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High-performance supercapacitor electrode from cellulose-derived, inter-bonded carbon nanofibers

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HIGHLIGHTS

- Bonded carbon nanofibers were prepared directly from separate cellulose nanofibers.
- The fiber inter-connection improves charge transfer through the fibrous structure.
- Electrodes from the bonded carbon nanofibers show large capacitance and stability.

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ABSTRACT

Carbon nanofibers with inter-bonded fibrous structure show high supercapacitor performance when being used as electrode materials. Their preparation is highly desirable from cellulose through a pyrolysis technique, because cellulose is an abundant, low cost natural material and its carbonization does not emit toxic substance. However, interconnected carbon nanofibers prepared from electrospun cellulose nanofibers and their capacitive behaviors have not been reported in the research literature. Here we report a facile one-step strategy to prepare inter-bonded carbon nanofibers from partially hydrolyzed cellulose acetate nanofibers, for making high-performance supercapacitors as electrode materials. The inter-fiber connection shows considerable improvement in electrode electrochemical performances. The supercapacitor electrode has a specific capacitance of ~241.4 F g^{-1} at 1 A g^{-1} current density. It maintains high cycling stability (negligible 0.1% capacitance reduction after 10,000 cycles) with a maximum power density of ~84.1 kW kg^{-1}. They may find applications in the development of efficient supercapacitor electrodes for energy storage applications.

1. Introduction

With the excessive consumption of fossil fuels, aggravating environmental pollution and energy crisis have urged the rapid development of new energy technologies from environmentally friendly, sustainable materials [1–3]. Supercapacitor (also called electrochemical capacitors) as a new-type electricity storage device has attracted considerable attention owing to the higher power density, faster charge-discharge rate, and longer cycle lifetime than batteries, which shows great potential for practical applications in portable electronics, hybrid electric vehicles, and stand-by power systems [4–15].

Electrodes play a key role in deciding the electrochemical performances of supercapacitors [2,16]. Nano-scaled carbons (e.g. carbon onions, nanotube, nanofiber, graphene, and quantum dot) [17–20] with large surface area, excellent stability, and electrical

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conductivity have been widely studied as electrode materials for supercapacitors. Among them, carbon nanofibers (CNFs) prepared by the carbonization of polymer precursor nanofibers have attracted interest because of the diversified fiber morphology, large surface-to-volume ratio, and unique fibrous structure. Electrospinning is promising for making polymer precursor nanofibers owing to the advantages in controlling fiber diameter, fiber alignment, and shape of the fibrous mat without the need of a tedious separation and dispersion process and use of harsh chemicals or catalysts [2,21–23].

Recently, our group and other researchers' studies have indicated that electrospun cellulosic nanofibers could be promising materials for making carbon nanofibers [24–27]. Cellulose is an abundant, low cost natural material. In comparison to other carbon precursors, such as polyacrylonitrile, polybenzimidazol, and pitch, cellulose does not emit toxic substance during carbonization. However, direct electrospinning of cellulose into nanofibers is difficult due to the poor solubility of cellulose in most of common solvents [28]. Alternatively, cellulose nanofibers can be obtained by electrospinning of cellulosic derivatives (e.g. cellulose acetate, ethyl cellulose, and methyl cellulose) and by subsequent regeneration [28–35].

In the previous study, we have demonstrated that carbon nanofibers fabricated by electrospinning of a cellulose acetate solution followed by deacetylation and pyrolysis can serve as a high performance supercapacitor electrodes [24]. In a separate study, we have also prepared inter-bonded carbon nanofibers by side-by-side bicomponent electrospinning and proven that fiber-fiber interconnection facilitates charge transfer and increase of capacitance [22]. However, interconnected carbon nanofibers prepared from electrospun cellulose nanofibers and their electrode behaviors have not been reported in the research literature.

Herein, we prove that electrospun cellulose acetate nanofibers after partial hydrolysis in a NaOH solution of ethanol-water mixture can be used as precursor for making inter-bonded carbon fibers. The carbon nanofibers are prepared by one-step pyrolysis of the partially hydrolyzed cellulose nanofibers (NFs) (presented in Fig. 1a, b). Supercapacitor electrode prepared by this bonded carbon nanofibers shows high specific capacitance (~241.4 F g^{-1} at the current density of 1.0 A g^{-1}), excellent cycling stability (99.9% capacitance retention after 10,000 cycles), and large power capability (~84.1 kW kg^{-1}). Ethanol-water ratio in the NaOH solution shows an effect on the morphology of cellulose nanofibers and resultant carbon fibers.

