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

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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 $349.3 \text{ m}^2 \text{ g}^{-1}$ 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 KCI 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.

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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

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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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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 KCI as the activation reagent. As for KCI, 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 KCI, the surface of silk fibers was full of KCI and K ions reacted with C and O of silk during high temperature carbonization, generating K₂CO₃ which would pyrolyze into K₂O and CO₂ further. When the CO₂ 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 $1 \times 1 \text{ cm}^2$ 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 (λ = 1.5406 Å), with a scan rate of 0.02 in the 2 θ 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 α source

(1486.6 Ev). The aluminum K α 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 H₂SO₄ (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 μ m 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/NH₃ atmosphere, the carbonized silk fibers (CS-900) indicate a few of micropores on the surface. However, after the treatment by KCI solution, the surfaces of the carbonized silk fibers (KCI-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 KCI-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 KCI-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 KCI-900 and CS-900, it may be ascribed to the activation of KCI.

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 KCI-400, KCI-600, KCI-700 and KCI-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 KCI-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 KCI-900 are determined by Brunauer-Emmett-Teller (BET) method. As depicted in Fig. 4a and b, the N₂ adsorption/desorption isotherms belong to IUPAC type-IV isotherm with a large slope at higher relative pressures²¹, which is typical of mesoporous materials. The pore-size distribution of CS-900 and KCI-900 calculated from the isotherm using the BJH model, demonstrates



Fig. 1. FE-SEM images of (a) CS-900 and (b) KCI-900 samples. TEM images of (c, e) CS-900 and (d, f) KCI-900 samples.

that the size of pores range from 2 to 10 nm and the average pore sizes are 5.4 nm and 4.8 nm, respectively in Fig. 4c and d. These pores possibly attribute to the effect of the activation of KCI on the surface of silk. And the BET specific surface areas of CS-900 and KCI-900 are calculated to be as high as about 246.7 m²/g and 349.3 m²/g, respectively.

Considering the specific surface areas increased by about 40% from CS-900 to KCI-900, the KCl can foster the activation of the silk fibers, subsequently, forming the graphene-like and porous structure. It is expected that the porous structure can expand the contact areas so as to accelerate effective electrolyte diffusion and the interfacial electrocatalytic reaction.

To further confirm the microstructure of the carbonized silk cocoon, the XRD patterns of the original silk fiber, KCI-900, KCI-800, KCI-700, KCI-600, KCI-400 and CS-900 are presented in Fig. 5a.

The silk cocoons exhibit only a main broad peak at 20.3°, and correspond to the (020) diffraction peak of silk, suggesting a typical β -sheet crystalline structure. After carbonization, the KCI-900 shows a typical diffraction peak at 24.2° corresponding to the (002) plane of graphite. No sharp peaks were found, indicating impurities were removed. When compared with CS-900, the characteristic peak (002) of CS-900 decreases to 23.0°. According to the Bragg's law, the interlayer distance (d-spacing) of the graphite layers of KCI-900 is determined to be 0.37 nm, which is closer to the result of TEM (Fig. 1f). However, there's a small shift of (002) peak from 24.2° to 23.8° approximately because of the different carbonization temperature and the KCI-800, KCI-700, KCI-600 and KCI-400 products display (002) plane of graphite at 24.2°, 23.7°, 23.4° and 23.8°, respectively. Obviously, it is found that another characteristic peak turns up at 43.6°, corresponding to the



Fig. 2. FE-SEM images of (a) KCI-400, (b) KCI-600, (c) KCI-700 and (d) KCI-800 samples.



Fig. 3. (a) HAADF-STEM and (b-e) STEM-EDS mapping images of KCI-900.

(100) lattice plane of typical turbostratic carbon²¹, which attributes to the high carbonization temperature (higher than 700 $^{\circ}$ C) and the intercalation of K ions.

Raman spectra were widely used to measure the structural disorder in carbon materials. Fig. 5b shows the Raman spectra of the carbonized silk fibers at different carbonization temperature. Two broad band peaks appear around 1579 cm⁻¹ and 1340 cm⁻¹, corresponding to the characteristic G and D bands of carbon materials, respectively. The D band is the representative of the disordered graphite structure, as well as the G band depends upon the percentage of graphitic domains containing layers of sp² hybridized carbon. To the best of our knowledge, the intensity ratio

of the G and D bands (I_G/I_D) is calculated to quantify the ordering of graphite. From the spectra, the I_G/I_D of CS-900, KCI-900, KCI-800 and KCI-700 are determined as 0.92, 0.99, 0.94, 0.92, respectively, indicating that the K activation and N-rich graphitic networks can promote the ordering of graphite and the degree of structural alignment. Notably, the carbon elements of sp³ hybridized carbon are not in the same plane and the plane is disordered, emphasizing the atomic-scale, not the microstructure. So the material disorder depends upon the type of hybridized carbon.

