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Original Research

Preparation of Si-doped and cross linked carbon nanofibers via electrospinning and their supercapacitive properties☆

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ABSTRACT

In this work, Si-doped cross linked carbon nanofibers (Si/CNF) were prepared by electrospinning polyacrylonitrile (PAN) solutions containing polyhedral oligomeric silsesquioxane (POSS) as Si source, followed by thermal treatments. Scanning electron microscope (SEM) observations showed the smooth surfaces of pure PAN nanofibers, while PAN/POSS nanofibers with obviously rough or porous surfaces were obtained with relatively high POSS content. X-ray diffraction (XRD) identified the presence of POSS in the composite nanofibers. After thermal treatments, cross linked Si/CNFs with various morphologies were obtained. Energy-dispersive X-ray (EDX) and X-ray photoelectron spectroscopy (XPS) analyses confirmed the successful incorporation of Si into CNFs. Raman spectra suggested the degree of carbon ordering of Si/CNFs reduced slightly when compared with pure CNF. The obtained nanofibers exhibited typical performances of electric double-layer capacitors (EDLC). The specific capacitance of Si/CNF showed a moderate increase with POSS content and reached a maximum of 175 F/g at 1 A/g with PAN:POSS equal to 100:5. Meanwhile Si/CNFs exhibited excellent cycling stability after 1000 cycles. The influence of POSS on the capacitive performance might be attributed to the combined effects of evolution of morphology, conductivity and surface properties of Si/CNFs.

1. Introduction

Owing to the growing demand for portable systems and electric vehicles, supercapacitors also known as electrochemical capacitors have been attracting intense research interests. As an emerging energy storage device, supercapacitors possess many advantages including long cycle life, high power density, fast charge-discharge process, etc [1–6]. Supercapacitors can be divided into faradaic pseudocapacitors and electric double-layer capacitors (EDLC) based on accumulation mechanism of electrostatic charges. Many efforts have been devoted to carbon-based EDLC due to its prominent merits of large surface area, excellent chemical & thermal stability, reasonable conductivity and low cost [3,4,7–9].

EDLC stores energy via accumulating ionic charges at the interface between electrode and electrolyte [10,11]. Carbon nanofibers (CNFs) involved with electrospinning is a promising type of electrode material for EDLC due to their simple preparation, tunable diameters, high specific surface area and convenient composition [7,8,12–15]. However the practical application of carbon-based EDLC is hampered by the shortage of low energy density. Extensive efforts have been made to improve the energy density [16,17]. Doping is an effective method to improve the performance of carbon-based supercapacitors. In the previous reports, various heteroatoms including nitrogen (N), sulphur (S), phosphorus (P) and silicon (Si), have been doped into CNFs to modify the electron/donor characteristics and increase the surface basic sites [18–22]. Atchudan et al. [23] provided N-doped carbon sheets from fruit extract via hydrothermal-carbonization method with a specific capacitance of 176 F/g at 0.1 A/g. Sun F. and Gao J. [24] reported the preparation of highly N-doped carbon nanospheres which showed fairly high specific capacitance (432 F/g at 1 A /g and 205 F/g at 100 A/g). S-doped hierarchically porous carbon prepared by Yang et al. [25] showed a high capacity of 394 F/g at a current density of 0.5 A/g. Also, co-doped carbon materials have been synthesized for the application in EDLC. Chen et al. [26] studied the rapid preparation of N/S co-doped nanoporous carbon materials. N/P/Si tri-doped carbon which showed a specific capacitance value of 318 F/g (scan rate = 5 mV/s) and excellent cycling stability, has been synthesized by Ramasahayam et al. [27] via microwave assisted one-pot method.

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Table 1
Structure parameters and specific capacitance of the obtained Si/CNFs[a].

Run	Concentration	PAN:POSS	$D_{average}$ of Si/CNF (nm)	I_D/I_G[b]	C_p[c] (F/g)
1	12%	100:0	260	0.967	153
2	12%	100:1	327	0.983	167
3	12%	100:3	286	1.013	170
4	12%	100:5	249	1.002	175
5	12%	100:10	379	1.012	152

[a] Other conditions: room temperature; concentration; working voltage = 18 kV; feed rate = 1.0 mL/h; distance from the end of spinneret to the collector is 15 cm.
[b] calculated based on Raman spectra.
[c] obtained from GCD curves with a current density of 1 A/g.

