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Direct synthesis of carbon-based microtubes by hydrothermal carbonization of microorganism cells

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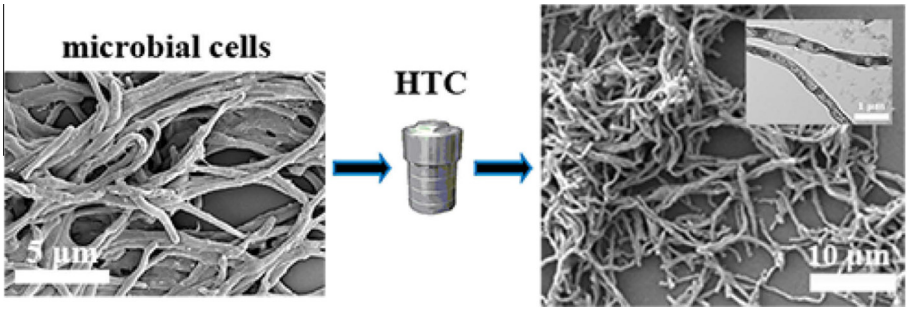
HIGHLIGHTS

- Tubular microbial cells were introduced to hydrothermal carbonization.
- Soft biomass conserved the biological structure in the carbonization process.
- Carbon-based microtubes were obtained and the formation mechanism was proposed.
- The resulted materials exhibited potential as non-metal electrocatalyst for hydrogen evolution reaction.

GRAPHICAL ABSTRACT



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ABSTRACT

Streptomyces sporoverrucosus dwc-3, a type of microbial biomass was used to prepare carbon-based microtubes (CMTs) due to their natural micro-tubular structure. After low temperature hydrothermal carbonization at 180 °C, CMTs with a diameter of 400–500 nm and a wall thickness of about 50 nm was obtained. It was demonstrated that the intrinsic biologic tissue of the soft biomass could also be well inherited during the formation process of CMTs. Electrochemical evaluations in 0.5 M Na_2SO_4 + 0.1 M H_2SO_4 solution at room temperature showed that the prepared CMTs exhibited high electrocatalytic activity for hydrogen evolution reaction. The significant outcomes in this work showed a novel approach to fabricate CMTs that can be used as non-metal electrocatalysts for hydrogen evolution reaction by using low temperature hydrothermal carbonization method.

1. Introduction

During the last two decades, carbon materials have attracted extensive attention because of their unique electrical, chemical, and mechanical properties [1]. These carbon materials can exist in various shapes like rods, spheres, cones, tubes, *etc.* Among the various structures, carbon nanotubes (CNTs) have been extensively investigated since Lijima's landmark discovery in 1991 [2]. Due to their superior physicochemical properties, CNTs have been used as nanoreactors for chemical reactions, as a test tube for catalysis, separation and storage, or as a nanochannel for the adsorption and transport of various molecules [3–5]. However, the potential of CNTs as nanoreactors or channels is hampered by their nanometer-size diameter (typically 1–100 nm) in the applications that require affixing CNTs with large sized molecules or particles, such as proteins, cells, inorganic clusters, *etc.* [6]. Therefore, CMTs with

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larger diameters are expected to be ideal candidates for the applications that need microscale level carbon materials (e.g., microfluidic pumps, flow channels, and microreactors). Recent studies also showed that CMTs had a great potential in serving as a mesoscale bridge from nano to bulk materials [7,8]. However, unlike CNTs, the synthetic methods of CMTs have not been fully investigated and most of the synthesis processes are complex, time consuming, and energy intensive [9].

Hydrothermal carbonization (HTC) is a rediscovered technique for the synthesis of functional carbon materials under very mild conditions ($\leqslant$200 °C). These functional carbon materials can then be designed for applications in crucial fields such as energy storage, biomedicine, separation and catalysis [10]. The idea of HTC can be dated back to 1913, when Bergius first described the hydrothermal conversion of cellulose into coal-like materials [11]. As the development of HTC, recent advances have demonstrated that low value and widely available biomass, including pure carbohydrates (glucose, sucrose, cellulose, starch, lignin, chitosan, *etc.*) and crude plant materials (pericarps, leaves, shrimp shells, pine needles, *etc.*) can be converted into interesting carbon nanostructures using environmentally friendly steps [12–14]. This avoids traditional harsh conditions such as strong acids or bases, high temperature and pressure, metal catalyst and long reaction times [15].

