The production of carbon microtubes by the carbonization of catkins and their use in the oxygen reduction reaction

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ABSTRACT
Willow or poplar catkins were carbonized to prepare carbon microtubes (CMTs) due to their natural micro-tubular structure. After carbonization at temperatures of 550–950 °C, CMTs with outer and inner diameters of 4–8 and 3–7 μm were obtained. In addition to having a large and accessible inner tube, a small amount of nitrogen (~1.8 at.%) and phosphorus (~0.4 at.%) dopants cause CMTs prepared at 750 °C to be a cheap metal-free catalyst with good catalytic activity in the oxygen reduction reaction.

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1. Introduction
Naturally occurring micro- and nanostructures are a topic of extensive interest in the world of nano- and ecotechnology, where their unique properties and sophisticated structures provide bio-inspiration and bio-template for material synthesis [1–4]. Learning from the natural phenomena such as “lotus effect” and “gecko foot”, researchers have created bio-inspired organic or/and inorganic materials including superhydrophobic films [5,6], highly adhesive surfaces [7,8], water-collection networks and so forth [9]. In biotemplating, a large variety of micro- and nanomaterials have been constructed based on the template of DNA, bacteria, viruses, etc. [3]. Additionally, biomass is a rich carbon resource for synthesizing carbon micro/nanomaterials [10]. Some biological materials such as filamentous silk and cotton could directly serve as both template and precursor for the preparation of carbon microfibers by simple carbonization [11–13]. Such carbon-material synthesis route is obviously simple, “free” and potentially abundant. But carbon micro- and nanomaterials with tubular structure, like one of the most important nanomaterials – carbon nanotubes, are still synthesized by artificial method including arc-discharge [14], chemical vapor deposition [15], and solvothermal synthesis method [16]. To meet some demands of large-diameter in nano/microfluid, drug-delivery and microreactor, carbon microtubes (CMTs) have also attracted great attention in recent years [17–22]. CMTs have been prepared by carbonizing hollow polymer fibers [17], and also could be grown by CVD using ZnS powder or Ga droplets as catalysts [18,19]. In this study, we used willow or poplar catkins as precursor to prepare CMTs by simple carbonization. The as-prepared CMTs have the outer and inner diameter of 4–8 and 3–7 μm, respectively. They contain about 1.8 at.% nitrogen and 0.4 at.% phosphorus species and exhibit good activity in the oxygen reduction reaction (ORR), demonstrating their promising potential in electrocatalysts for fuel cells.

2. Experimental
2.1. CMT preparation
The willow (scientific name: Salix babylonica Linn.) and poplar (Populus euramevicana cv.'I-214') catkins were collected in...
The willow catkins were carbonized at 550, 750, or 950 °C. After carbonization for 60 min, about 12 mg black products were collected when the reactor was cooled to room temperature under Ar gas protection.

2.2. Sample characterization

The structure of the willow catkins before and after carbonization was characterized by scanning electron microscopy (SEM, Hitachi S-4800), transmission electron microscopy (TEM, JEM1005 at 100 kV), X-ray diffraction (XRD, Philips X’pert Pro X-ray diffractometer with Cu Kα radiation of 1.5418 Å), Raman spectroscopy (Renishaw inVia Raman Microscope with an argon-ion laser at an excitation wavelength of 514 nm) and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250). The Brunauer–Emmett–Teller (BET) surface area and Barret–Joyner–Halenda (BJH) pore distribution of the samples were measured using nitrogen adsorption isotherm measurements at 77 K (V-Sorb 2800P).

2.3. Electrocatalytic evaluation

The capability of CMTs for the ORR were evaluated by cyclic voltammetry (CV) and rotating ring-disk electrode (RRDE) voltammetry. This electrochemical measurements were carried out at 25 °C with a CHI 760C workstation (CH Instruments). Ag/AgCl and platinum wire served as reference and counter electrodes, respectively. CV was collected with a glassy carbon (GC) electrode (5 mm diameter). The RRDE voltammetric experiments were performed on a modulated speed rotator electrode rotator (Pine Instrument Co.) using a GC disk electrode (5 mm diameter) surrounded by a Pt ring (6.5 mm inside diameter). The GC electrode was modified as following. Simply, 5 mg CMTs was dispersed into 5 mL mixture of water, ethanol and Nafion (DuPont, 5 wt.%), with the volume ratio of 1:3.85:0.15. The GC electrode was further confirmed by Raman spectra (Fig. 2b). Compared with the featureless spectrum of the catkin precursor, the spectra for the carbonized samples display two obvious peaks (D-band, 1353 cm⁻¹, and G-band, 1591 cm⁻¹) which might be a sign from the complete transformation of catkins to carbon-based materials. The graphitic structure of the carbonized samples was further confirmed by Raman spectra (Fig. 2b). Compared with the featureless spectrum of the catkin precursor, the spectra for the carbonized samples display two obvious peaks centered at ~1353 cm⁻¹ (D-band) and ~1591 cm⁻¹ (G-band), attributed to defected carbon crystallites and crystalline graphite, respectively [25].

