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Research paper

A facile method to synthesise reduced graphene oxide/carbon nanotube hybrid fibers as binder-free electrodes for supercapacitors

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ABSTRACT

The reduced graphene oxide/carbon nanotube hybrid fibers (G/CNTs) were prepared by a facile chemical reduction and self-assembly strategy at low temperature. SEM images indicate a certain degree of reduced graphene oxide nanosheets and carbon nanotube orientation along the main axis of the obtained hybrid fibers. The reduced graphene oxide/carbon nanotube hybrid fibers exhibit large surface area of 149.85 $m^2 g^{-1}$ and good mechanical strength. The electrochemical performances of hybrid fibers as flexible and binder-free electrodes are evaluated by using a three-electrode system, and it displays high specific capacitance of 243.0 Fg^{-1} at a current density of 200 mA g^{-1}, which is mainly ascribed to porous structure and large specific surface area. The as-synthesized reduced graphene oxide/carbon nanotube hybrid fibers will be potential candidate for flexible and binder-free electrodes for supercapacitors.

1. Introduction

With the increasing requirements of wearable, portable and flexible electronic products, the miniaturized, lightweight and flexible supercapacitors, with high power density and high energy density, have attracted significant attention as promising energy storage devices [1–6]. Flexible and binder-free electrode materials play an important role in future applications for high-performance supercapacitors. Flexible electrodes have mainly been fabricated using carbon-based materials, such as amorphous carbon, carbon nanotube (CNT) and graphene in previous published papers [1,7,8]. To meet flexibility and binder-free requirements, carbon nanotube or graphene based 3D aerogels, 2D membranes, and 1D fibers electrode materials have been widely researched. The 1D fiber-typed electrodes have been developed to realized wearable storage devices and smart textiles due to combining easily with textiles [9,10].

The 1D linear graphene fibers, with good mechanical flexibility, wearable and electrical properties in contrast to graphene-based aerogels and membranes, can be fabricated by individual graphene nanosheets [11]. In the synthesis processes, the graphene fibers tend to restack into graphite-like structure due to the aggregating nature caused by strong π-π interactions, which destroy the excellent characteristics of the individual graphene nanosheets, such as high surface area [5,12,13]. The flexible CNT fibers possess many combined advantages including low density, high tensile strength and high electrical conductivity. But the CNT fibers exhibit relatively low electrochemical activities that are found to be critical for electronic applications [14]. To overcome these problems, the graphene and carbon nanotube hybrid fibers can be prepared by solution spinning, which can reduce the aggregation of graphene nanosheets to obtain larger specific surface area, and improve the electrochemical properties [15–17].

In this paper, the reduced graphene oxide/carbon nanotube hybrid fibers (G/CNTs) were prepared by a facile low temperature induced self-assembly strategy, and the synthesis process is shown in Fig. 1. The G/CNTs are fabricated at different temperature of 90 °C and 120 °C until the hybrid fibers fully form, which is beneficial to controlling ordered and porous structure. The as-prepared G/CNTs exhibit large specific surface area of 149.85 $m^2 g^{-1}$, and good flexibility, which can be conveniently woven into variety patterns. The G/CNTs deliver high specific capacitance of 195.1 Fg^{-1} after 500 cycles at a current density of 200 mA g^{-1}, which is mainly ascribed to the designed structure and synergistic effect between reduced graphene oxide and carbon nanotube. These reduced graphene oxide/carbon nanotube hybrid fibers will be an ideal candidate of electrode materials for flexible and bendable supercapacitors, and the development can promote more engineering applications of graphene and carbon nanotube.

2. Experimental

2.1. Synthesis of materials

Natural graphite power with 20–30 μm were received from Qingdao

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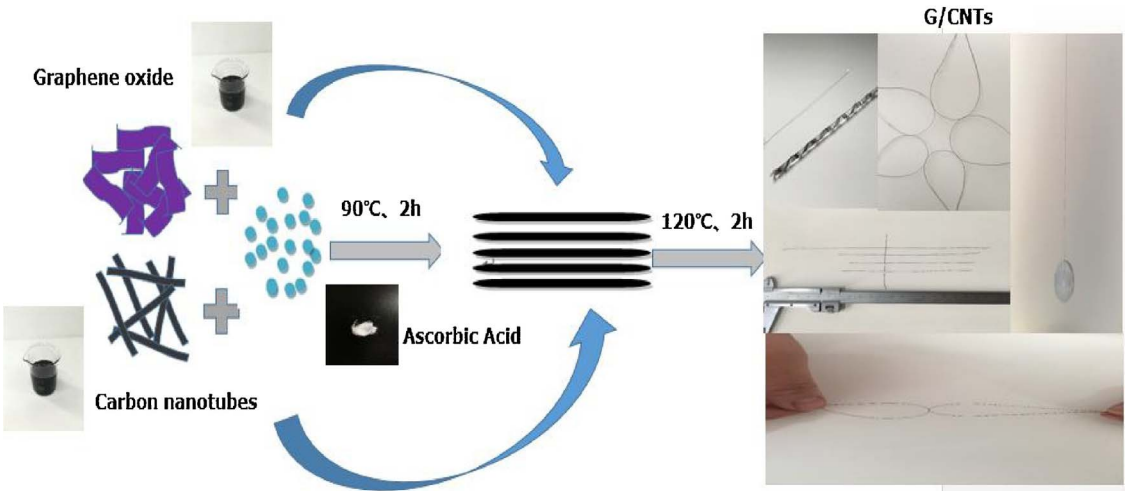

Fig. 1. Scheme of G/CNTs synthesis processes.

