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## Enhancing capacitive deionization performance of electrospun activated carbon nanofibers by coupling with carbon nanotubes

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### ABSTRACT

Capacitive deionization (CDI) is an alternative, effective and environmentally friendly technology for desalination of brackish water. The performance of the CDI device is highly determined by the electrode materials. In this paper, a composite of carbon nanotubes (CNTs) embedded in activated carbon nanofiber (ACF) was prepared by a direct co-electrospinning way and subsequent CO<sub>2</sub> activation. The introduction of CNTs can greatly improve the conductivity while the CO<sub>2</sub>-mediated activation can render the final product with high porosity. As such, the hybrid structure can provide an excellent storage space and pathways for ion adsorption and conduction. When evaluated as electrode materials for CDI, the as-prepared CNT/ACF composites with higher electrical conductivity and mesopore ratios exhibited higher electrosorption capacity and good regeneration performance in comparison with the pure ACF.

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### 1. Introduction

In recent years, water crisis has swept the globe and resulted in a lot of emergency threats for humans that are related to health, environment, economy and politics [1,2]. In response to these threats, several techniques including reverse osmosis, multistage flash distillation and electrodialysis have been developed in 50 years to produce purified fresh water from abundant seawater and brackish water [3,4]. However, these techniques are still insufficient to solve such great global threats in an economic manner [5]. Therefore, capacitive deionization (CDI), as a new robust, energy efficient and cost effective alternative strategy for desalination, has drawn a lot of attention [6,7]. According to the electrical double layer (EDL) theory, carbon materials are the most promising electrode materials because of their high adsorption capacitance and readily availability, such as carbon aerogels [8–10], activated carbon [11,12], activated carbon cloth [13], mesoporous carbon [14,15], carbide derived carbon [16–18], carbon nanotubes (CNTs) [19,20] and graphene [21,22]. The CDI plants equipped with high performance carbon electrodes will present remarkably both high salt removal and energy efficiency, specially

for brackish water [7,23,24]. According to the electrosorption mechanism and kinetics, porous carbon with good electrical conductivity, hierarchical pore distribution and high specific surface area is the key for high CDI performance [25,26]. In addition, considering the negative effect of non-conducting and pore-blocking polymer binder, self-sustainable carbon materials are more preferred for large scale CDI. Hence, some binder-free carbon materials, carbon nanotube sponges [27] and sponge-templated graphene [28], were fabricated and present higher electrosorption capacity due to the continuous monolithic structure for higher solid phase conductivity and controllable pore size distribution. Nevertheless, some intrinsic problems, such as low mechanical properties, combined with high cost, have limited the practical use of the concerned carbon materials as the electrode materials in CDI.

Electrospinning, an electrostatically induced self-assembly technology for the fabrication of ultra-fine nanofiber webs, recently has been demonstrated to be able to fabricate high performance functional activated carbon nanofiber (ACF) for energy storage, structure strengthening, catalyst supports, and many other applications [29,30]. In light of the good monolithic structure, high electrical conductivity, and controllable pore size distribution of electrospun ACF, it is obviously expected to have a high electrosorption capacity for CDI, which has been partly demonstrated recently by our group [25,31,32]. As a promising alternative for CDI electrode, the electrospun ACFs feature high specific surface

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area and tuned pore size distribution for higher electrosorption capacity compared to other traditional materials [25]. Nevertheless, the limited diffusion rate of hydrated ions within micropores, which contributed to most of the specific surface area of carbon nanofibers, could restrain the full access of hydrated ions onto the electrode and then resulted in a low apparent capacitance.

To our knowledge, the mesopore ratio of the CDI electrode materials is one of the key factors for a higher electrosorption capacity and ion sorption–desorption speed, which is significant for large-scale industrial applications of CDI [33,34]. Carbon nanotubes, as a novel one-dimensional carbon material with extremely high electrical conductivity and abundant easy accessible surface area, have already shown high electrosorption capacity and efficiency in CDI applications according to the literatures [27,35].

In this work, CNT/ACF composite was prepared by a direct electrospinning way and subsequent heat treatment and CO<sub>2</sub> activation at 800 °C. It is found that CNTs are successfully embedded in the ACF framework and a large quantity of hierarchical pores is created on the ACF surface, which not only increases the conductivity of CNT/ACF but also provides an excellent storage space and pathways for ion adsorption and conduction. Compared with pure ACF, the as-fabricated CNT/ACF composite electrode shows a higher desalination capacity of 6.4 mg g<sup>-1</sup> and an excellent current efficiency of 25% for CDI at a working potential of 1.2 V.

