

Direct synthesis of graphene-based hybrid films as flexible supercapacitor electrodes

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ABSTRACT

Excellent carbon nanotubes and graphene have attracted more and more attention due to their fascinating properties of combining advantages. In this report, graphene/multi-walled carbon nanotube composite films (G/MWNTs) with excellent mechanical flexibility and high electrical conductivity were prepared by one-step and self-assembly strategy. Importantly, G/MWNTs were equipped with high specific surface areas, which are conducive to growing the micropores and active sites. The electrochemical measurement results indicate that G₁/MWNTs exhibit a specific capacitance of 249.3 F g⁻¹ at a current density of 200 mA g⁻¹ and still remain 91.3% of the original specific capacitance after 8000 cycles, indicating an excellent electrochemical performance. Furthermore, the flexible and mechanically stable graphene-based films can be bent to various angles on demand, which is a necessary condition in practical application. The as-prepared G/MWNTs show enormous potential in supercapacitors as high performance electrodes and may be favorable for some other research fields as well.

1. Introduction

Supercapacitor, as energy storage devices, occupies an important place in our daily life for years due to their promising performance, including long working life, high energy density, and fast charging/discharging efficiency [1–4]. In order to find and design original active electrode materials with excellent storage ability, enormous efforts have been paid. Among all electrode materials in previous published papers, carbon materials have been known as flexible electrodes for supercapacitors, such as activated carbon, carbon nanofiber and carbon aerogels [5–7]. Carbon-based materials display absolute potential advantages owing to their unique sizes and perfect structures. Particularly, graphene, as active electrode materials, has been confirmed that it possess tremendous potentials in energy storage devices [8,9]. However, due to the aggregation of graphene nanosheets and deficiency of effective channel, the performances of graphene is greatly limited [10]. To overcome the above problems, one possible strategy is to use one-dimensional carbon nanotubes to bring in distance between two-dimensional graphene nanosheets with preventing restacked structures and forming an emerging three-dimensional hierarchical architecture, which is beneficial to facilitate the ion permeability to electrode surfaces.

Graphene with a honeycomb lattice structure is an outstanding and rising material owing to the excellent mechanical flexibility, large

surface areas, and favorable electrochemical performance [9,11–14]. Since the discovery of graphene in 2004, a lot of efforts have been dedicated to its synthesis, characterization, and investigations of its properties. Moreover, carbon nanotubes and graphene exhibit a lot of similar properties, but differ in some aspects due to the morphological structure differences. The pure carbon nanotube materials display oppositely poor electrochemical performance, which is necessary for electronic applications [15]. Therefore, many methods have been explored to combine these two carbon materials in order to develop their advantages [16–18].

In this study, graphene/multi-walled carbon nanotube (G/MWNTs) hybrid films were combined by one-step and self-assembly strategy, and the process of synthesis is shown in Fig. 1. The graphene-based films were prepared at the temperature of 160 °C for about 10 min until the composite films completely formed. We tested the capacitive behavior of as-synthesized G/MWNTs by using a three-electrode system. The results represented that the specific capacitance of G₁/MWNTs were 249.3 F g⁻¹ when the current density is 200 mA g⁻¹, which is higher compared with that of pure graphene films (GFs), and still remained at 91.3% of its original capacitance after 8000 cycles, suggesting its outstanding electrochemical stability. This is primarily attributed to the designed specific structures and synergistic effect between reduced graphene oxide nanosheets and multi-walled carbon nanotubes. Furthermore, the flexible and mechanically stable graphene-based films

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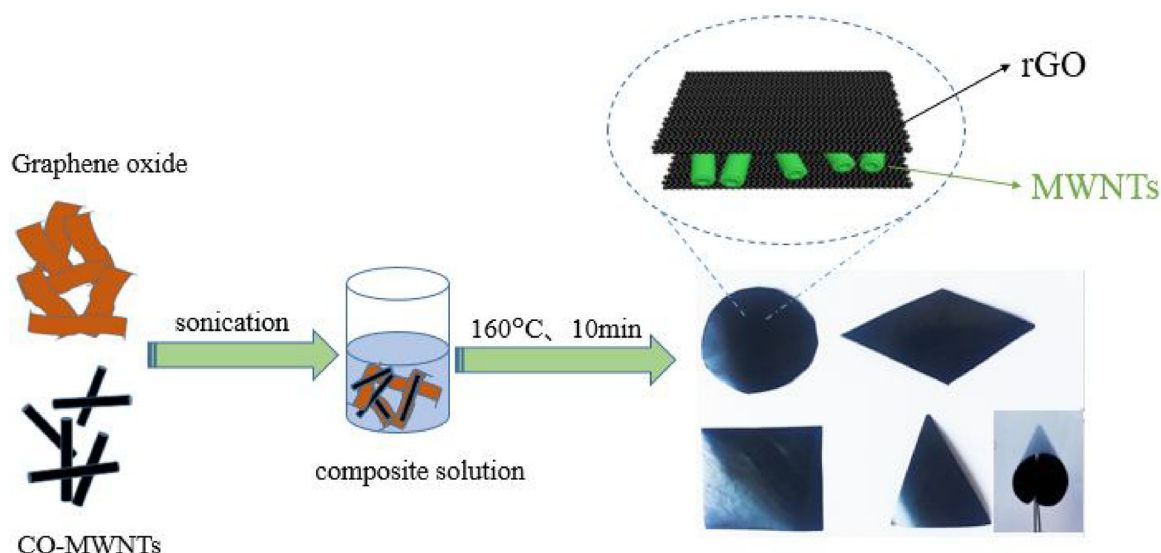


Fig. 1. Scheme of graphene-based films synthesis processes.

can be bent to various angles on demand, suggesting its promising application in flexible and wearable electronics as powerful electrodes.

