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Freestanding supercapacitor electrode applications of carbon nanofibers based on polyacrylonitrile and polyhedral oligomeric silsesquioxane

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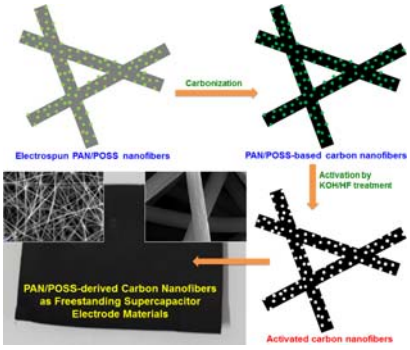
HIGHLIGHTS

- Precursor nanofibers were prepared by electrospinning of PAN/POSS solutions.
- Carbon nanofibers (CNFs) were fabricated by carbonizing the precursor nanofibers.
- KOH and HF treatments were effective for activating CNFs.
- Activated CNFs can serve as self-standing high performance supercapacitor electrodes.

GRAPHICAL ABSTRACT



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ABSTRACT

The microstructures and electrochemical performance of polyacrylonitrile/polyhedral oligomeric silsesquioxane (PAN/POSS)-derived carbon nanofibers (CNFs) were investigated in terms of POSS content (0–60 wt%) and activation process for their potential utilization as freestanding supercapacitor electrodes. For the purpose, a series of CNFs were manufactured by stabilization and carbonization of electrospun PAN/POSS nanofibers. The CNFs were then activated by potassium hydroxide (KOH) treatment to etch carbon and by hydrofluoric acid (HF) treatment to remove the POSS filler. Scanning electron microscopic images and energy dispersive X-ray spectra of PAN/POSS-based CNFs revealed the efficient removal of the POSS filler by KOH and HF treatments. The effect of POSS content on the porous structures of KOH/HF-treated CNFs was also confirmed by the specific surface area and pore size distribution analyses. The electrochemical performance of the CNFs was evaluated by using cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) test. KOH/HF-treated CNFs, which were fabricated from electrospun nanofibers with 40 wt% POSS, were found to have high specific capacitance of 257.7 F g^{-1} at a scan rate of 5 mV s^{-1} and 116.9 F g^{-1} at 100 mV s^{-1}. The GCD results demonstrated that the CNFs have high specific capacitance of 138.7 F g^{-1}, energy density of 12.2 Wh kg^{-1}, and power density of 79.6 W kg^{-1}.

1. Introduction

Supercapacitors, composed of two electrodes with electrolyte in between, are one of the most promising electrochemical energy storage devices, because of their desirable characteristics such as high power

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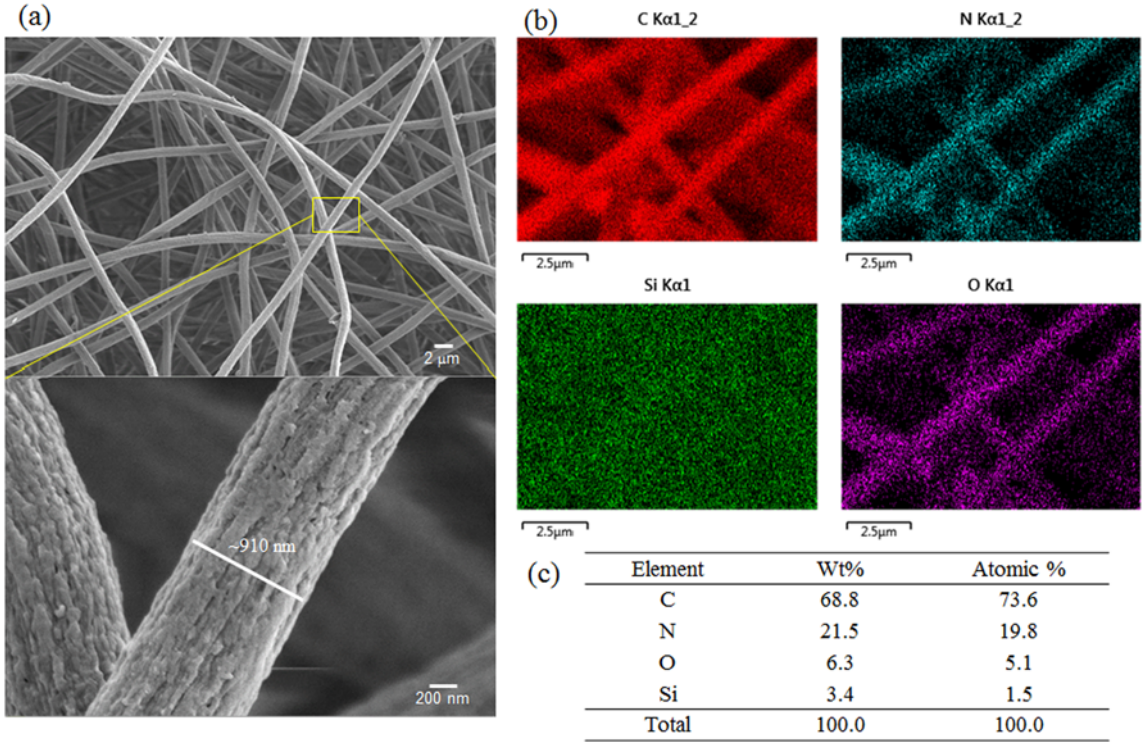
density, rapid charging/discharging rate, superior cycling stability, and wide operating temperature range [1–3]. Therefore, they have been widely used in various applications such as electric vehicles, power back-up, pacemakers, and vehicle airbags [4]. The difference of supercapacitors from conventional capacitors is that ion-conducting electrolytes are used in the supercapacitor instead of dielectrics [5]. There are two kinds of supercapacitors. The first is the electrochemical double layer capacitors storing electrical energy by a charge separation at the electrode-electrolyte interface [6–8]. The second is the pseudocapacitors based on Faradaic pseudo capacitance by incorporating transition metal oxides or conductive polymers to achieve better electrochemical performance of devices [9–11]. Lots of researches have been directed to developing high quality electrodes to improve the electrochemical performance of supercapacitors, which has a great relationship to the specific surface area and pore size distribution of the electrodes [12]. Porous carbon materials with high surface area are considered as the promising supercapacitor electrode materials, because they exhibit high capability for charge accumulation at the electrode-electrolyte interface and are favorable for the fast transport of electrolyte ions [4,13,14].