Nanjing, China. Hundred milligrams catkins were placed in a quartz tube and set in central zone inside a horizontal tube furnace. Then the furnace was heated to the reaction temperatures of 550, 750, or 950 °C at a rate of 10 °C/min in Ar atmosphere. After carbonization for 60 min, about 12 mg black products were collected when the reactor was cooled to room temperature under Ar gas protection.

Fig. 1 – (a) Photograph of willow catkins and their carbonized samples; SEM images of willow catkins (b) and their carbonized samples at 550 °C (c), 750 °C (d) and 950 °C (e). The insert in (b) is the typical TEM image of willow catkins.

3. Results and discussion

The willow catkins were carbonized at 550, 750, or 950 °C for 60 min and the weight loss of the catkins carbonized at 950 °C is about 88%. Fig. 1a shows a photograph of willow catkins (white one) and their carbonized samples (black). The carbonized samples with catkin-like morphology still kept certain mechanical resilience, though it was lower than that of the pristine catkins. The structures of the willow catkins before and after carbonization were characterized by SEM and TEM, which are shown in Fig. 1b–e. The catkin fibers have a diameter of 5–10 μm (Fig. 1b) and microtubular structure (the insert of TEM image in Fig. 1b). After calcination, these microtubes became brittle and tend to break to short pipes. The high-magnification SEM images (the inserts in Fig. 1c and d) show several broken, open-ended microtubes with the outer and inner diameter of 4–8 and 3–7 μm, respectively, suggesting that the tubular structure is well maintained during carbonization.

The XRD curves for the willow catkins and their carbonized samples are shown in Fig. 2a. The diffraction peaks at 21.7°, 23.2°, 23.9° and 25.0° are corresponding to d spacings of 0.41, 0.38, 0.37 and 0.36 nm respectively. The peak for willow catkins around 21.7° should arise from the cellulose they owned, similar to that of wheat straw or cotton fibers [23,24]. With increasing annealing temperature, the peak shifts gradually to higher diffraction-angle side accompanied by the slight increase of its intensity, finally approaching a d spacing close to 0.34 nm, i.e., d₀₀₂ in graphite. XRD curves for the samples annealed at 750 and 950 °C also displays a weak peak at 43.4° corresponding to graphite (1 0 0), which might be a sign from the complete transformation of catkins to carbon-based materials. The graphitic structure of the carbonized samples was further confirmed by Raman spectra (Fig. 2b). Compared with the featureless spectrum of the catkin precursor, the spectra for the carbonized samples display two obvious peaks centered at ~1353 cm⁻¹ (D-band) and ~1591 cm⁻¹ (G-band), attributed to defected carbon crystallites and crystalline graphite, respectively [25].

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The carbon materials prepared from biomass usually contain nitrogen species, which is derived from the –NH₂ group in amino acids/proteins [12,13]. In this case, the chemical state and surface concentration of C, N, O, and P elements existed in the samples were analyzed by XPS (Fig. 3). All the binding energies (E_b) are referenced to C1s at 284.60 eV. The C1s spectra (Fig. 3a) could be identified into five chemically different carbon entities: sp² C=C (284.6 eV), sp³ C–C (285.2–285.5 eV), C–O (286.1–286.6 eV), >C=O (287.1–287.8 eV), and O–C=O (288.8–289.2 eV) [26]. Accordingly, the peaks for C=O and C-O type oxygen can be fitted out in their O1s XPS spectra (Fig. 4b). The oxygen functionalities for the samples decreased with increasing heating temperature (Table 1), indicating that the weight loss during the catkin carbonization mainly come from dehydration, decarbonylation, and decarboxylation [27,28]. The N1s spectra in Fig. 4c can be deconvoluted into four components: C–N (397.0–397.3 eV), N–C=O (400.4–400.5 eV), Imidazole (401.3–401.5 eV), and pyridine (401.5–401.7 eV) [29,30].

![Fig. 2 – XRD curves (a) and Raman spectra (b) of willow catkins and their carbonized samples.](image)

![Fig. 3 – XPS spectra of willow catkins and their carbonized samples. (a) C1s; (b) O1s; (c) N1s; (d) P2p spectrum.](image)
luted into four peaks. Specifically, the three peaks centered at higher binding energy can be assigned to three different nitrogen species: graphitic nitrogen at 401.3–401.5 eV, pyrrolic nitrogen at 400.1–400.4 eV, pyridinic nitrogen at 398.3–398.8 eV [29]. While the last peak at 397.9 may be correspond to P–N=P bonds [30], accompanying by the co-existence of P at. % phosphorus in the CMTs (Fig. 4d and Table 1). The nitrogen surface atomic concentrations for the carbonized samples are around 1.2–1.8 at.%, higher than that for the catkin precursor (~1.0 at.%) due to the considerable removal of other components including oxygen and carbon species after the degradation of the catkins. In the three as-prepared CMTs, the one carbonized at 750 °C has the highest pyridinic nitrogen content. From the P2p XPS spectra (Fig. 4d), it is seen that the phosphorus signal at 133.0 eV is neglectable for the catkin while obviously visualizable for the CMTs. This should be caused by the increase of phosphorous concentration after the remarkably removal of carbon and oxygen species during the carbonization.