So far, there are few researches employing HTC method to synchronize novel carbon micro/nanomaterials in which microorganisms were used as carbon precursors, although they can easily be obtained from food and pharmaceutical industry waste or large-scale cultivation in laboratory study [16]. Compared with the biomass that have already been applied in the HTC process, especially the crude plant materials, microorganism can inhabit and replicate rapidly under suitable conditions. Therefore, HTC from certain tubular bacteria may provide a technically feasible and economical approach to obtain CMTs besides the already reported methods, such as carbonization of hollow polymer fibers [17], chemical vapor deposition [18] as well as solvothermal synthesis method [19]. It has been demonstrated that, through mild hydrothermal carbonization, polysaccharides can be transformed into highly functional carbonaceous materials with great strength and stability [20]. As pointed out by Vollmer et al. [21], the cell wall of most microorganism consists of polysaccharide (named as peptidoglycan), which indicates the possibility of the cell wall being processed into carbon material via carbonization process. Recently, as Zhu et al. reported [22,23], several microorganisms were used as precursor to fabricate carbon materials for supercapacitors by high temperature inothermal or commonly-used carbonization method. Although most of the final materials prepared in their study were amorphous and had no conformed shape similar to the crude biomass, their study already indicated that microorganisms could have potential applications in material preparation.

As pointed out by Titirici, biomass used in the low temperature HTC could be classified into hard biomass and soft biomass [1]. Generally, the soft biomass, without crystalline cellulose scaffold, was first liquefy during the aqueous hydrothermal treatment process, then carbonized, which finally produces hydrophilic and water-dispersible spherical particles in the size range of 20–200 nm [24]. The microorganism cells obviously belong to the soft biomass, which means that it is difficult to preserve the natural structure of these precursors into the final hydrothermal carbon. To overcome this problem and prepare CMTs by employing HTC on such biomass, further studies are required. In the present study, *Streptomyces sporoverrucosus* dwc-3 (*S. sproroverrucosus* dwc-3), a tubular bacterium for laboratory study was chosen as the carbon precursor for a low temperature HTC research for the first time. Our goal is to preserve the intrinsic morphology of the microorganism during the carbonization process, thereby to develop a template free, low cost and simple one-pot synthetic method to fabricate CMTs.

2. Experimental

2.1. Chemicals and reagents

Chemicals and reagents such as glutaraldehyde (GA), soluble starch, K_2CO_3, NaCl, $FeSO_4{\cdot}7H_2O$, $MgSO_4{\cdot}7H_2O$, K_2HPO_4, and KNO_3 used in this research were purchased from Chengdu Kelong Chemical Reagent Co., Ltd. (China). All chemical reagents were analytical grade and used as received without further purification. The strain of *S. sporoverrucosus* dwc-3 was isolated from soils in Southwest China and cultured in Gause medium, which was described in details during our previous work [25], and also shown in Supplementary material.

2.2. Synthesis of CMTs

After cultivation, the *S. sporoverrucosus* dwc-3 cells (SSDC) were harvested by centrifugation (4000×*g*) with three times wash using deionized water. In a typical CMTs synthesis procedure, the wet SSDC (4–5 g) were dispersed as homogeneously as possible in 2–6% (v/v) GA aqueous solution (30 mL). The suspension was then transferred to a 50 mL Teflon-lined stainless steel autoclave which was then sealed and heated to 180 °C in 2 h. After remaining at 180 °C for 24 h, the product was cooled down to room temperature naturally. The yellowish-brown powders were obtained by filtering, and washed alternatively by deionized water and ethanol till the filtrate was colorless. The final products were then dried at 60 °C in a vacuum oven for 24 h. Note that part of SSDC were directly dried at 60 °C overnight and stored as the control sample for comparison.

2.3. Sample characterization

The morphology of the CMTs products was observed by scanning electron microscopy (SEM, JSM-7500F, Japan) and transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN, USA). The crystalline phase of the products was examined using an X-ray diffractometer (XRD, DX-2700, China) equipped with a rotating anode and a Cu Ka radiation source (λ = 1.54178 Å). The contents of carbon, nitrogen, oxygen and hydrogen were confirmed by elemental analyzer (Carlo-Erba 1106, Italy). Elemental chemical states on the surface of the resulting materials were measured by X-ray photoelectron spectroscopy (XPS, XSAM800, UK). Fourier transform infrared (FT-IR) spectra were obtained from a PerkinElmer IR-843 spectrometer (USA). The chemical environment was obtained by ^{13}C solid-state CP-MAS NMR spectra (^{13}C SSNMR, AV II-400 spectrometer, 500 MHz, Bruker).

2.4. Electrocatalytic evaluation

The electrochemical measurements were carried out at 25 °C with a PARSTAT 2273 Electrochemical System (Princeton Applied Research, USA). Saturation calomel electrode (SCE) and graphite electrode served as reference electrode and auxiliary electrode, respectively. The working electrode was prepared by mixing CMTs with polytetrafluoroethylene (PTFE) and acetylene black at a weight ratio of 80:10:10 to form slurry. The slurry so obtained was loaded on a clean Ni foam (1 cm × 1 cm) using a brush, and dried under vacuum for 30 min at 110 °C. As a reference point, Ni electrode without active material was used as corresponding working electrode for control experiments. In order to express easily and intuitively, the two working electrodes described above