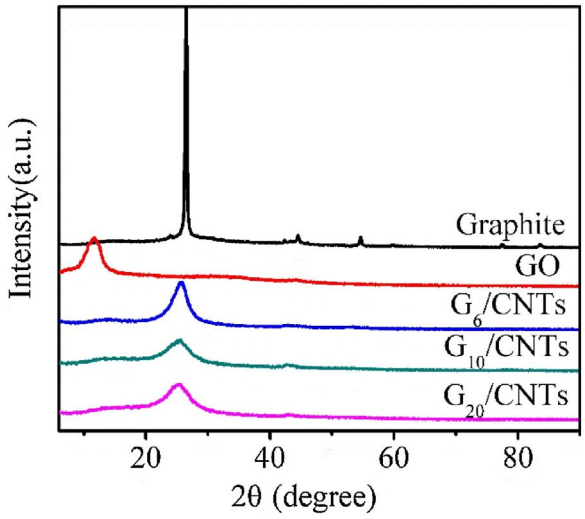

Fig. 2. XRD patterns of Graphite, GO, G_6/CNTs, G_{10}/CNTs, and G_{20}/CNTs.

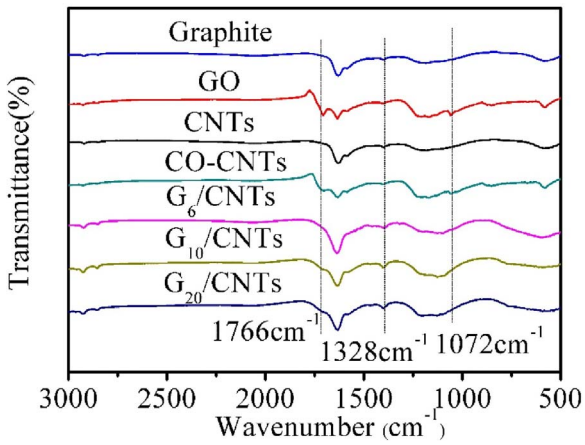

Fig. 3. FTIR spectra of Graphite, GO, CNTs, CO-CNTs, G_6/CNTs, G_{10}/CNTs and G_{20}/CNTs.

Ruisheng Graphite Co., Ltd. Other chemicals were of analytical grade and used as received from Sinopharm Chemical Reagent Co., Ltd., without further purification. Using graphite power, the graphite oxides (GO) suspension (GO dispersed in water) with high concentration were prepared by modified Hummers method, which could keep a long time at room temperature. The mixtures of 3.6 g carbon nanotube, 90 ml H_2SO_4 and 30 ml HNO_3 was put in an ultrasonic bath for 2 h, it was transferred into oil bath at 120 °C for 2 h, the carboxylic carbon nanotube (CO-CNTs) were obtained from carbon nanotube (CNTs), then the CO-CNTs were washed by deionized water to form uniform CO-CNTs suspension. As shown in Fig. 1, graphene oxide and carboxylic carbon nanotube were combined by a facile chemical reduction and self-assembly strategy at low temperature, the preparation of reduced graphene oxide/carbon nanotube hybrid fibers (G/CNTs) could be divided into three steps: first, the obtained GO solution was diluted to 7 mg ml^{-1}, and the mixed suspension of GO and CO-CNTs was put in an ultrasonic bath for 30 min. Second, 0.12 g reducing agent (ascorbic acid) was added into the mixed suspension and make the mixtures well-distributed. Third, the obtained mixtures were sealed into the specified diameter glass tube by using PTFE membrane and put it in an oven at 90 °C for 2 h, and the gel-fibers were preliminarily formed, then the temperature increased to 120 °C until fibers fully formed. The synthesis process of hybrid fibers was continually accompanied by the volatilization of water. The forming of hybrid fibers is mainly due to capillary forces and surface-tension-induced sheet interactions. The G/CNTs with different mass ratio values of 6:1, 10:1 and 20:1 could be named G_6/CNTs, G_{10}/CNTs, G_{20}/CNTs, respectively. The graphene oxides were reduced by ascorbic acid to obtain reduced graphene oxide under the same synthesis processes.

2.2. Characterization

The structures and morphologies of G/CNTs were characterized by Field emission scanning electron microscopy (FESEM, JEOL JSE-7500F). The tensile strength of G/CNTs were evaluated by Dynamic Mechanical Analyzer (DMA, Q800). The Brunauer-Emmet-Teller (BET) surface area of the as-synthesized samples were measured using a surface area detecting instrument (Kubo X1000) analyzer by N_2 physisorption at liquid nitrogen temperature. In addition, other auxiliary information of the products was observed by X-ray diffraction (XRD, X Pert MDP) and Fourier transform infrared spectra (FTIR, Nicolet Nexus 670).

2.3. Electrochemical testing

The electrochemical performance of the as-synthesized G/CNTs were performed in 6 M KOH solution as flexible and binder-free electrode materials in a three-electrode system, using Pt as a counter electrode and Hg/HgO as a reference electrode. The galvanostatic charge-discharge performance were conducted on LAND instrument at