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Nitrogen-doped carbon mesh from pyrolysis of cotton in ammonia as binder-free electrodes of supercapacitors

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A B S T R A C T

Conductive and porous carbon plays critical roles as electrode material for electrochemical energy storage devices, including supercapacitors. Using commonly available biomass cellulous fibers as the raw material to produce porous carbon is a promising approach to achieve high-performance and low-cost electrodes. Herein, carbon microfiber (CMF) membranes were prepared via a direct carbonization method using cotton fiber meshes as precursors. The nitrogen doping content, carbon surface area and pore density could be well adjusted by the carbonization atmosphere and temperature. With CMF membranes as freestanding electrodes in supercapacitors, remarkable electrochemical performances were demonstrated. In particular, the CMF membrane obtained at 800 °C in ammonia (CMFs-800) can achieve a high capacitance of 172 F g^{-1} at the current density of 0.1 A g^{-1}, meanwhile it shows excellent rate capability and superior cycling stability. This study indicates that the pyrolyzed cotton mesh, due to its large pore density, high specific surface area, and heteroatom doping, has potential to be used as cost-effective electrode for supercapacitors.

1. Introduction

Supercapacitors, also known as electrochemical capacitors or ultracapacitors, have sparked great research interest in recent years due to their ultrahigh power density, long cycling stability, improved safety, low maintenance cost and environmental friendliness [1,2]. They have been used as the power source in a number of applications that require pulse power or short charge time, such as portable electronics, digital communication devices and electric vehicles.

Electrode materials play a dominant role in determining the performance of supercapacitors. A variety of delicately designed materials and structures have been investigated as supercapacitor electrodes, among which the most widely reported are porous carbonaceous materials that offer merits such as high electronic conductivity, well-controlled architecture, excellent chemical stability and facile heteroatom doping [3–5]. Most of the reported nanocarbon materials, however, face challenges for large-scale production due to the usage of expensive precursors, the complex fabrication procedures, and the large amount of chemicals used that cause environmental pollution, among others.

Nowadays, sustainable development is a major technology trend [6]. Biomass cellulose and biopolymers provide a sustainable and economic resource for the production of activated carbon because they contain abundant cellulose, hemicellulose, and lignin, and could be converted into carbon materials under high temperature. Up to now, the activated carbons derived from biomass such as loofah sponge [7], banana peel [8], lotus stems [9], coffee grounds [10] and biomass cellulose [11] have been used as electrode materials of supercapacitors and exhibited remarkable electrochemical performance. Cotton, abundant in cellulose, is well known as one of the most important and common commodities in the world. Selecting cotton fiber as the precursor to prepare porous carbon can not only reduce its preparation costs and simplify its preparation process but also achieve mass production. Cotton fiber membrane is endowed with a natural porous network structure composed of interconnected microfibers and the unique structure could be well retained after pyrolysis. It has been reported that cotton-derived carbons have remarkable performance when used as anodes of lithium-ion batteries [12], lithium-sulfur batteries [13] and sodium-ion batteries [14]. Even so, very few studies have reported the usage of cotton-derived carbon as the electrode material of supercapacitors.

In this work, we report a facile process to prepare carbon microfiber (CMF) membranes using cotton fiber meshes as a precursor. The CMFs were prepared by carbonization of cotton in ammonia or argon atmosphere at different temperatures. The nitrogen doping content and CMF architecture could be well adjusted by controlling the carbonization atmosphere and temperature. In particular, the CMF membrane obtained at 800 °C in ammonia (CMFs-800) shows high specific capacitance, outstanding rate capability, and excellent cycling stability, which are attributed to the double layer capacitance resulting from its high specific surface area and high pore density, and the pseudocapacitance

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resulting from appropriate nitrogen doping content. This study opens a novel route to economical production of high-performance carbon electrodes for energy storage devices.

2. Results and discussion

2.1. Morphology, composition and structure of CMFs

Fig. 1(a) shows a photo of cotton plantation. Cotton is planted principally in dry areas around the world with a worldwide production of 24.5 million tons in 2013 and is widely used in textile industry and medical field [15]. In our experiment, the cotton mesh (Fig. 1(b)), made of woven fibers, was purchased from a CVS store. The cotton fibers have a diameter of approximately 20 μm and show characteristic X-Ray diffraction (XRD) peaks of cellulose polymer (Figure S1) [16]. Due to the high content of carbon in cellulose, cotton is considered to be a desirable precursor for preparing activated carbon. During pyrolysis, with the loss of oxygen and hydrogen elements and small amount of carbon atoms, the pellicle size was significantly reduced from 6.5 cm to 3 cm (Fig. 1(b)). The carbonized cotton pellicle exhibited remarkable flexibility (Fig. 1(c)), suitable as electrodes for flexible energy storage devices. As shown in Fig. 1(d) and Figure S2, the carbonized pellicle retained the woven network structure, but the fiber diameter was reduced to a few micrometers, which further confirmed the loss of oxygen and hydrogen elements during pyrolysis.

The crystalline structure of CMFs was analyzed via XRD and Raman spectroscopies. As shown in Fig. 1(e) and Figure S2, the XRD pattern of CMFs shows two broad peaks, a dominant one at around 21° and a minor one at 43°, ascribing to the diffraction from graphite (002) and (100) planes, respectively [17]. The Raman spectra of sample CMFs-800 is shown in Fig. 1(f). There are two prominent peaks at around 1350 and 1580 cm^{-1}, corresponding to the structural defects and disorders in the carbon (D band) and E_{2g} vibration mode of the sp^2-bonded carbon atoms (G band), respectively [18], further suggesting the successful conversion of cellulose into carbon at high temperatures.

