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Superior performance of highly flexible solid-state supercapacitor based on the ternary composites of graphene oxide supported poly(3,4-ethylenedioxythiophene)-carbon nanotubes

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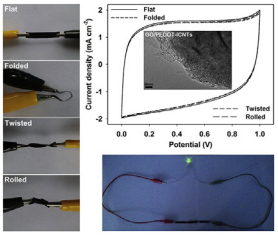
HIGHLIGHTS

- GO/PEDOT-CNTs ternary composites are prepared via a facile electrochemical method.
- The long CNTs more effectively improve the capacitive performance of GO/PEDOT.
- A lightweight and thin solid-state highly flexible supercapacitor is fabricated.
- The supercapacitor device shows a high specific capacitance and cycle stability.

GRAPHICAL ABSTRACT



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ABSTRACT

Ternary composite electrodes based on carbon nanotubes thin films (CNFs)-loaded graphene oxide (GO) supported poly(3,4-ethylenedioxythiophene)- carbon nanotubes (GO/PEDOT-CNTs) have been prepared via a facile one-step electrochemical codeposition method. The effect of long and short CNTs-incorporated composites (GO/PEDOT-lCNTs and GO/PEDOT-sCNTs) on the electrochemical behaviors of the electrodes is investigated and compared. Electrochemical measurements indicate that the incorporation of CNTs effectively improves the electrochemical performances of the GO/PEDOT electrodes. Long CNTs-incorporated GO/PEDOT-lCNTs electrodes have more superior electrochemical behaviors with respect to the short CNTs-incorporated GO/PEDOT-lCNTs electrodes, which can be attributed to the optimized composition and specific microstructures of the former. To verify the feasibility of the prepared composite electrodes for utilization as flexible supercapacitor, a solid-state supercapacitor using the CNFs-loaded GO/PEDOT-lCNTs electrodes is fabricated and tested. The device shows lightweight, ultrathin, and highly flexible features, which also has a high areal and volumetric specific capacitance (33.4 m F cm^{-2} at 10 mV s^{-1} and 2.7 F cm^{-3} at 0.042 A cm^{-3}), superior rate capability, and excellent cycle stability (maintaining 97.5% for 5000 cycles). This highly flexible solid-state supercapacitor has great potential for applications in flexible electronics, roll-up display, and wearable devices.

1. Introduction

Developing highly flexible energy storage devices with superior performance can meet the requirement for flexible electronics of

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the next generation, which has potential technological applications in various fields, including but not limited to roll-up displays, artificial electronic skin, and wearable devices. For personal electronics and modern market, such devices follow the trend toward lightweight, thinness, miniaturization, and flexibility, and may be even rolled up [1–6]. Supercapacitors (also called electrochemical capacitors) are the promising candidates for flexible devices, due to their advantages including inherent electrochemical properties (high power density, rapid charge-discharge performance, and long-term cycle stability), relatively simple structures, as well as the easy production on large scale [7–10].

Commonly, supercapacitors can be divided into two categories based on the energy storage mechanism. One is the electrochemical double-layer capacitors (EDLCs), which usually use carbon materials with high power density as the accumulation of pure electrostatic charges in the electric double layers. The other is the Faradaic pseudocapacitors that employ conducting polymers and transition metal oxides/hydroxides, whose high energy density derives from the surface or near-surface redox reactions of electroactive species [11–14]. The electrode materials are crucial to the performance of supercapacitors. However, each electrode material has its advantages and disadvantages. For instance, carbon materials show high power density and long cycle stability, but they have low capacitance. Transition metal oxides exhibit higher energy density than carbon materials and a better cycle life than conducting polymers, but they also present a drawback of poor conductivity. Conducting polymers have high energy density, and yet they reveal the disadvantages of a low cycle life because swelling and shrinkage occur during the doping/dedoping of counter-ions [15–17]. Therefore, extensive attempts have been made to prepare composite electrode materials that can compensate for the limitation of each individual material used for supercapacitors. For instance, the hierarchical NiMn layered double hydroxide/carbon nanotubes [18], three dimensional (3D) carbon-metal oxide composite [19], and carbon@MnO_2 core-shell hybrid nanospheres [20], and so on.