Polar groups of Si-O-C/Si-O-Si introduced into CNFs could improve the electrochemical performance by modifying the chemical structure and wettability of CNFs [1,8,13]. Yang et al. [28] reported the preparation of composite CNFs containing Si-O-C groups from electrospun polyacrylonitrile/polyphenylsilane nanofibers. The composite CNFs exhibited increased specific surface, high thermal stability and improved electrochemical performance. Using tetraethyl orthosilicate as the pore generator and Si source, porous CNFs containing Si-O-C with a high surface area (up to 1386.9 m^2/g) were prepared. The composite CNFs showed increased specific capacitance in the organic electrolyte [8]. Kim B. H. et al. [29] fabricated silica decorated porous activated CNFs with superior specific capacitance via electrospinning of PAN solutions containing $PhSiH_3$ followed by activation process.

Also the morphology of CNFs shows notable influence on the electrochemical properties. CNFs with cross-linked structures prepared respectively by Lin et al. [3] and Ying et al. [4] exhibited enhanced capacitance due to the reduced contact-resistance. Polyhedral oligomeric silsesquioxane (POSS) which could be deemed as silicon particles with diameters of 1–3 μm, has been used widely to prepare various composites [30–32]. In this work, polar Si-O-C/Si-O-Si structures were incorporated into cross-linked CNFs using POSS as Si source simultaneously pore generator. The morphologies, structures and electrochemical performances of obtained Si/CNFs and Si/CNF were investigated and valuated as the electrode materials of supercapacitors.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, M_w~150000) and *N,N*-dimethylformamide (DMF) were provided by Shanghai Macklin Biochemical Co., Ltd. and Tianjin Zhiyuan Chemical Reagent Co. Ltd., respectively. Aminopropylisobutyl polyhedral oligomeric silsesquioxan (POSS) was from Hybrid Plastics Inc. The chemicals were all used as-received.

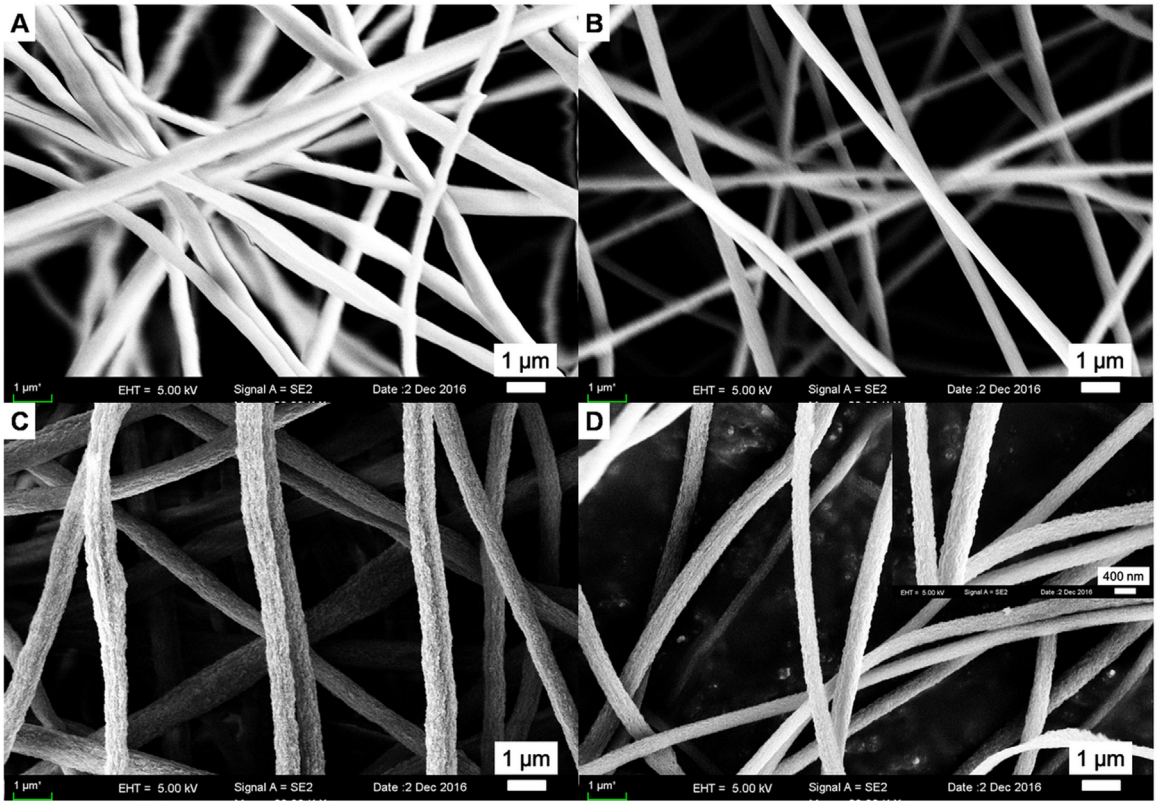

Fig. 1. SEM images of PAN composite fibers with various ratios of PAN to POSS (A: 100:0; B: 100:1; C: 100:5; D: 100:10).