X-ray photoelectron spectroscopy (XPS) was studied to determine the chemical composition of CMFs (Fig. 2(a)) and bonding states of nitrogen dopants. The data is summarized in Table 1. The CMFs, including CMFs-argon, CMFs-600, CMFs-700, CMFs-800 and CMFs-900, contain high carbon content, further indicating the successful carbonization of cellulose under high temperature. The four samples pyrolyzed in ammonia environment, CMFs-600, CMFs-700, CMFs-800 and CMFs-900, also contain nitrogen element in addition to carbon and oxygen, while no detectable nitrogen element was found in CMFs-argon, suggesting that nitrogen could be doped into carbon in the cellulose pyrolysis process conducted in an ammonia environment. It was also noticed that CMFs-600, CMFs-700, CMFs-800 and CNFs-900 possessed a much higher percentage of oxygen element than in CMFs-argon. The introduction of oxygen and nitrogen in carbon would enhance the capacitive performance through the pseudocapacitive effect [19]. The functional groups related to these heteroatoms would also improve the wettability of porous carbon surfaces, thus ensuring fully access of these surface area by an electrolyte for a large double layer capacitance. Both effects would contribute to a large capacitance. To clarify the types of bonding configuration of nitrogen introduced in CMFs, high-resolution XPS spectra of N_{1s} peak were analyzed. As presented in Fig. 2(b) and S3, the N_{1s} spectra of CMFs-600, CMFs-700, CMFs-800 and CMFs-900, all can be fitted into four peaks at around 398.5, 400.5, 401.1 and 403.0 eV. They are ascribed to pyridinic nitrogen (N-6), pyrrolic nitrogen (N-5), quaternary nitrogen (N-Q), and oxidized pyridinic nitrogen (N-PO), respectively [20]. With pyrolysis temperature increased, N atoms within the pentagonal ring of polypyrrole (N-5) were progressively converted to N-Q during the carbonization process. N-Q would enhance the conductivity of carbon materials and provide chemically active sites for pseudocapacitive charge storage, thus improving the power density of supercapacitors [21,22]. Therefore, CMFs-800 was considered to be superior to CMFs-600 and CMFs-700 when used as the electrode of supercapacitors.

Fig. 2(d) and (e) show the N_2 adsorption-desorption isotherms and pore-size distribution curves of the CMFs, respectively. The measured pore properties are summarized in Table 2. The pyrolysis temperature and gas used had dramatic impacts on the pore property. The BET surface area for samples CMFs-argon, CMFs-600, CMFs-700, CMFs-800 and CMFs-900 is 23.5, 478.8, 847.3, 1071.9 and 708.2 $m^2 g^{-1}$, respectively. The CMFs-argon merely possesses a low density of mesopores, probably caused by the escape of oxygen and hydrogen at high temperature, while the four samples pyrolyzed in ammonia contain both micropores and mesopores. In particular at a high pyrolyzed

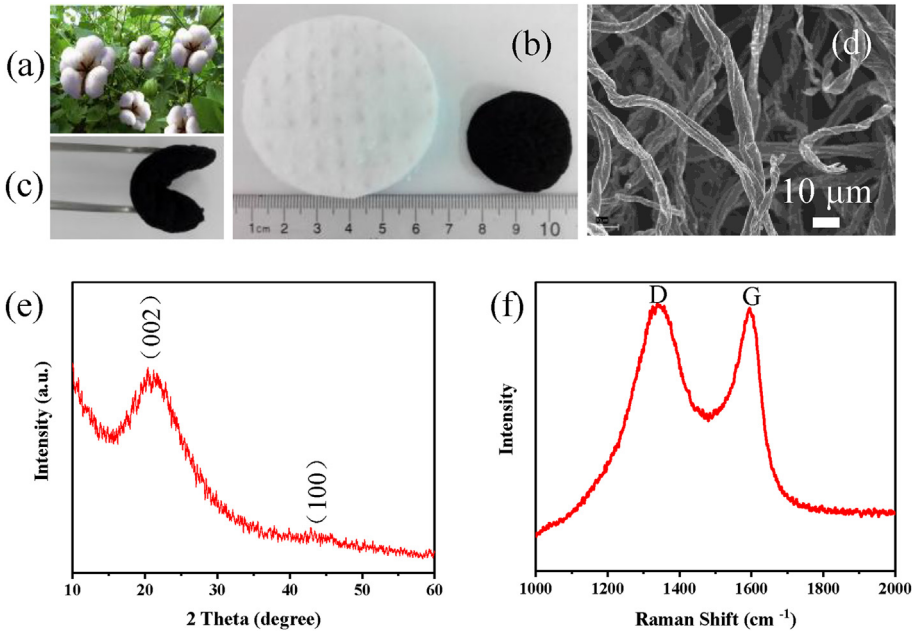

Fig. 1. Photos of (a) cotton plants, (b) the used cotton pellicle (white) and the CMF membrane (black) obtained after pyrolysis, (c) CMF membrane bending test, (d) SEM image, (e) XRD pattern and (f) Raman spectra of the CMFs-800 membrane.