2. Experimental

2.1. Synthesis of materials

Graphene oxide (GO) was prepared from natural graphite (20–30 μm , Nanjing XFnano Co., Ltd) flakes by an improved Hummers' method as reported in our previous papers [19], which could keep at room temperature for a long time. MWNTs (diameters around 10–20 nm, Sinopharm Chemical Reagent Co., Ltd) were oxidized by HNO_3 and H_2SO_4 reflux for 4 h to obtain CO-MWNTs, and the CO-MWNTs were washed by deionized water to form uniform CO-MWNTs suspension. Graphene oxide solution and carboxylic multi-walled carbon nanotubes solution were synthesized by one-step and self-assembly strategy as shown in Fig. 1. Firstly, 10 ml GO aqueous solution and 10 ml CO-MWNTs were ultrasonic for 30 min, respectively, and then the mixture of GO and CO-MWNTs was ultrasonically stirred for 30 min again. Secondly, the dispersion with 0.2 g reducing agent (ascorbic acid) was poured into the specified petri dish. Finally, CO-MWNTs/GO aqueous dispersions was put in an oven at 160 $^\circ\text{C}$ for about 10 min until the graphene-based films fully formed. The G/MWNTs with various mass ratio values of 1:0 and 1:1 could be named GFs and G_1 /MWNTs, respectively.

2.2. Characterization and electrochemical testing

The morphologies and structures of samples were characterized by field emission scanning electron microscopy (FE-SEM; Ultra55). The tensile strength of G/MWNTs were evaluated by Dynamic Mechanical Analyzer (DMA, Q800). The chemical composition of samples was obtained via Fourier transform infrared spectra (FT-IR, Nicolet 57000) from 400 to 4000 cm^{-1} . In addition, Powder X-ray diffraction patterns of samples were recorded by using Cu K α radiation, scanning from 6 to 90 $^\circ$ (in 2 θ) (XRD; ARL XTRA). Raman spectroscopy was recorded from 500 to 2500 cm^{-1} by using a 514 nm argon ion laser (HR800, Horiba Jobin Yvon). The electrical conductivity of samples was obtained by four-point probe measurement. The electrochemical performance of the as-synthesized samples were carried out in a three-electrode system as flexible electrode materials at room temperature, using a pure Pt wire and Hg/HgO as a counter electrode and a reference electrode, respectively. 6M KOH aqueous solution was used as electrolyte. The

electrochemical techniques included cyclic voltammetry, galvanostatic discharge-charge, and impedance spectroscopy. The galvanostatic discharge-charge performance of the samples were investigated using LAND instrument at various current densities. Cyclic voltammetry curves were collected with a potential window from 0 to 0.8 V at scan rate from 10 to 100 mV s^{-1} . Impedance spectroscopy measurements were carried out with 100 kHz (initial) and 0.1 Hz (final) at amplitude voltage of 5 mV [20,21].

3. Results and discussion

As indicated in the XRD curves of G_1 /MWNTs, GFs, GO, and Graphite (Fig. 2a), respectively. The prepared GO displays the typical dominant peak located at 11.2 $^\circ$ due to the reflection of plane. The calculated interlayer d-spacing of GO was about 0.76 nm, which is approximately twice than that of natural graphite (0.34 nm). As can be seen, a similar diffraction peak of the reduced GFs and G_1 /MWNTs were discovered at about $2\theta = 25.8^\circ$, corresponding that of the characteristic of natural graphite, which explains the increasing the reduction of carboxylic multi-walled carbon nanotubes and graphene oxides [22,23]. Fig. 2b displays FTIR spectra of MWNTs, CO-MWNTs Graphite, GO, GFs and G_1 /MWNTs, Clearly, the spectrum of CO-MWNTs contained three obvious absorption bands in contrast to the pure carbon nanotubes, situated at 1069 cm^{-1} (C–O–C), 1260 cm^{-1} (C–OH), and 1734 cm^{-1} (C=O) [24,25] respectively, which represents the presence of a large number of oxygen functional groups in the CO-MWNTs. At the same time, the GO also displayed the similar characteristic peaks with that of CO-MWNTs. In addition, it was observed that almost all the oxidized groups of GFs and G_1 /MWNTs radically weakened and some of them even disappeared completely after the reduction progress by using the reducing agent, which agrees with the XRD results. The electronic structure of carbon materials are usually investigated by using the Raman spectroscopy. The Raman spectra of GO, CO-MWNTs, GFs and G_1 /MWNTs were provided as shown in Fig. 2c. As can be seen, all of them displayed the typical D bands (1349 cm^{-1}) and G bands (1588 cm^{-1}), which is attributed to the presence of disordered portions of carbon and ordered graphitic crystallites of carbon [15]. Both the GFs and G_1 /MWNTs showed a relatively high D band after reduction with ascorbic acid. In addition, the I_D/I_G values of GO, CO-MWNTs, GFs and G_1 /MWNTs are respectively 0.84, 0.92, 1.26 and 1.36, which is mainly due to the decreased sp^2 bonded carbon domain by chemical reduction.

SEM was used to investigate the surface morphologies of CO-

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