Fig. 4 shows adsorption–desorption isotherms and pore size distributions of the CMTs prepared at 750 and 950 °C. The CMTs exhibit an adsorption isotherm of type I according to IUPAC (Fig. 4a). The adsorbed amount to nitrogen of CMTs largely increases with increasing carbonization temperature. BET specific surface areas (S_{BET}) for CMTs prepared at 750 and 950 °C calculated using adsorption data are 137 and 257 m²/g. The corresponding pore sizes evaluated using BJH for them are 2–4 and 4–7 nm respectively, as displayed in Fig. 4b. While for the CMTs prepared at 550 °C, its S_{BET} is about 0.5 m²/g and adsorption–desorption isotherm can not be depicted probably due to overrun of the detection limit, indicating that the CMTs prepared at 550 °C do not own micropores. The pores formed in the walls of CMTs should be activated by the H₂O and/or CO₂ during their dehydration, decarbonylation, and decarboxylation at a high temperature, e.g. 750 or 950 °C.

The above experimental results indicate that, by simple carbonization, CMTs with large internal diameter as well as a certain amount of nitrogen and phosphorous species could be obtained from the naturally occurring catkins. According to the above results, CMTs prepared at 750 °C and 950 °C are suitable for oxygen reduction reaction applications. RRDE tests were conducted at a rotation rate of 1200 rpm and the Pt ring electrode was polarized at 0.5 V.

<table>
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<th>Samples</th>
<th>Elements</th>
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<th>Ols</th>
<th>P2p</th>
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<tr>
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<td>1.82</td>
<td>11.32</td>
<td>0.45</td>
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<tr>
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<td></td>
<td>90.14</td>
<td>1.23</td>
<td>8.22</td>
<td>0.41</td>
</tr>
</tbody>
</table>

**Fig. 5 –** CV (a) and RRDE (b) voltammetric curves of CMTs in O₂-saturated 1 M NaOH electrolyte at a scan rate of 10 mV s⁻¹. RRDE tests were conducted at a rotation rate of 1200 rpm and the Pt ring electrode was polarized at 0.5 V.

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to the high electrocatalytic activity owned by the nitrogen doped carbon nanotubes (NCNTs) [31,32], the as-prepared CMTs are attractive for electrocatalyzing ORR due to the active sites generated by the dopants on the available outer- and inner-wall. The electrocatalytic performances of the CMTs were firstly examined by CV (Fig. 5a). The onset potential and peak potential of the oxygen reduction for the CMTs prepared at 750 °C in CV curve (Fig. 5a) are around 0.19 and −0.34 V, which are higher than those for the CMTs obtained at 550 (−0.28, −0.39 V) and 950 °C (−0.20 V, −0.37 V). The CMTs prepared at 750 °C owns the highest electrocatalytic activity, which is likely contributed to the synergistic effect of its good graphitization, highest pyridinic nitrogen content and highest specific surface areas [29]. The electrocatalytic properties of the CMTs prepared at 750 and 950 °C were further studied by RDDE voltammetry (Fig. 5b). As seen, the changes of disk current curves are in consistent with that in RDE testing (S1 in Supplementary data). Compared with the CMTs prepared at 950 °C, the ones obtained at 750 °C have lower ring currents, i.e., higher selectivity for the reduction of O2 towards H2O. Using the equation of \( n = 4I_{\text{dis}}/(I_{\text{disk}} + I_{\text{ring}}/N) \) [32], here \( I_{\text{dis}} \) and \( I_{\text{ring}} \) are faradic current at 0.60 V, \( N = 0.26 \) is the collection efficiency, the precise transferred electron number (n) per O2 for CMTs prepared at 750 and 950 °C was calculated to be 2.73 and 2.35. This implies that the ORR on CMTs is a combination of two-electron and four-electron reactions, which is similar to the catalysis process taken place on some types of NCNTs [32,33]. The good ORR activity owned by CMTs indicates their great potential in advanced electrocatalysts.

4. Summary

Willow and poplar catkins provide a sophisticated microtubular structure for preparing CMTs by simple carbonization. (CMTs prepared from poplar catkins are shown in S2 in Supplementary data) The as-prepared CMTs have large inner-diameter of 3–7 μm and contain about 1.8 at.% nitrogen and 0.4 at.% phosphorous dopants. The ones prepared at 750 °C have exhibited good activity for electrocatalyzing the ORR with a transferred electron number of 2.73, suggesting their potential in electrocatalyst. The large and accessible inner tube of CMTs makes them suitable for wide applications beyond fuel cells such as supercapacitors, ion batteries, drug delivery and microreactors.

Acknowledgements

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Appendix A. Supplementary data


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