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Carbon nanotube/hematite core/shell nanowires on carbon cloth for supercapacitor anode with ultrahigh specific capacitance and superb cycling stability

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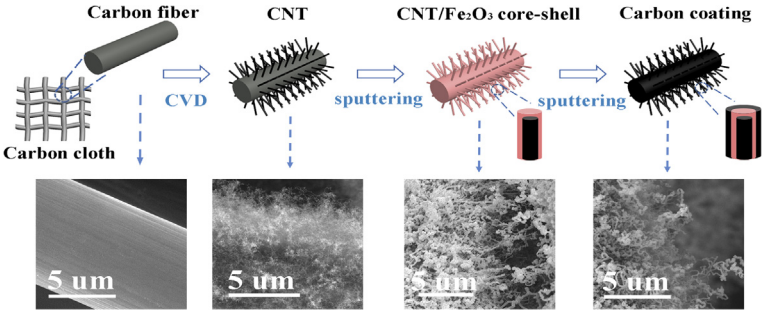
HIGHLIGHTS

- Sandwiched core–shell carbon nanotubes/hematite@carbon arrays were fabricated.
- The conformal coating of hematite and carbon were achieved by magnetron sputtering.
- The composite electrode exhibits high specific capacitance and high stability.

GRAPHICAL ABSTRACT



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ABSTRACT

Rationally designed carbon-based conductive nanostructures are highly demanded to improve the electrochemical performance of hematite-based supercapacitors. In this research, we have successfully designed and synthesized three-layer sandwiched core–shell carbon nanotubes/Fe_2O_3@carbon arrays on carbon cloth substrate via commercially available magnetron sputtering and chemical vapor deposition methods. The carbon nanotube core (prepared by chemical vapor deposition) and the carbon shell (prepared by magnetron sputtering) both can improve the specific surface area and electrical conductivity of Fe_2O_3 (prepared by magnetron sputtering), restrain the active materials and thus enhance its electrochemical performance and long-term stability. X-ray diffraction and Raman results demonstrate the obtained hematite is α phase. Scanning electron microscopy and high-resolution transmission electron microscopy images indicate the Fe_2O_3 and carbon shell are conformally coated on the carbon nanotube core. Consequently, under the optimal mass of Fe_2O_3 and carbon shell, the carbon nanotube/Fe_2O_3@carbon composite electrode exhibits a high specific capacitance of 787.5 F g^{-1} at the scan rate of 5 mV s^{-1} and a high stability (92% of the initial capacitance remains after 7000 cycles). The remarkable performance of these binder-free carbon cloth/carbon nanotube/Fe_2O_3@carbon electrodes suggest their huge potential use as negative electrode material for high performance supercapacitors.

1. Introduction

Supercapacitor (SC), also call electrochemical capacitor (EC), with excellent performance such as superior power density, fast

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recharge capability and long-cycle lifetime, wide range of operating temperature (−40 to −70 °C), environmental friendliness and high safety [1–5], has attracted much attention in recent years and will be a promising candidate energy storage device in many applications such as hybrid electric vehicles, back-up power devices, portable and wearable electronics [6–9]. However, supercapacitor suffer from its low energy density and need further improvement from its electrode materials and device structures [10–12]. Asymmetric supercapacitor (ASC), consisting of carbonaceous anode material as the power source and pseudocapacitive cathode material as the energy source, has a wider working voltage window and deliver a considerable high energy density as well as power density [13,14]. However, the low specific capacitance of carbonaceous anode materials cannot match the high specific capacitance of pseudocapacitive cathode materials, thus severely limiting the energy density of ASC. Therefore, it is highly valuable and significant to explore the new and state-of-art anode materials with high specific capacitance.

So far, many anode materials such as MoO_{3-x} [23], Co_9S_8 [24], FeO_X [25,26], V_2O_5 [27], VN [28], have been investigated. Among them, hematite (Fe_2O_3) has attracted considerable attention owing to its large theoretical specific capacitance (3625 F g^{-1}), suitable working voltage window, low cost, abundance, non-toxicity, and eco-friendliness [7,29]. Nonetheless, the inherently poor conductivity (10^{-14} S cm^{-1}) and small surface area of Fe_2O_3 hinder its specific capacitance and power capability [14]. To address these issues, much research has been devoted to nanostructured Fe_2O_3 composite electrodes, namely combing nanostructured Fe_2O_3 (nanoparticles [30,31], nanotubes [32,33], nanoflakes [34,35], etc.) with conductive materials like carbonaceous materials (activated carbon [36], carbon nanotubes/carbon nanofibers [17], graphene [37]) and conductive polymers (PEDOT [38], PPy [18], PANI [39]). Some typical researches on nanostructured Fe_2O_3 composite electrodes are summarized in Table 1. As can be seen that most Fe_2O_3-based composites output superior performance compared to barely Fe_2O_3 but do not have both high specific capacitance (C_{sp}) and long-term stability. For example, the CNT/nanoparticle α-Fe_2O_3 composite which synthesized by hydrothermal exhibits a high C_{sp} of 296.3 F g^{-1} but a low capacitance retention (50–60% after 1000 cycles), and α-Fe2O3 nanorods based on carbon fiber paper show long-term cycling stability (97.5% of the initial capacitance remains after 10000 cycles) but a low C_{sp} of 125.6 F g^{-1}. It is worth noting that the hierarchical graphite foam-CNT@Fe_2O_3 structures prepared by chemical vapor deposition (CVD) and atomic layer deposition (ALD) present a C_{sp} of 580.6 F g^{-1} and a good cycling stability. However, the ALD method is relatively time-consuming and expensive. Therefore, specially designed hierarchical conductive Fe_2O_3 based electrodes through mature preparation methods are highly desirable.

