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Turning *gelidium amansii* residue into nitrogen-doped carbon nanofiber aerogel for enhanced multiple energy storage

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ABSTRACT

Three-dimensional (3D) carbonaceous aerogels assembled by one-dimensional (1D) carbon nanofibers (CNF) have attracted much attention, because their unique interconnected and hierarchical porous structure can offer a wide range of applications in environmental remediation and energy storage. Herein, the residue of *gelidium amansii* (mainly endofibers, ~1.6 µm) after extraction of agar were used as precursor to fabricate nanofibrilated cellulose by using facile ultrosonication treatment. The nanofibrilated celluloses are highly engineered nanofibers with average diameter of ~90 nm. Then the 1D cellulose nanofibers could be assembled into 3D nanofiber aerogels after freeze drying. The subsequent pyrolysis in NH_3 and activition could result in the formation of N-doped CNF areogel (N-PCNFA), where the oxygen-containing groups in cellulose macromolecules converted to H_2O, CO, and CO_2. The N-PCNFA with hierarchically porous structure, high surface area (2290 $m^2 g^{-1}$), N-doping, and 3D interconnected channels are beneficial to electrolyte ions and electron transportation. The N-PCNFA displayed high capacity and long-term stability as energy storage material. This work highlights a new strategy in highly efficient utilizing the marine biomass waste for developing low-cost and functional carbon aerogel for multiple energy storage.

1. Introduction

Carbon nanomaterials, including carbon nanotube, carbon nanosphere, graphene, and carbon nanofiber (CNF) etc, have been considered as the promising energy storage materials for lithium ion batteries (LIBs) and supercapacitors (SCs), due to their relatively high electronic conductivity, high specific capacity, accessibility, and excellent stability [1–3]. Particularly, one-dimensional (1D) CNF has been extensively explored for energy storage because of its oriented electronic/ionic transport pathway, excellent mechanical property, and high surface to volume ratio [4,5]. However, the ordinary CNF usually cannot meet the increasing requirement for excellent performance energy storage devices due to its dissatisfactory electrolyte ions and electron transports. Constructing porous structure in CNF with high surface area offer sufficient porous channels and large interface between active sites and electrolyte for promoting the electrolyte ion diffusion, which can achieve the high requirement of energy storage devices [6–9]. Recently, three-dimensional (3D) carbonaceous aerogels assembled by 1D porous CNF have been attracted much attention. The adequate space of hierarchically 3D interconnected CNF-based framework and high length-diameter ratio of 1D CNF could synergistically promote electrolyte ions diffusion and electron transport, further enhancing the energy storage performance.

Generally, the fabrication of such 3D hierarchical porous CNF depends on the pyrolysis of polymer (such as poly(vinyl alcohol), polyacrylonitrile, and polyimide) nanofiber through simple electrospinning synthetics, generating continuous nanofibers with

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controlled size [10,11]. The non-renewable polymer precursors and toxic by-products hinder the sustainable applications of such CNF. Thus, low-cost, sustainable, and large-scale production of 3D porous CNF with cheap and renewable precursors is still a vital research demand. Nowadays, many valuable CNF derived from sustainable biomass have been developed through innovative strategies, which show great potential in energy storage [12–15]. For example, bacterial cellulose is a promising candidate for the fabricating of CNF, opening a green and sustainable biomass-converting method. Lu et al. controllably synthesized a series of 3D porous CNF aerogel with different dimeters using earth-abundant bamboo as precursors [12]. With the fast exploration of ocean, the abundant algae resources, mainly including brown, red, and green algas, have been extensively concerned [16–25]. Similar to bamboo, some of abundant seaweed (~30,000,000 tons per year) contain high cellulose, making them possible to produce CNF aerogel *via* a sustainable route. For instance, *Gelidium amansii* (GA), one of the most abundant red algae species, mainly is composed of mucilaginous materials and endofibers. After the extraction of agar or carrageenan from polysaccharide complexes of the mucilaginous materials, the remaining solid endofibers are cellulose (8%–11%) [26,27]. However, the GA residue shows low value for further utilization at present.

Herein, we used such GA residue (mainly endofibers, ~1.6 μm) as precursor to fabricate nanofibrilated cellulose by using facile ultrosonication treatment, since the ultrosonication process could break the weak macromolecular interfibrillar hydrogen bonding and Wander Waals force. The nanofibrilated celluloses are highly engineered nanofibers with average diameter of ~90 nm. Then the 1D cellulose nanofibers could be assembled into 3D nanofiber aerogels after freeze drying. The subsequent pyrolysis in NH_3 and activition could result in the formation of N-doped porous CNF areogel (N-PCNFA). When used as energy storage material, the important characteristics of N-PCNFA, such as 3D interconnected network, high surface area (2290 $m^2 g^{-1}$), porous structure and N-doping, not only increase the contact surface area of active material and electrolyte to decrease ion diffusion distance, but also enhance the conductivity of electrode material. For instance, as lithium storage material, N-PCNFA exhibits a high specific capacity and good cycling stability (572 $mAh g^{-1}$ at 1 $A g^{-1}$ after 600 cycles), and excellent rate performance (220 $mAh g^{-1}$ at high current density of 10 $A g^{-1}$). It also displays the excellent capacitive behavior (in a three-electrode system, 320 and 248 $F g^{-1}$ at 1 and 100 $A g^{-1}$, respectively) for SCs.