2. Experimental

2.1. Materials

Acetone (Chem-Supply), N, N-Dimethylacetamide (DMAc, Sigma-Aldrich), sodium hydroxide (Merck KGaA), potassium hydroxide (Chem-Supply), high purity nitrogen (4.0, Migomag) and carbon dioxide (Foodgrade, Migomag) were used as received.

2.2. Preparation of cellulose nanofibers

Cellulose acetate (CA) nanofibers were prepared using a purpose-made electrospinning setup [24]. Electrospun CA fibrous mats were then placed in a NaOH solution (0.05–0.2 M) at room temperature for 6–24 h to convert cellulose acetate into cellulose (see Supplementary data Fig. S1). After being rinsed with deionized water, these samples were dried in an oven at 80 °C for 24 h.

2.3. Synthesis of inter-bonded carbon nanofibers

The hydrolyzed cellulose nanofiber samples were stabilized by heating to 240 °C in air at a rate of 3 °C min^{-1}, followed by a 1 h isothermal treatment at 240 °C. The stabilized samples were then carbonized in N_2 flow (1 L min^{-1}) by heating up to 1000 °C with the heating rate of 5 °C min^{-1} and kept at this temperature for 2 h. To activate carbon fibers, the products were then heated in CO_2 at 850 °C for 1.5 h before cooling down in flowing nitrogen (1 L min^{-1}).

2.4. Characterizations

The fibers were observed on a scanning electron microscope (SEM, Supra 55VP). The crystallographic structure was analyzed on a powder X-ray diffractometer (XRD, X'pert Pro MRD XL) equipped with Cu Kα radiation ($\lambda = 0.15{,}406$ nm). Surface chemical composition was determined using an X-ray photoelectron spectrometer (XPS, Kratos AXIS Ultra DLD) equipped with a 165 mm hemispherical electron energy analyzer. Raman spectra were collected on a Renishaw inVia Raman microscope with a 633 nm excitation laser. A 50 × objective lens was used and the laser power was set at around 1.7 mW. Fourier transform infrared spectroscopy (FTIR) was performed using a Bruker VERTEX 70 spectrometer with ATR mode. Differential scanning calorimeter (DSC) was carried out with a TA Q200 equipment at 10 °C min^{-1} heating rate. BET surface area was measured by the nitrogen adsorption method with Quantachrome Autosorb-1 instrument.

2.5. Electrochemical measurement

All electrochemical measurements were carried out on a CHI 760D electrochemical workstation at ambient temperature. The electrochemical tests of individual electrodes were measured with a three-electrode system using 6.0 M aqueous KOH solution as the electrolyte, Pt foil as the counter electrode, and Hg/HgO electrode as the reference electrode. The electrodes were prepared by mixing active material, carbon black (CB), and poly-(vinylidene fluoride) (PVDF) in *N*-methylpyrrolidone at a mass ratio of 80:15:5 to obtain slurry. The slurry was then pressed onto a nickel foam current collector (size: 1 cm × 1 cm; loading: ~2 mg) and dried at 80 °C overnight. The supercapacitor device was fabricated using two electrodes and a piece of filter paper (as separator). The two electrodes were separated by the filter paper, and a 6.0 M KOH aqueous solution was used as the electrolyte. The device was tested in two-electrode model. Electrochemical impedance spectroscopy (EIS) was measured in the frequency range of 10 mHz to 10 kHz at the open circuit voltage with an AC amplitude of 10 mV. The key parameters of the supercapacitor, power density (P) (W g^{-1}) and energy density (E) (J g^{-1}), were calculated using following equations [3,36–39]:

$$C_m = \frac{I \times \Delta t}{M \times \Delta V} \tag{1}$$

$$E = \frac{1}{2} \times C_m \times (\Delta V)^2 \tag{2}$$

$$P_{av} = \frac{E}{\Delta t} \tag{3}$$

where C_m (F g^{-1}) is the specific capacitance of supercapacitor, ΔV (V) is the potential change within the discharge time Δt (s), and M is the total mass of active materials on the two electrodes of the capacitor (g).