In view of the above consideration, in this work, we have successfully designed and synthesized a three-layer sandwiched core–shell arrays via combined chemical vapor deposition and magnetron sputtering methods. CNTs were first grown on conductive carbon fiber cloth substrate by CVD (CC-CNT), then Fe_2O_3 and successive carbon shells were prepared onto the CNT core by magnetron sputtering (CNT/Fe_2O_3@C). In such unique architecture, Fe_2O_3 are conformally sandwiched by the CNT core and carbon shell forming sandwiched core–shell arrays. The carbon shell can effectively serve as conductive protective outer layer for Fe_2O_3 and hinder the diffusion of intermediate Fe-based oxide/hydroxide. These three components are intimately merged together and achieve synergistic effects with enhanced electrical conductivity and superior electrochemical stability. Consequently, under the optimal mass of Fe_2O_3 and carbon shell, the CNT/Fe_2O_3@C composite electrode shows a high C_{sp} of 787.5 F g^{-1} at the scan rate of 5 mV s^{-1} and a high stability of 92% after 7000 cycles. Meanwhile,our research provides a new approach for fabricating advanced multicomponent composite electrodes for application in energy storage.

2. Material and methods

2.1. Fabrication of composites

Firstly, the carbon fiber cloth (W0S1002, CeTech) was pretreated with 3:1 H_2SO_4/HNO_3 mixed acid at 65 °C for 2 h and then cleaned by sonication in deionized water. Secondly, CNTs were grown on a piece of $Ni(NO_3)_2$ catalyst-coated carbon fiber cloth substrate (1 cm ×1 cm) by CVD. Flow rates of C_2H_2, H_2, and Ar were set to 10, 20, 200 SCCM (standard cubic centimeters per minute), respectively. The growth time was set to 30 min at 700 °C. The obtained mass loading of CNT is from 1.50 to 1.90 mg cm^{-2}. Thirdly, Fe_2O_3 was coated on the CNT core by direct current magnetron sputtering of 70 mm-diameter Fe target (99.999% purity) at a pressure of 1.0 Pa in a gas mixture of argon (30 SCCM) and oxygen (8 SCCM). The sputtering process was done at room temperature for a sputtering time between 10 and 50 min under a power of 16 W. Finally, the outer carbon shell was coated on CNT/Fe_2O_3 by radio-frequency magnetron sputtering of 70 mm-diameter graphite target (99.999% purity) at a pressure of 1.0 Pa in argon gas (30 SCCM) under a power of 200 W. The CNT/Fe_2O_3@C composites with different content of Fe_2O_3 and C were obtained. According to the sputtering time for Fe_2O_3 and C, the samples are named as CNT/Fe_2O_3-XX@C-YY, where XX and YY denote the sputtering time for Fe_2O_3 and C, respectively.

Materials characterization

The morphologies and microstructures of the as-prepared samples were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and transmission electron microscopy (TEM, FEI Tecnai F30) coupled with an energy dispersive X-ray spectrometer. Crystal structures were tested by X-ray diffraction (XRD, Philips, X'pert Pro, Cu Kα, 0.154056 nm) and micro-Raman spectroscopy (JY-HR 800, 532-nm wavelength YAG laser).

2.2. Electrochemical measurements

The electrochemical properties were tested in a standard three-electrode system at room temperature on an electrochemical work station (CHI 760). The 2 M KOH aqueous solution was used as the electrolyte, a Pt plate as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and the CNT/Fe_2O_3@C on carbon cloth (CC) as the binder-free working electrode. Electrochemical impedance spectroscopy (EIS) results were obtained in frequencies from 100 kHz to 0.01 Hz at open circuit voltage with an AC voltage perturbation amplitude of 50 mV. The mass of the active material was weighed by a microbalance (Mettler, XS105DU) with a tolerance of less than 0.01 mg.

3. Results and discussion

The entire synthetic procedure of the sandwiched core/shell CNT/Fe_2O_3@C arrays on CC substrate is schematically illustrated in Fig. 1a. Primarily, CNTs were grown on carbon cloth substrate via a facile CVD method. Then, the CNTs serve as the skeleton for the uniform growth of Fe_2O_3 by magnetron sputtering. Finally, the carbon shell on CNT/Fe_2O_3 was constructed by another