



Fabrication and characterization of TiO₂-NTs based hollow carbon fibers/carbon film composite electrode with NiO_x decorated for capacitive application



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HIGHLIGHTS

- Applied TiO₂-NTs array as carrier for capacitive application.
- Designed a unique structure consisted of TiO₂-NTs, HCFs and CF layer.
- Discussed impacts of Ni addition on the capacitive performance of composite electrode.

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ABSTRACT

This work designs a novel structure of TiO₂ nanotubes (TiO₂-NTs) based hollow carbon nanofibers (HCFs)/carbon film (CF) composite electrode with NiO_x decorated for capacitive deionization application. The TiO₂-NTs array is obtained through anode oxidation method on the titanium substrate, while the HCFs/CF is synthesized by thermal decomposition of a mixture of C₆H₁₂O₆ and Ni(CH₃COO)₂·4H₂O inside the nanochannels and over the caps of TiO₂-NTs array, then followed by carbonization and HNO₃ activation. The nickel possesses multi-functional effects during the synthesis process as carbon catalyst (Ni(II)), molecule binder (NiTi) and pseudo-capacitance supplier (NiO_x). FE-SEM, XRD, Raman spectroscopy and water contact angle measurement reveal a uniform carbon distribution, favorable nickel dispersion, high stability and ideal hydrophilicity for this structure. With the addition of C₆H₁₂O₆ and Ni(Ac)₂·4H₂O controlled at 10% (wt) and 2% (wt), respectively, a composite electrode with specific capacitance of 244.9 F·g⁻¹, high oxygen evolution potential of 2.15 V and low water contact angle of 41.77° is obtained as well as minimum polarization impedance and efficient capacitive ability, which exhibits promising applications for practical employment.

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1. Introduction

Growing water pollution and fresh water shortage have stimulated a considerable interest in desalination technologies of brackish water [1]. Currently, traditional separation techniques including reverse osmosis, multi-stage flash distillation, ion exchange and electrodialysis are widely used in water desalination, but it is well-known that these techniques produce high energy consumption, high cost and secondary pollution [2]. Capacitive

deionization (CDI) is a promising electrosorption technology which aims at removing charged ions from the salty solution and store them within the electrical double layers (EDL) formed at interface between the solution and porous electrodes [3–5]. Such captured ions can be further released when the charge induced on the electrodes is cancelled and simultaneously the energy employed to create the electrode/electrolyte interface can be recovered [6,7].

According to the principle of CDI process, the electrosorption capacity is closely dependent on the properties of porous electrode, such as pore structure, conductivity and specific surface area [8,9]. Therefore, carbon based materials including activated carbon [10], carbon aerogel [11] carbon nanofiber [12], carbon nanotubes [13] and graphene [14] are often employed as electrodes due to their high specific surface area, large pore volume, good conductivity and

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chemical stability. Among porous carbons, activated carbons (ACs) are by far the commercially most commonly used and usually the most cost efficient materials for scale applications [15]. However, the AC based CDI often suffers a low capacitance due to the strong hydrophobicity and the presence of micropores with pore size less than 0.5 nm which are not contribute to the CDI process [16]. In this case, one effective solution is the incorporation of finely dispersed metal oxides to the carbon material to offer an extra faradaic pseudocapacitance [17]. It has been extensively reported for applications such as catalytic activity [18], supercapacitor [19] and lithium batteries [20], but merely for water reuse. Another method is nitric acid treatment for it's a simple, yet efficient way to introduce oxygen containing functional groups and modify hydrophilicity of carbon materials and has been widely investigated [21].

The current collector is regarded as the other important unit for CDI electrodes. It is a common method to assemble an electrode by mechanically pressing capacitive materials that mixed with electroconductive binders onto a current collector sheet [22]. However, only a few materials applied as current collectors have been reported on the synthesis process for capacitive application [22–24], and the weak interaction force between the conductive substrate and the capacitance layer have caused concerns for practical applications. In view of this, the designing and optimizing of electrode structure for CDI process is much necessary. Due to the good hydrophilicity, larger specific surface area and high orientation and uniformity, the vertically aligned TiO₂ nanotubes (TiO₂-NTs or TNTs) in situ growing on Ti substrate is considered as excellent carriers for the further loading of functional materials [25–27]. The TiO₂-NTs have been applied in diverse environment related fields such as electrochemical oxidation [28], photochemical catalysis [29] and gas sensors progress [30]. Through simple method, it can act as a hard template to prepare carbon based materials like hollow carbon fibers (HCFs) [31]. But to today, using TiO₂-NTs as capacitor carriers for CDI process has rarely been reported. Herein, we have designed a novel structure of CDI electrode by selecting glucose solution with certain ratio of nickel acetate (NiAc₂) as a precursor, then induced them into columnar pore channels of TiO₂-NTs and cast a liquid film above the nanotubes. A TiO₂-NTs based and NiO_x decorated active carbon film (ACF) capacitor with HCFs embedded in the TiO₂-NTs as a structure bonder would shape up after carbonization and nitric-acid activation. The structure and morphological properties of the electrodes have been characterized by structural and spectroscopic techniques and the capacitive behavior has been elucidated by electrochemical and deionization experiments.