X-ray photoelectron spectroscopy (XPS) was used to verify the different valence states of individual elements of silk derived carbon. From Fig. 6a, the survey spectra of KCI-900 and CS-900



Fig. 4. Nitrogen adsorption/desorption isotherm plots and the BJH pore-size distribution curves of (a,c) KCI-900 and (b,d) CS-900.



Fig. 5. (a) The XRD patterns of the original silk fibers, CS-900, KCI-900, KCI-800, KCI-700, KCI-600 and KCI-400 samples. (b) Raman spectra of the CS-900, KCI-900, KCI-800 and KCI-700 samples.

reveal the presence of C, N and O elements without K or CI elements. The high resolution C 1 s spectrum is probed in Fig. 6b, the spectrum of KCI-900 are fitted into four peaks with binding energy at nearly 284.7 (-C--C/H), 285.4 (-C--N), 286.6 (C--OH/C--N) and 288.2 eV (-O=C--N). The peak at 288.2 eV (-O=C--N) is an evidence of the existence of the peptide backbone, while the peak at 284.7 eV (-C--C/H) assigns to the aliphatic C--C carbons of the amino acid pendant groups. Additionally, the N1 s spectrum can be deconvoluted into four peaks centered at 398.1, 398.6, 400.7 and 404.1 eV, which are consistent with pyridinc (N-5), pyrrolic (N-6), graphitic (N-Q) and oxidized nitrogen, respectively (see Fig. 6c), indicating that nitrogen in amino group has transformed into N-5, N-6 and N-Q during the carbonization process.

Furthermore, based on the two survey spectra in Fig. 6d and e, there is no difference between CS-900 and KCI-900, indicating that the K intercalation does not bring about any effect on carbon species. The XPS spectra of KCI-400, KCI-600, KCI-700 and KCI-800 are provided in Fig. S2. To determine the contents and types of nitrogen in the obtained products with different carbonization temperature, the results are calculated in Table S1 and shown in Fig. 6f. Generally speaking, with the increased carbonization temperature, the contents of nitrogen decrease from 14.3 wt% to

4.7 wt%. Interestingly, the N-6 species takes up the major part of the total content at low temperature but the N-Q species is the dominant when the temperature is high, indicating that nitrogen in amino group has transformed into N-Q more easily than N-6 under higher carbonization temperature.

The electrocatalytic activities of the silk-derived N-doped carbon nanomaterials are measured by the typical three-electrode system in $0.5 \text{ M }_2\text{SO}_4$ at room temperature. The carbon rod was used as the counter electrode to avoid introducing Pt onto the working electrode. The KCI-900 is investigated and the other catalysts are conducted as control experiments. As shown in Fig. 7a, the CS-900 exhibits a poor HER catalytic activity with high onset potential of 187 mV and a low cathodic current density (see Table 1). However, after activation by KCl, the silk-derived carbon materials exhibit incredible high electrocatalytic activity. Hydrogen bubbles release more vigorously with more negative potentials.

Typically, the KCI-900 achieves the onset potential of only 63 mV, which is a little higher than that of 20 wt% Pt/C (about 45 mV). In addition, the KCI-400, KCI-600, KCI-700 and KCI-800 catalysts also show amazing electrocatalytic performances with onset potentials in a range from 75 to 83 mV, indicating that the



Fig. 6. (a) XPS survey spectra of KCI-900 and CS-900. High-resolution (b,d) C 1 s and (c,e) N 1 s of KCI-900 and CS-900. (f) The nitrogen contents of the as-prepared products.

electrocatalytic activity of N-rich carbon materials derived from silk is indeed promoted by KCI activation. To further investigate the HER performances of the catalysts, the Tafel plots derived from the polarization curves are fitted by the well-known Tafel equation (η = a + blog[j]), in which j is the current density, b is the Tafel slop and a is the exchange current density (see Fig. 7b). The Tafel slope of KCI-900 is 131 mV dec⁻¹, which is much lower than that of CS-900 (172.9 mV dec⁻¹). At the same time, the Tafel slopes of KCI-800, KCI-700, KCI-600 and KCI-400 are 152, 185, 179 and 191 mV dec⁻¹, respectively. It is found that the nitrogen in amino groups were transformed into N-5, N-6 and N-Q species and the content of N-Q increases with carbonization temperature rises, leading to the enhancement of HER activity.

