



Novel hybrid nanocomposite based on poly(3,4-ethylenedioxythiophene)/multiwalled carbon nanotubes/graphene as electrode material for supercapacitor



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ARTICLE INFO

Article history:

Received 16 October 2013

Received in revised form

18 December 2013

Accepted 2 January 2014

Available online 28 January 2014

Keywords:

Graphene

Poly(3,4-ethylenedioxythiophene)

Multiwalled carbon nanotubes

Electrode material

Nanocomposite

Supercapacitor

ABSTRACT

The hybrid nanocomposite based on poly(3,4-ethylenedioxythiophene)/multiwalled carbon nanotubes/graphene was prepared by reducing the graphene oxide with hydrazine in the presence of multiwalled carbon nanotubes (MWCNTs) and the anchored poly(3,4-ethylenedioxythiophene) hollow spheres (b-PEDOT). The transmission electron microscope (TEM) images of b-PEDOT/MWCNTs/rGO nanocomposite reveal that the b-PEDOT and MWCNTs were sandwiched between layers of graphene sheets. The b-PEDOT nanoparticles act as spacers to create gaps between neighboring graphene sheets, resulting in a higher surface area compared to pure graphene. Furthermore, it shows a significant pseudo-capacitance energy storage mechanism during the charge/discharge process. And the MWCNTs improve electric conductivity of the nanocomposite and contribute to a low equivalent series resistance (ESR). Utilizing this composite material, a specific capacitance of 225 F g^{-1} at a current density of 0.1 A g^{-1} has been achieved.

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1. Introduction

With the rapidly growing market in portable electronic devices, electric vehicles and hybrid electric vehicles, there has been an ever increasing demand for environmentally friendly, high-performance energy-storage systems. Supercapacitors, also known as electrochemical capacitors (ECs) or ultracapacitors, have attracted much attention in the automotive and consumer electronics industry due to their high capacitance, long cyclic life (>100 000 cycles), low maintenance cost and fast dynamics of charge propagation [1–3]. Electrochemical supercapacitors with relatively high energy and power densities are part of a significant field of electrochemical energy storage because they bridge the gap between conventional capacitors and batteries [4]. Supercapacitors have two energy storage mechanisms, namely the electrical double-layer capacitance (EDLC) and the pseudocapacitance. These two mechanisms can function simultaneously, depending on the nature of the electrode materials. The capacitance of EDLCs is generated from the electric double layer due to charge separation at the electrode and electrolyte interface, which exhibits strong dependence on accessible surface area of the electrode materials.

The capacitance of pseudo-capacitors is typically generated from the faradic of electrode materials in addition to electric double layer charges [5–7]. Generally, the supercapacitor performance is mainly determined by electrode materials. The main materials used for supercapacitor electrode preparation include carbon materials, such as graphene, activated carbon, carbon nanotubes, activated carbon fibers [8–10], and electroactive materials with several redox states or structures, such as transition-metal oxides (e.g., oxides of ruthenium, nickel, cobalt, and manganese) [11–16] and conducting polymers [17–20].

Graphene oxide (GO), with a low fabrication cost and an environmentally friendly nature, can be obtained on a large scale by the chemical oxidation of graphite, and it possesses a number of hydroxyl and epoxide functional groups anchored on sp^3 -hybridized carbon atoms on both surfaces of each sheet and considerable amounts of sp^2 -hybridized carbon-atom-containing carboxyl and carbonyl groups at the sheet edges [21–23]. Unfortunately, the functional groups and poor electrical conductivity resulting from the oxidation of the graphite can be obstacles for electrolyte motion between the sheets. Graphene is a single-atom-thick, two dimensional sheet of sp^2 -hybridized carbon atoms arranged in a honeycomb crystal structure with exceptionally high strength, surface area, thermal conductivity, and electronic conductivity [24,25]. These superior properties make graphene a very promising candidate in many applications, such as sensors [26],

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fuel cells [27], batteries [28,29], and supercapacitors [30–32]. Bulk quantities of chemically reduced graphene (rGO) can be obtained by chemically exfoliating graphite powders, followed by reducing the graphene oxide product [33–35]. Due to its electrical conductivity and high surface area, chemically modified graphene has attracted significant interest as an electrode material for supercapacitors [30,31,36–39]. Chemical exfoliation has been the most employed method to fabricate graphene based devices due to its advantages of facile aqueous synthesis, low cost, and easy scale up [40–42].

Conducting polymers have been regarded as alternative electrode materials for electrochemical supercapacitors because of their pseudocapacitive behaviors. Conducting polymers, such as polyacetylene, polypyrrole, polyaniline, polythiophene, and their derivatives, are amongst the more promising materials for a polymer-based pseudocapacitor [43]. Conducting polymers are able to store charge, not only in the electrical double layer, but also throughout the body of the polymer by rapid faradaic charge transfer i.e. a three-dimensional charge storage mechanism resulting in far higher capacity. However, the redox reaction in pseudocapacitors is a slower process compared with the double layer process in EDLCs and the pseudocapacitor has lower charge/discharge performance than an EDLC capacitor. One solution is to incorporate carbon materials into the conducting polymers, which has been shown to increase its capacitance while maintaining high level of power density [44]. Among conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) exhibits not only a high conductivity but also an unusual stability in the oxidized state, being considered as perhaps the most stable conducting polymer currently available [45] and, therefore, many researchers have studied PEDOT as the electrode materials for supercapacitors [46,47].