2. Experimental section

2.1. Materials preparation

The GA was firstly decolorized by $NaClO_2$ solution to produce bleached GA pulp, and washed with H_2O to pH = 7. Then, the obtained sample was treated with 1 M KOH solution at 85 °C for 2 h, which has a significant and positive effect on solubilizing the agar from the GA. After filtration, the filtered residue was endofiber (mainly cellulose). To fabricate cellulose nanofiber, the typically ultrasound method was used. The residue was put in a beaker with water, and then the pulsed high-intensity (60 KHz, 300 W) ultrasonication was performed with the water/ice bath for 30 min (setting 50% duty cycle for reducing temperature variation). The nanofibrillated cellulose was obtained, and the cellulose nanofiber/water dispersion was frozen to −70 °C. The freeze-drying was used to dry it to get the cellulose nanofiber aerogel. Then, the cellulose nanofiber aerogel was pyrolyzed at 700 °C for 1 h under the ammonia or nitrogen atmosphere (heating rate: 2 °C min^{-1}) to fabricate the N-doped carbon nanofiber aerogel (N-CNFA) and carbon nanofiber aerogel (CNFA), respectively. The N-CNFA and CNFA were activated by KOH at 800 °C for 1 h (weight ratio of KOH/samples = 4/1) under nitrogen atmosphere and then washed with 1 M HCl and deionized water until pH = 7 to obtain the N-PCNFA and PCNFA, respectively.

2.2. Characterization

Scanning electron microscopy (SEM) images were obtained using a JSM-7001F instrument. Transmission electron microscopy

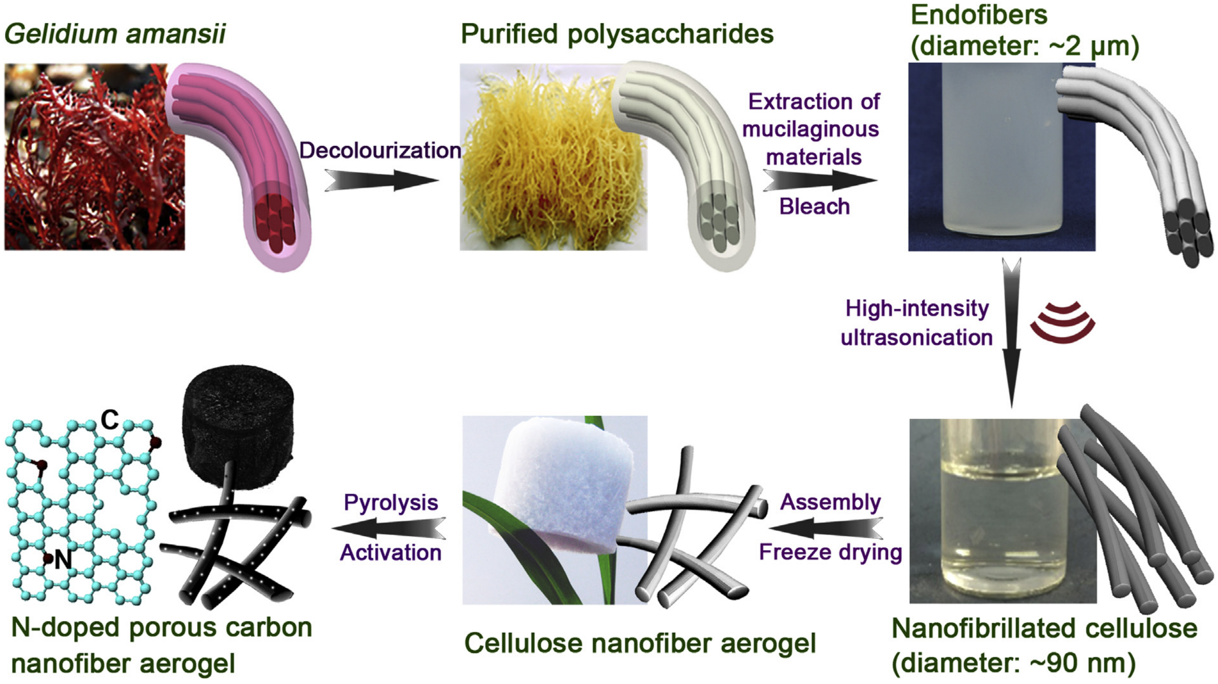

Fig. 1. Schematic illustration on the synthesis process of N-PCNFA. (A colour version of this figure can be viewed online.)