## 2. Experimental

### 2.1. Preparation of CNT/ACF

Polyacrylonitrile (PAN,  $M_w = 150,000$  g mol<sup>-1</sup>, Aldrich Chemical Co., USA) was pre-dissolved in dimethylformamide with a ratio of 10 wt.% and then a certain amount of multi-walled carbon nanotubes (5 wt.% vs. PAN) were added. The mixture was stirred at 80 °C for 6 h and further ultrasonicated to obtain a homogeneous CNT/PAN suspension. The web-like CNT/PAN fibers were made by a home-built electrospinning apparatus at room temperature. Fig. 1a shows the schematic representation of the electrospinning setup in this study. The CNT/PAN suspension solution was subsequently loaded into a 10 mL glass syringe with a hypodermic needle (the inner diameter is 0.2 mm). The applied electrospinning voltage, the distance between the needle tip and the collector and the feeding rate of the CNT/PAN suspension solution were 22 kV, 15 cm and 0.8 mL h<sup>-1</sup>, respectively. Then, the web-like CNT/PAN fibers were pre-oxidized from room temperature to 280 °C and held for 2 h in air with a flow rate of 300 cm<sup>3</sup> min<sup>-1</sup>, thereafter, further heated to 800 °C in N<sub>2</sub> for 2 h (200 cm<sup>3</sup> min<sup>-1</sup>), and maintaining the final temperature (800 °C) for 1 h in CO<sub>2</sub> (150 cm<sup>3</sup> min<sup>-1</sup>) to obtain the CNT/ACF composites material. For

comparison, the pristine ACF webs were also prepared as previously reported [31].

### 2.2. Characterization

The electrical resistance of ACF and CNT/ACF were measured using a four-point probe meter (Keithley, 2400). Then the conductivity was calculated by the equation  $\sigma = \frac{I}{V \cdot \delta \cdot F(D/S) \cdot F(\delta/S) \cdot F_{sp}}$ , where  $\sigma$  is the electrical conductivity (S m<sup>-1</sup>),  $I$  is the current (A),  $V$  is the voltage (V), and  $\delta$  is the thickness of the electrode (m),  $D$  is the diameter of the electrode (m),  $F(D/S)$ ,  $F(\delta/S)$  and  $F_{sp}$  are the correction factor of the diameter of the electrode, the thickness of the electrode and the distance of probe, respectively. Field emission scanning electron microscopy (FESEM, FEI, Nova 450) and transmission electron microscopy (TEM, FEI TecnaiG20, 200 kV) were carried out to observe the surface morphologies of pure ACF and CNT/ACF composites. The specific surface area and pore size distribution were measured by nitrogen adsorption/desorption technique at 77 K (Micromeritics, ASAP2020).

Prior to the measurements, all the samples were degassed at 523 K for 5 h in a vacuum line. The Brunauer–Emmett–Teller (BET) technique was used to calculate the total specific surface area ( $S_{BET}$ ) from the nitrogen adsorption–desorption data. The total pore volume ( $V_{total}$ ) is calculated from the amount adsorbed at a relative pressure ( $P/P_0$ ) of 0.99, and the micropore volume ( $V_{micro}$ ) and the micropore surface area ( $S_{micro}$ ) are calculated by  $t$ -plot model. The pore size distribution plot is derived from the desorption branch of the isotherm based on the BJH model. The electrochemical impedance spectroscopy (EIS) of ACF and CNT/ACF was investigated with a wide frequency range from 0.01 Hz to 100 kHz in a typical three-electrode system using an electrochemical workstation (Bio-logic Science Instrument, France). An Ag/AgCl electrode, a platinum electrode and 1 M NaCl solution were used as the reference electrode, the counter electrode and the electrolyte, respectively.

### 2.3. CDI measurements

The CDI experiments were performed in a continuous recycle system, including a CDI cell, a peristaltic pump (Longer BT100-2J, China), an electrochemical workstation (CHI760E, Shanghai Chenhua, China), an ion conductivity meter (ET915, eDAQ TECH, Australia) and a water tank (Fig. 1b). Two CNT/ACF electrode materials with an area of 45 × 55 mm<sup>2</sup> were directly attached to the current collector (graphite paper) and separated by an insulated rubber spacer. For each experiment, the conductivity variation of the NaCl solution was continuously monitored online and measured at 298 K using the ion conductivity meter. In the present work, the electrosorption capacity ( $Q$ , mg g<sup>-1</sup>) was defined as the adsorbed

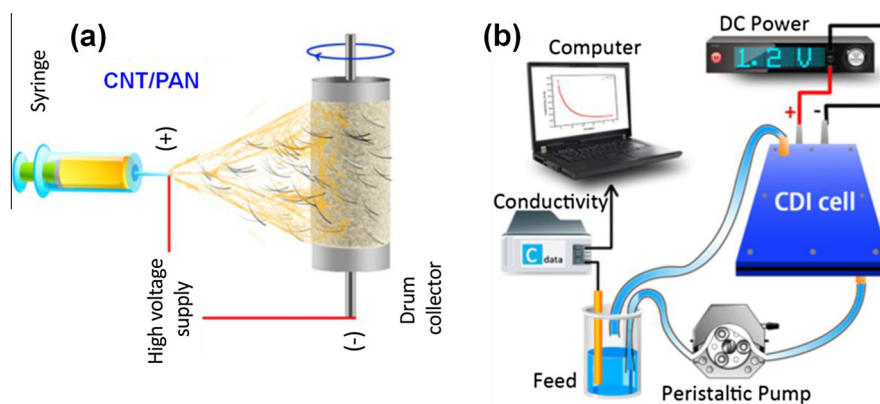


Fig. 1. Schematic diagram of the synthesis and electrospinning process (a) and the CDI set-up (b).

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