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Enhancement of electrosorption capacity of activated carbon fibers by grafting with carbon nanofibers

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ABSTRACT

The composite films of activated carbon fibers (ACFs) and carbon nanofibers (CNFs) are prepared via chemical vapor deposition of CNFs onto ACFs in different times from 0.5 to 2 h and their electrosorption behaviors in NaCl solution are investigated. The morphology, structure, porous and electrochemical properties are characterized by scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, N_2 adsorption at 77 K, contact angle goniometer and electrochemical workstation, respectively. The results show that CNFs have been hierarchically grown on the surface of ACFs and the as grown ACF/CNF composite films have less defects, higher specific capacitances, more suitable mesoporous structure and more hydrophilic surface than the pristine ACFs, which is beneficial to their electrosorption performance. The ACFs/CNFs with CNFs deposited in 1 h exhibit an optimized NaCl removal ratio of 80%, 55% higher than that of ACFs and the NaCl electrosorption follows a Langmuir isotherm with a maximum electrosorption capacity of 17.19 mg/g.

1. Introduction

As a result of the rise in population rates and the expansion of industrial and agricultural activities, currently many countries in the world are suffering from a shortage of fresh drinking water. Seawater desalination has emerged as an important source of fresh water because about 97% of the earth's water is seawater. The conventional desalination technologies such as membrane separation and thermal separation require either high-pressure pumps, membranes, distillation columns, or thermal heaters, resulting in high capital or operational expenditure [1,2]. Therefore, further exploration of low-cost desalination technology is neccesary.

Electrosorption, also called as capacitive deionization (CDI), has been recently receiving great interests and offers an attractive, energy-efficient alternative to thermal and membrane desalination processes [3–6]. This electrochemical process operates by adsorbing ions in the double layer formed at the electrode surface by applying a low direct current (DC) potential (normally less than 2 V) and exhibits several advantages, such as high capacity, no secondary waste and good reversibility which render the electrosorption process attractive for water desalination. The efficiency of electrosorption strongly depends upon the properties of electrode materials. Conventionally, activated carbon (AC) materials including AC powders [7–9], AC sheets [10], AC cloths [11–14] and AC fibers (ACFs) [15,16] have been widely used as electrosorption electrodes due to their large surface area, high chemical stability, relatively low cost and environmental friendliness. However, intrinsic drawbacks of conventional AC electrodes for electrosorption have been encountered recently, such as irregular pore structures and high mass transfer resistance. In order to improve the desalination capacity, two strategies are taken into consideration: the exploration of novel electrode materials such as carbon aerogels (CAs) [17–19] with small (<50 nm) interstitial pores, ordered mesoporous carbons (OMCs) [20–23] with regular mesopore arrangement, carbon nanofibers (CNFs) or carbon nanotubes (CNTs) with high mechanical strength [24,25] and graphene with remarkable electrical conductivity [26–28]; the modification of AC materials by strong acid oxidation, alkaline treatment, alkoxides reaction [29–31] or the combination with nanoscale materials [32,33]. Though, in the latter method, the electrosorption performance of AC materials is significantly enhanced after modification, chemical reaction to increase the adsorption sites may easily introduce other impurities even toxic substances and damage the mechanical strength and electrical conductivity of the pristine ACs. The composite electrodes proposed by Dai et al. [32,33] were fabricated by directly mixing ACs and CNTs while the uniform distribution of CNTs within ACs is difficult to obtain and the contact resistance between ACs and CNTs is innegligible. In this paper, we use chemical vapour deposition (CVD) method to deposit CNFs onto ACFs to form ACF/CNF composite materials. Such a method can form good contact between CNFs and ACFs. The ACF/CNF composite materials are employed as electrosorption electrodes and exhibit