Polyacrylonitrile (PAN) is a widely used carbon precursor material for supercapacitor electrodes due to its good spinnability, stability during thermal treatments, and high carbon yield [12,15–21]. Variety of methods have been also adopted to activate PAN-based carbon materials to design micro- or meso-pores, for example, CO_2 activation [21], KOH activation [19], incorporating nanofillers [19], mixing with sacrifice polymers [16], and so on.

Polyhedral oligomeric silsesquioxane (POSS) with an empirical formula of $(RSiO_{1.5})_n$, typically composed of an cubic inner core of inorganic siloxane (Si_8O_{12}) and organic substituent moieties (R_8) at each of the eight vertices, is regarded as the smallest possible versions of silica with 1–3 nm in size. POSS has been generally incorporated in polymers as nanofillers to improve the oxidation resistance, mechanical and thermal properties [22–24]. Recently, POSS has attracted more attention and been used in advanced applications. For example, it was added in solid polymer electrolyte membranes of lithium ion batteries to enhance the dimensional stability as well as the ionic conductivity due to the additional free volume formed by the steric effect between POSS groups [25]. Additionally, POSS begins to playing significant role in supercapacitor electrodes. Liu et al. manufactured hierarchically porous carbon structures by a block copolymer-assisted method using POSS as carbon source [22]. The obtained carbon materials possess high specific surface area of >2000 $m^2\ g^{-1}$ and specific capacitance of 210 $F\ g^{-1}$ in 1 M H_2SO_4 aqueous electrolyte at a current density of 0.25 $A\ g^{-1}$ in a symmetrical two-electrode cell. Tang et al. synthesized N-doped nanoporous carbon materials through pyrolysis of copolymer made from octa(aminophenyl)-silsesquioxane (OAPS) and resol, followed by etching silica domains [26]. The symmetric supercapacitor assembled by the electrodes with OAPS to resol ratio of 95:5 in 1 M H_2SO_4 electrolyte exhibited specific capacitance of 230 $F\ g^{-1}$ at 1 $A\ g^{-1}$. However, the above carbon materials must be assisted with conductive additives and binding agents for the final supercapacitor electrode applications.

Electrospinning technique is an efficient method to manufacture nanofiber materials in quantity with uniform structures and high surface areas. After carbonization and activation, the carbon nanofibers (CNFs) as electrode materials can still keep a plane shape and freestanding structure to be used directly [12]. Herein, we have prepared a series of CNFs as freestanding supercapacitor electrodes by using electrospinning of PAN/POSS precursor solutions with different POSS contents, followed by stabilization and carbonization. Then, the pristine CNFs were treated with potassium hydroxide (KOH) to realize chemical activation and with hydrofluoric acid (HF) to remove silica-like residues formed by the degradation of POSS filler. Raman spectra and SEM images were obtained to identify the microstructures and morphological features of the pristine and activated CNFs. The relative amounts of Si atom on the surfaces of CNFs were determined by energy-dispersive X-ray spectroscopy (EDS). Surface areas and pore volumes of CNFs are evaluated from low temperature N_2 adsorption-desorption isotherm results. Electrochemical performance of CNFs, which are manufactured from PAN/POSS precursors with different POSS contents, are evaluated by cyclic voltammetry and galvanostatic charge/discharge method using H_3PO_4-polyvinyl alcohol (PVA) gel as an electrolyte.



(c)

Element	Wt%	Atomic %
C	68.8	73.6
N	21.5	19.8
O	6.3	5.1
Si	3.4	1.5
Total	100.0	100.0

Fig. 1. (a) SEM images, (b) elemental mapping images, and (c) relative elemental composition of as-electrospun precursor nanofibers with 40 wt% POSS.