Electrochemical impedance spectra (EIS) measurements are recorded at -0.121 V vs. RHE, in order to explore the interface reactions and electrode kinetics of catalysts during the HER process, as shown in Fig. 7c. The Nyquist plot of KCI-900 shows a much smallest arc among the all catalysts and a dramatically decreased charge-transfer resistance (R_{ct}) for KCI-900 (19.99 Ω) relative to the CS-900 (30.74 Ω), KCI-800 (22.26 Ω), KCI-700 (23.53 Ω), KCI-600 (21.77 Ω) and KCI-400 (44.56 Ω), signifying the highest conductivity and fastest electron transfer of silk derived carbon owing to the high content of N-Q and the large ratio of I_G/I_D.

Apart from the electrochemical activity, the long term durability of a catalyst electrode in the HER is another important factor for practical application, therefore, the durability test of KCI-

900 is evaluated and the time dependence current density plots under static overpotential (-0.365 V) is depicted in Fig. 7d. KCI-900 exhibits almost negligible decay during the electrocatalytic process even after 10h continuous operations, indicating a virtually invariant current response. To investigate the morphology of the products after stability tests, we further characterize the KCI-900 after long-term electrochemical stability tests. The porous structure of KCI-900 still does not change a lot as illustrated in Fig. S3. But nanosheets are not observed obviously, which can be attributed to the collapse of nanosheets caused by the generation of the bubbles during the HER process. Similarly, the KCI-800 and KCI-700 are conducted as the same way with a small attenuation of catalytic activity. Stability of KCI-400 and KCI-600 is further measured by cycling continuously for 1000 cycles ranging from 0 to +0.8 V vs. RHE at a scan rate of 100 mV s^{-1} under 0.5 M H₂SO₄ in Fig. 7e and f. It is obvious that HER current lost slightly after 1000 cycles of cyclic voltammetry.

Above all, the silk-derived nanosheets carbon fibers are successfully obtained through KCI activation, which would offer a novel and effective method for the preparation of non-preciousmetal HER catalysts derived from naturally sustainable biomass. KCI-900 is endowed the promising performance by porous formation. And the effect of porous formation can be ascribed to the following parts: 1) With the help of KCI activation, the rich content of nitrogen in amino groups were transformed into N-5, N-6 and N-Q and the content of N-Q increases with increased



Fig. 7. (a) Polarization curves, (b) Tafel plots and (c) Nyquist plots of CS-900, KCI-800, KCI-800, KCI-700, KCI-400 and 20% Pt/C catalysts in N₂-saturated 0.5 M H₂SO₄ solution, respectively. (d) Time dependence current density under static potential (η = -0.365 V). Polarization curves of (e) KCI-400 and (f) KCI-600 recorded before and after 1000 cycles in 0.5 M H₂SO₄ solution.

 Table 1

 Electrochemical parameters of the obtained products.

| Samples | Onset overpotential (mV) | $\eta @ j = 10 mA cm^{-2}$ (mV) | Tafel slope (mV/dec) | Exchange current density $(mA cm^{-2})$ | Charge-transfer resistance Rct (Ω) |
|---------|-----------------------------|------------------------------------|-------------------------|---|---|
| KCI-400 | 83.4 | 184 | 191.2 | 0.185 | 44.56 |
| KCI-600 | 80.0 | 165 | 179.4 | 0.150 | 21.77 |
| KCI-700 | 81.1 | 165 | 184.7 | 0.056 | 23.53 |
| KCI-800 | 75.3 | 146 | 151.9 | 0.035 | 22.26 |
| KCI-900 | 63.3 | 137 | 131.6 | 0.003 | 19.99 |
| CS-900 | 187.0 | 317 | 172.9 | 0.1157 | 30.74 |

carbonization temperatures, providing much effective active sites, which is essential for HER catalytic activity. 2) The high surface area and nanoporous structure offer more exposed active sites and larger contact area, which can accelerate effective electrolyte diffusion and the interfacial electrocatalytic reactions. 3) The high graphitization degree of silk-derived nanosheets carbon fibers affords remarkably fast electron transport.

4. Conclusions

In summary, we developed a facile method to synthesize porous and N-rich carbon materials derived from Bombyx mori silk cocoons with an effective KCl activation and a thermal carbonization process at controlled temperature. The products consist of a porous and multilayer structure, endowing the materials with high surface area as high as 349.3 m²/g and much exposed active sites and the rich N elements (4.7%) in the silk cocoons are introduced into the carbon network, forming N-6 and N-Q. The silk derived nanosheets carbon fibers were employed as electrocatalyst toward HER and exhibit incredible catalytic activity and durability. Typically, the KCI-900 affords Tafel slope of 131.6 mV dec⁻¹, a lower onset potential of -63.3 mV (vs. RHE), and a low overpotential of 137 mV at 10 mA cm⁻². The present study may offer a novel and effective method for the preparation of non-preciousmetal HER catalysts derived from naturally sustainable biomass and accelerate the development of biomass-derived carbon material catalysts for electrocatalytic reactions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2016. 08.091.

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