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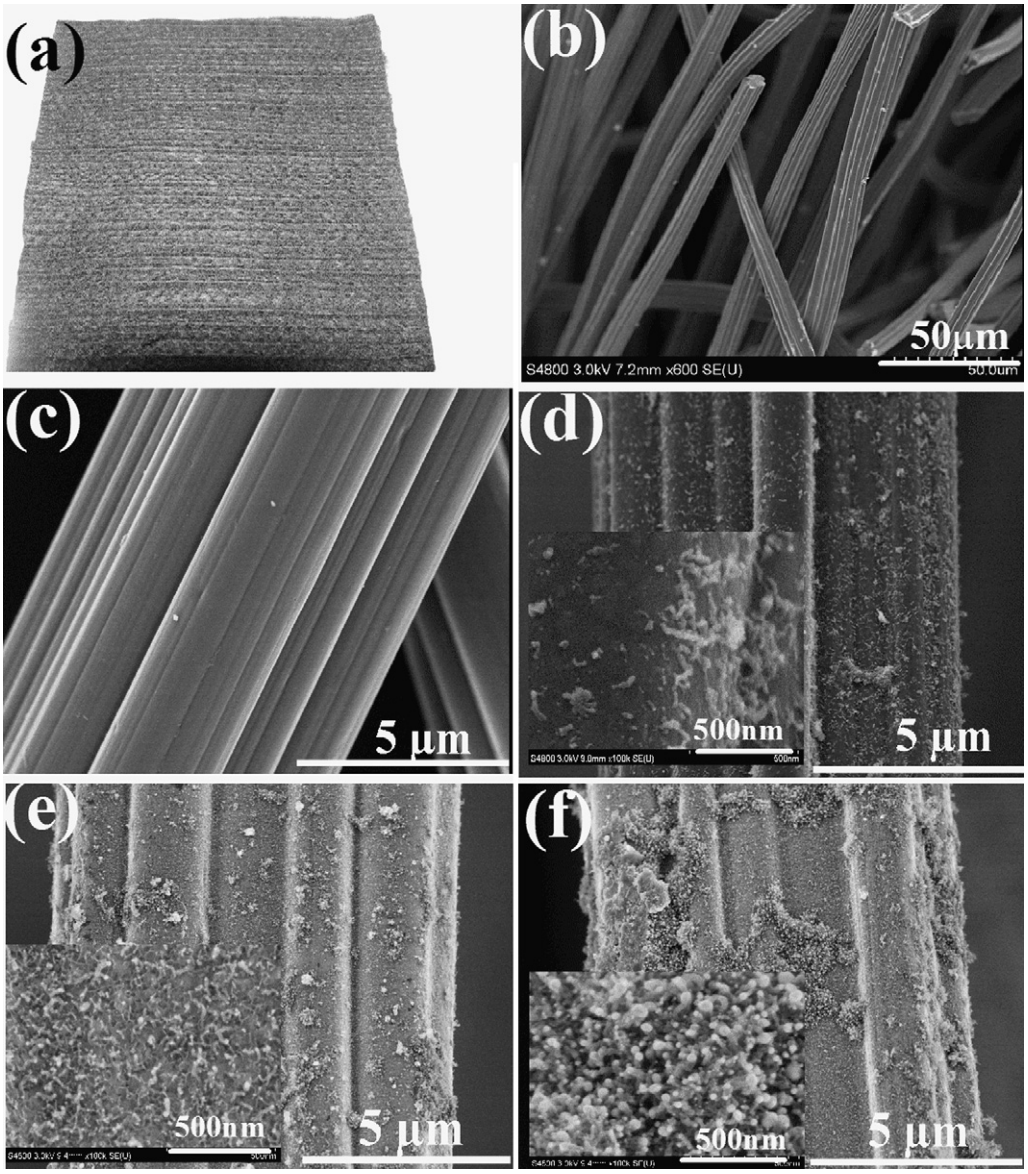

Fig. 1. (a) Optical photograph of ACF cloth (dimensions: 80 mm × 80 mm); (b) and (c) FESEM images of ACFs; (d–f) FESEM images of ACFs/CNFs-0.5 h, ACFs/CNFs-1 h and ACFs/CNTs-2 h. Insets are corresponding high magnification images.

highly enhanced efficiency to remove sodium chloride (NaCl) from water by comparing with the pristine ACFs.

2. Experimental

2.1. Preparation of ACFs/CNFs

ACF films (80 mm width × 80 mm length × 3 mm thickness) were purchased from Nantong Senyou Carbon Fiber Co. Ltd., China. The ACFs were washed by deionized water, and then dried at 373 K before use. Subsequently, the ACFs were immerged in a 300 mL Ni–Al catalyst precursor solution with $Ni(OH)_2$ and $Al(OH)_3$ obtained by an in situ chemical co-precipitation method and the molar ratio of Ni–Al was 4:1 [34]. The reduction of the Ni–Al catalyst was performed in the thermal CVD system at 823 K for 30 min with a hydrogen gas flow rate of 100 mL/min. In situ growth of CNFs was carried out on the surface of ACFs by introducing acetylene and hydrogen mixture gas into the CVD chamber at a flow rate of 50 and 100 mL/min at 823 K, respectively. The ACF/CNF electrodes with CNFs deposited in 0.5, 1 and 2 h (named as ACFs/CNFs-0.5 h, ACFs/CNFs-1 h and ACFs/CNFs-2 h) were obtained. The Ni–Al catalyst particles were removed before electrosorption experiment by immersing the electrodes in acid solution.

2.2. Characterization

The surface morphology and structure were characterized by field emission scanning electron microscopy (FESEM, JEOL-4700), transmission electron microscope (TEM, JEM-2100) and Raman spectroscopy (Renishaw inVia, resolution: 1 cm^{-1}), respectively. The contact angles of water on the surface of electrodes were measured by the contact angle goniometer (JC2000D, Powereach) using digital micrographs of deionized water droplets. The Brunauer–Emmett–Teller (BET) specific surface area was determined by the surface analyzer (Quantachrome, O2108-KR-1) using N_2 as adsorbate at 77 K. The potential sweep cyclic voltammetry (CV) measurement was examined in 1 M NaCl solution by using Autolab PGSTAT 302N electrochemical workstation in a three-electrode mode, including a standard calomel electrode as reference electrode and a platinum foil as counter electrode.