Multiwalled carbon nanotubes (MWCNTs), which is an excellent form of carbon, attract much attention as supercapacitor electrode material because of their unique mesoporous network, outstanding electrical conductivity, and excellent chemical stability. Furthermore, MWCNTs provide conducting pathway to facilitate a fast electrochemical kinetic process during high current density charge/discharge [48,49]. And a kind of PEDOT hollow spheres (b-PEDOT) through a one-step self-assembly process was reported before [50]. Herein, we fabricated a supercapacitor electrode material with good electrochemical performance based on the interpenetrative nanocomposite of chemically modified graphene (rGO), b-PEDOT and MWCNTs. Compared to early studies, the difference of this new research is the design to enable synergistic effects of rGO, PEDOT and MWCNTs by using graphene as a high-surface-area substrate for direct growth of b-PEDOT and MWCNTs because graphene has been widely considered as an ideal substrate for ultrathin coating of functional materials due to its unique structural and electrical properties, while b-PEDOT is a conducting polymer which may favor adhesion onto the GO surface and the MWCNTs is highly conductive that is beneficial for electronic and ionic transport.

2. Experimental details

2.1. Instruments

The main instruments used in the experiment are as follows: KH7200DE ultrasonic (Hechuang, Kunshan) was used for synthesis of the nanocomposite. CHI660 C electrochemical workstation (Chenhua, Shanghai) was used for the electrochemical measurement. The morphologies of the samples were characterized by an field emission scanning electron microscopy (FEI, Netherlands) and a JEM-100CX transmission electron microscope (JEOL, Japan).

2.2. Materials

The main materials used in the experiment are as follows: Graphite powder was purchased from Shanghai HuaYi Group HuaYuan Chemical Industry Co. Ltd. Multiwalled carbon nanotubes were purchased from Timesnano Co. Ltd. and 3,4-ethylenedioxythiophene (EDOT) was purchased from Best-reagent Co. Ltd. and all were used as received. Other reagents were purchased from China in the reagent grades and used without further purification.

2.3. Preparation of b-PEDOT

Polyvinylpyrrolidone (PVP, 30 mg) was added to 20 ml deionized water in a 250 ml flask, and then sonicated for 30 min. EDOT monomer (60 μ l, 80 mg) and naphthalene-1, 5-disulfonic acid tetrahydrate (60 mg) were added into the flask under stirring, and the mixture was sonicated for 30 min. Ammonium persulfate (APS, 500 mg) was added into the flask with stirring. The polymerization was allowed to proceed for 15 h at room temperature. Finally, the solid b-PEDOT was obtained by filter through a mixed cellulose ester membrane and the obtained filter cake was then vacuum dried at 60 °C for 12 h. The b-PEDOT dispersion (5 mg ml⁻¹) was prepared by sonication of dried b-PEDOT.

2.4. Preparation of GO

GO was synthesized from natural graphite by the modified Hummer's method. In an ice bath, 23 ml H₂SO₄ (98%) was added into a 250 ml flask filled with graphite (1 g) and NaNO₃ (0.5 g), followed by slow addition of KMnO₄ (3 g) with stirring and cooling to keep the temperature in the reactor below 20 °C. The mixture was stirred continuously for 1 h and heated to 35 °C, then stirred at 35 °C for another 30 min. Deionized water (50 ml) was slowly added and increase the temperature to 98 °C, and the mixture was maintained at that temperature for 15 min. The product was washed by the addition of deionized water followed by 10 ml of a 30% H₂O₂ solution. The solid graphite oxide product was separated by centrifugation, washed repeatedly with a 5% HCl solution until sulfate could not be detected with BaCl₂, and then washed three to four times with deionized water and dried in a vacuum oven at 60 °C for 24 h. The GO dispersion was prepared by simple sonication of graphite oxide that obtained previously. Then, the GO dispersion was subjected to centrifugation at 8000 rpm for 5 min to remove the unexfoliated GO. The resulting GO colloid solution is able to remain stable for a few months.

2.5. Preparation of purified MWCNTs

MWCNTs (200 mg) was added to 40 ml mixed acid (30 ml H₂SO₄ (98%) and 10 ml HNO₃ (~65%)), the mixture was then sonicated for 5 h. After the sonication, deionized water (80 ml) was added to the mixture. The product was obtained by filtered and washed with deionized water and dried at 60 °C for 24 h in vacuum. The final MWCNTs dispersion (2 mg ml⁻¹) was prepared by sonication of purified MWCNTs.

2.6. Synthesis of the nanocomposite of b-PEDOT/MWCNTs/rGO

The nanocomposite was prepared by reducing the mixture of the graphene oxide with hydrazine in the presence of MWCNTs and the anchored b-PEDOT. GO dispersion (0.5 mg ml⁻¹, 200 ml) was added into a flask, b-PEDOT dispersion (5 mg ml⁻¹, 6 ml) was added, and the mixed solution was stirred for 30 min and then subjected to sonication for 1 h. Afterward, MWCNTs dispersion (2 mg ml⁻¹, 5 ml) was added and sonicated for 20 min to ensure good mixing. Subsequently, a hydrazine solution was added into the mixture, and the mixture was stirred and heated at 95 °C for 5 h. Finally,

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