined lattice fringes, corresponding to the (002) plane of carbon with an interlayer spacing of 0.37 nm (see Fig. 1f). Considering the different nanostructures between KCl-900 and CS-900, it may be ascribed to the activation of KCl.

It is noted that carbonization temperatures have strong influences on the morphology and structure of the silk derived carbon nanomaterials, and the silk derived carbon prepared at different temperatures are denoted as KCl-400, KCl-600, KCl-700 and KCl-800, as shown in Fig. 2a-d. Comparing the four products, the surface become rougher and more nanosheets and hierarchical porous structure are distributed uniformly with increasing carbonization temperature. The HAADF-STEM image of KCl-900 in Fig. 3a confirms the porous structures and the element mapping images from Fig. 3c-e reveal well distribution of C, N and O elements, demonstrating the successfully preparation of N-doped carbon nanomaterials.

The specific surface area and the porous nature of CS-900 and KCl-900 are determined by Brunauer-Emmett-Teller (BET) method. As depicted in Fig. 4a and b, the N_2 adsorption/desorption isotherms belong to IUPAC type-IV isotherm with a large slope at higher relative pressures[21], which is typical of mesoporous materials. The pore-size distribution of CS-900 and KCl-900 calculated from the isotherm using the BJH model, demonstrates