2. Experimental

2.1. Synthesis of TiO₂ nanotube arrays

TiO₂ nanotube arrays were prepared by anode oxidation according to our earlier work [28]. First, the titanium sheets (0.5 mm thick, 99.9% purity) were polished and ultrasonically cleaned in distilled water and acetone successively. Then they were etched in 18% hydrochloric acid at 85 °C for 30 min to remove the oxide layers. The etched titanium sheets were anodized in an electrolyte (0.075 M KF, 0.075 M HF and 1 M H₂SO₄) at 20 V for 60 min in a two-electrode configuration with a stainless steel cathode (spaced 1.2 cm). After anodization, the as-prepared TNTs were annealed at 500 °C in oxygen ambient for 3 h with a cooling rate of 1 °C/min to obtain stable nanotubes.

2.2. Preparation of TiO₂-NTs/HCF/CF composite electrode

As shown in Table 1, four precursors labeled N-1, N-2, N-3 and N-

4 were obtained by dissolving 10 g glucose to 100 mL Ni(CH₃-COO)₂·4H₂O aqueous solution (5 g·L⁻¹, 10 g·L⁻¹, 20 g·L⁻¹ and 40 g·L⁻¹), respectively [31]. First, the TiO₂-NTs arrays on Ti substrate were placed in a glass reaction kettle, with the precursor in a constant pressure funnel. After evacuating, the funnel cock was opened, and the nanochannels of the TiO₂-NTs were subsequently filled with precursor dominated by the atmospheric pressure. Second, after proper cleaning, a certain volume of precursor was dropped on the TiO₂-NTs top surface to form a homogeneous liquid film. After drying at room temperature for 12 h, the sample was kept in vacuum for 12 h at 60 °C. This step was repeated to control the thickness of the carbon film. Third, the sample was heated in air for 2 h at 200 °C, and subsequently calcined at 600 °C with a heating rate of 1 °C·min⁻¹ in N₂ atmosphere for 3 h. The TiO₂-NTs/HCF/CF composite electrode was obtained after slow cooling to room temperature, labeled CN-1, CN-2, CN-3 and CN-4 in consistent with N-1, N-2, N-3 and N-4. Last, the sample was treated by 5 M nitrite acid solution for 24 h at 50 °C to modify its hydrophilic ability.

2.3. Characterization

Scanning electron microscopy (SEM) and EDS were recorded with a Quanta 250 F SEM filed emission scanning electron microscope with primary electron energy of 20 KV. Raman spectra were performed on an Aramis spectrometer at 532 nm. The sample crystallization behavior was examined using an X-ray diffraction meter using Cu K_α radiation (XRD, D8 Advance, Bruker Inc., Germany). The contact angles of droplets on the electrodes were tested using a goniometric method (DSA30, KRUSS).

The CV, EIS and LSV were evaluated on a CHI660e (CH Instruments, Inc.) electrochemical workstation. CV measurements were executed in the potential range of 0–1 V at a potential scan rate of 50 mV·s⁻¹ in 1 M Na₂SO₄ solution. EIS measurements were carried out in the frequency range from 100 kHz to 0.1 Hz in 1 M and 0.1 M Na₂SO₄ solution. LSV (Linear Sweep Voltammetry) was conduct from 0.7 V to 2.8 V with scan rate of 2 mV·s⁻¹. All of CV, EIS and LSV measurements were performed with a three-electrode system (with an effective surface area of 1 cm² as the work electrode, while a platinum sheet electrode and an SCE were applied as the auxiliary and reference electrodes, respectively).

2.4. Desalination test

To measure the desalination performance of electrodes, batch-mode experiments were conducted in a cell with a dimension of 5 cm (length) × 1.6 cm (width) × 5 cm (height). The conductivity of 100 μs·cm⁻¹ Na₂SO₄ solution in the test was 60 mL. The loading materials of the electrodes were controlled around 5 mg·cm⁻² – cast 400 μL precursor on the electrode surface (5 cm × 5 cm) by 10 times. The electrodes were placed face to face at both sides with a distance of 1 mm and connected with a direct-current (DC) power supply. The DC power supply maintained a constant voltage at 1.6 V during CDI process.

In our experiments, the desalination ratio was calculated according to Eq. (1):

$$\text{Desalination ratio (\%)} = (C_0 - C_1)/C_0 \times 100\% \quad (1)$$

where C₀ is the initial Na₂SO₄ conductivity (μs·cm⁻¹), C₁ is the final Na₂SO₄ conductivity (μs·cm⁻¹).

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