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Silica decorated on porous activated carbon nanofiber composites for high-performance supercapacitors

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HIGHLIGHTS

- ACNF-PSs are prepared by electrospinning and steam activation process.
- ACNF-PSs at various PS contents are examined the morphological and textual structure.
- ACNF-PS electrodes showed superior electrochemical performance.
- Improved capacitance was related to ACNF's high surface area and SiO_2's hydrophilicity.

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ABSTRACT

A hybrid of silica decorated on porous activated carbon nanofibers (ACNFs) is fabricated in the form of a web via electrospinning and an activation process as an electrode material for electrochemical capacitors in an organic electrolyte. The introduction of $PhSiH_3$ (PS) into the polyacrylonitrile (PAN) solution induces a porous ACNF structure containing silica nanoparticles (NPs) via the spontaneous sol-gel process of PS by steam in the subsequent physical activation process. These inorganic-organic hybrid composites of porous ACNF containing silica NPs show superior specific capacitance and energy density in electrochemical tests, along with good rate capability and excellent cycle life in an organic electrolyte, which is attributed to the combination of ACNF's high surface area and silica's hydrophilicity. The electrochemical performance decreases with increasing PS concentration, and this trend is consistent with the specific surface area results, which reveal the rapid formation of a double layer.

1. Introduction

Supercapacitors have many attractive characteristics such as high power density, excellent reversibility, environmental protection, and long cycle life [1–3]. Their electrochemical performance largely depends on carbon electrode materials with highly developed surface area and proper pore size distribution because the energy storage mechanism of electric double-layer capacitors (EDLCs) is an electrostatic attraction with charge accumulation at the electrode/electrolyte double-layer interfaces [4]. However, the use of carbon materials in supercapacitors introduces the weakness of low specific capacitance, which limits their further wide application as electrode materials [5]. Therefore, expanding their range of applications by enhancing their electrochemical performance requires nanoporous carbon materials with tailored pore structures and controlled surface properties. Inorganic-organic composite materials/membranes represent an opportunity for the design of materials with improved flexibility, processability, heat-stability, chemical resistance, charge propagation dynamics, and enhanced energy storage capabilities, due to the combination of the merits of inorganic and organic materials [6–8]. Among those inorganic supercapacitor materials, silica (SiO_2) nanoparticles (NPs) offer unique properties such as high surface area (>500 m^2g^{-1}), relatively high differential capacitance (up to 180 μFcm^{-2}), and hydrophilicity [9,10]. However, little research has investigated the application of silica electrodes for electrochemical capacitors, because silica NPs are not a pseudocapacitor oxide capable of storing charge by electron transfer reactions.

In this work, an organic polymer based on the highly spinnable polyacrylonitrile (PAN) and an inorganic material based on phenylsilane ($PhSiH_3$, PS) were combined to prepare inorganic-organic

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hybrid materials with activated carbon nanofibers (ACNFs) and silica by electrospinning, followed by stabilization and activation process. We used PS to generate the porous ACNF structure as well as silica NPs by eliminating organic moieties and spontaneous sol-gel process of PS by steam without the need for any acid/base catalyst in the subsequent physical activation process. The study aim is to gain insight into the nanoporous structure according to the PS content and to examine the electrochemical performance of the inorganic-organic hybrid ACNFs with a silica (ACNF-PS) structure in an organic electrolyte. These inorganic-organic hybrid composites combine the advantages of the high electrical conductivity and large surface area of ACNFs and the hydrophilic property of silica [3,11]. In particular, incorporation of silica into ACNFs increases the hydrophilicity and modifies the polarity of the ACNF-PS composite, which improves the wettability of the carbon matrix between the electrolyte and electrode materials, thereby enhancing the electrochemical performance.

2. Experimental

2.1. Materials and fabrication

PAN, PS, and dimethylformamide (DMF) were purchased from Aldrich Chemical Co. (USA) and used as received. Electrospinning solutions were prepared by dispersing an appropriate amount of PS (5, 10, 20 wt% relative to PAN) in a 10 wt% PAN solution in DMF. The blended solution of PAN and PS was electrospun into nanofibers (NFs) using an electrospinning apparatus. Oxidative stabilization was then performed at 280 °C in air to thermally stabilize the NFs, which were then activated by exposure to 20 vol% steam in a nitrogen carrier gas for 1 h at 800 °C to develop the microstructure of the ACNFs. During this activation process, stabilized NFs shrink in diameter, losing about 50% of its weight. The activated samples, denoted as ACNF-PS5, ACNF-PS10, and ACNF-PS20, indicate concentrations of 5, 10, and 20% PS relative to PAN, respectively, with ACNF without PS also prepared for comparison of the electrochemical properties.