Graphene oxide (GO) can be easily synthesized from natural graphite and forms stable dispersions in water. It has a low fabrication cost and is environmentally friendly in nature. GO also exhibits a high specific surface area that results in the large electrical double-layer. On the other hand, conducting polymers (CPs) have high Faradaic pseudocapacitance. Thus, a number of recent studies have been devoted to synthesizing the composites of CPs and GO nanosheets in order to achieve the large specific capacitance and long cycle life for electrochemical capacitors. Cao et al. reported the 3D GO/polypyrrole (GO/PPy) composite electrodes by electrochemical deposition [21]; Wu et al. demonstrated a facile and effective synthesis of GO/CPs (CPs, PANI and PPy) composites via an in situ oxidative polymerization [22]; Li et al. investigated the GO/PPy nanowire composite material using an in situ chemical polymerization method [23]; and Li et al. prepared the GO/PANI composites using an in-situ polymerized method [24]. In our previous study, the PPy/GO composites have been also investigated through an electrochemical codeposition method [25].

Although the above GO/CPs composites exhibit good capacitive performances due to the hydrophilic nature of GO and the π–π stacking between GO layers and polymer rings, the GO still hinders their charge storage properties as a result of the insulating nature of GO (conductivity of 1.28×10^{-9} S cm^{-1}), which is caused by a large number of oxygen containing functional groups in its structure [21]. Carbon nanotubes (CNTs), owing to their high conductivity, low specific weight, ideal specific surface area and chemical stability, have been widely used as the supercapacitor electrode materials [26–28]. So incorporating CNTs into the GO/CPs composites has the potential to improve their electrochemical behaviors. Poly(3,4-ethylenedioxythiophene) (PEDOT) as an electrode material for supercapacitors has been extensively investigated. It exhibits not only a high conductivity, but also an unusual stability in the oxidized state as compared to other CPs [29,30]. In this contribution, we shall devote our effort to improving the electrochemical performances of the GO/PEDOT composites by incorporating the CNTs. The ternary GO/PEDOT-CNTs composites are readily prepared via a facile one-step electrochemical codeposition method. To our knowledge, no prior research has been made to prepare the ternary composites consisting of CPs, GO and CNTs for supercapacitor applications. Furthermore, we will investigate the effect of two types of CNTs (long versus short) on improving the electrochemical behaviors of the GO/PEDOT composites.

Carbon nanotube films (CNFs) are one kind of favorable substrate for flexible electric devices due to its superior flexibility, excellent electrical conductivity, and mechanical strength [31]. In this study, CNFs are used as the electrode substrate (mechanical support) as well as current collector to obtain a highly flexible, ultrathin, and lightweight electrode architecture. The CNFs-loaded long and short CNTs incorporated GO/PEDOT ternary composite electrodes (GO/PEDOT-lCNTs and GO/PEDOT-sCNTs) are prepared via a facile one-step electrochemical codeposition method. Their electrochemical behaviors were investigated and compared using the cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) measurements, and electrochemical impedance spectroscopy (EIS). To verify the feasibility of the prepared composite electrodes for use as flexible supercapacitor, a flexible solid-state supercapacitor was assembled by two identical composite electrodes of CNFs-loaded GO/PEDOT-lCNTs, with the PVA/H_3PO_4 gel as solid electrolyte. The capacitive performances and cycle stability of this highly flexible supercapacitor were tested, which successfully lighted a light-emitting diode (LED). This result is anticipated to stimulate practical applications.

2. Experimental

2.1. Materials

Natural graphite powder (325 mesh) was purchased from Guangfu Research Institute (Tianjin, China). Short and long carboxylated multi-wall carbon nanotubes (sCNTs-COOH and lCNTs-COOH) were obtained from Chengdu Organic Chemicals Co., Ltd., which were made by chemical vapor deposition (CVD) method, and their length was 0.5–2 and 10–30 μm, respectively. Carbon nanotubes thin films (CNFs, thickness of 20 μm) were supplied by Hengqiu Tech. Inc. (Soochow, China). 3, 4-ethylenedioxythiophene (EDOT, Ourchem®, 99%) and polyvinyl alcohol (PVA)-124 were purchased from Sinopharm (Shanghai, China).

2.2. Preparation of the electrode and supercapacitor

Graphite oxide was prepared from natural graphite powder with the modified Hummers method [32,33], and GO was obtained by subsequent exfoliation by ultrasonication. The flexible ternary composite electrodes of CNFs-loaded GO supported poly(3,4-ethylenedioxythiophene)-CNTs (GO/PEDOT-CNTs) were fabricated through a facile electrochemical codeposition method. The aqueous deposition bath containing 0.01 M EDOT monomer, 1 mg mL^{-1} GO, and 1 mg mL^{-1} sCNTs-COOH or lCNTs-COOH was dispersed adequately under ultrasonication for about 15 min. After that, the electrodeposition was performed with a three-electrode system, in which CNFs with 0.5 cm × 1 cm conductive areas serve as the working electrode, large areal Pt sheet acts as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. A