2.2. Characterization

The surface morphology of the nano-structured materials was examined by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4700). The chemical state of the surface was characterized by X-ray photoelectron spectroscopy (XPS) on a VG Scientific ESCALAB 250 spectrometer with an Al Kα X-ray source (15 mA, 14 kV). Transmission electron microscopy (TEM) images were obtained with a Tecnai-F20 system operated at 200 kV. Samples for analysis were prepared on a carbon-coated Cu grid by dip-coating

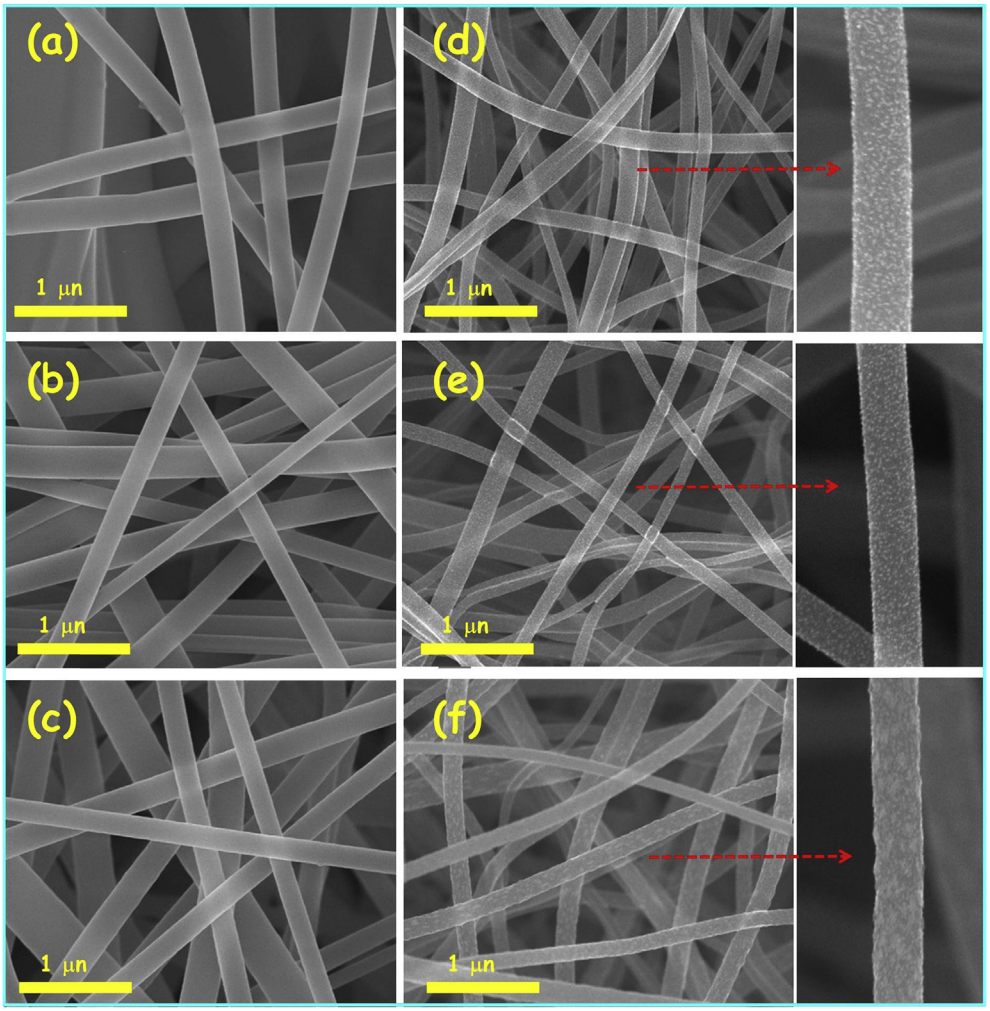

Fig. 1. FE-SEM images of electrospun NFs (a–c) and carbonized NFs (d–f) with three $PhSiH_3$ contents: (a and d) 5 wt%, (b and e) 10 wt%, (c and f) 20 wt%. The red arrows indicate the highly magnified images of an individual fiber. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)