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Preparation and characterization of PEDOT:PSS wrapped carbon nanotubes/MnO_2 composite electrodes for flexible supercapacitors

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ABSTRACT

A great deal of researches have been dedicated to achieve thin, lightweight, and flexible energy storage devices for wearable electronics. However, the electrodes used for flexible supercapacitors usually have poor electronic and ionic conductivities, resulting in their limited performance in power density and cycling stability. Herein, we developed a flexible, high-performance and low-cost electrode based on PEDOT:PSS wrapped MWNT/MnO_2 composite for the high performance supercapacitor applications. Triton X-100 was used to improve the wettability of the MWNT surface and achieve better dispersion effect in the solution. PEDOT:PSS can further penetrate into the Triton X-100 wrapped MWNTs with enhanced electric conductivity and electrochemical stability. A high specific capacitance of 428.2 F/g, with a high energy density of 63.8 Wh kg^{-1} and good cycle stability can be obtained. These results demonstrated the great potential of the as-fabricated PEDOT:PSS wrapped MWCNT/MnO_2 composite for flexible, low-cost, high-performance energy storage devices.

1. Introduction

The demand for flexible energy storage devices has prompted significant research efforts for their potential applications in modern electronic devices including roll-up display, electronic paper, distributed sensors, wearable multimedia computing, flexible biosensors, and implantable medical products [1–4]. In particular, the development of flexible supercapacitors with high power density and long cycling life represents a promising strategy toward safe, light-weight, and wearable energy storage devices [5–7]. However, improving energy density while maintaining high power density of supercapacitors still remain a primary research focus in the field. In general, potential materials for supercapacitor applications include nanostructured transition metal oxides such as Co_3O_4, NiO, RuO_2, SnO_2 and MnO_2 because of their exceptional electrochemical pseudocapacitive properties [8–11]. Among the metal oxides, manganese oxide (MnO_2) is regarded as the most attractive oxide material due to its high pseudocapacitance, low cost, and environmental benignity. Nanostructured MnO_2 exhibits larger surface area and shorter conduction lengths for electrons and cations, making it highly attractive for application as electrodes for supercapacitor devices. Recently, a porous hierarchical MnO_2 nanowires deposited by using a simple two-step electrochemical deposition process has exhibited high specific capacitance and good cycle stability [12]. However, pure MnO_2 usually shows low conductivity. Therefore, combination of highly conductive carbon based materials with MnO_2 is one possible strategy to overcome the problem.

Typically, two-dimensional (2D) and rigid substrates such as Ti foil, fluorine-doped tin oxide glass, and carbon fabrics are widely used as current collectors through which the loading mass of active materials can be controlled to minimize the charge diffusion path [13]. However, the method used results in a low volume utilization rate of the supercapacitor, leading to diminished specific capacitance and energy density. Furthermore, the development of facile preparation procedures for fabricating soft, thin, and flexible low-cost supercapacitors with high mass loading density and high specific capacitance is often limited due to high electrode resistance and a low electrochemically active surface area [14–16].

In the present work, we develop thin, highly electrically conductive, and flexible electrodes based on poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) wrapped multi-wall carbon nanotubes (MWNT)/MnO_2 composites for supercapacitor applications. In the prepared composite, the non-ionic surfactant polymer, Triton X-100, was used to improve the wettability of the MWNT surface and achieve better dispersion effect in the solution. PEDOT:PSS can further penetrate into the Triton X-100 wrapped MWNTs with enhanced electric conductivity and electrochemical stability. The PEDOT:PSS wrapped MWNT composite not only provides a mechanical reinforcement effect, but also acts as an electronic transport medium for MnO_2 to ensure its remarkable electrochemical performance.

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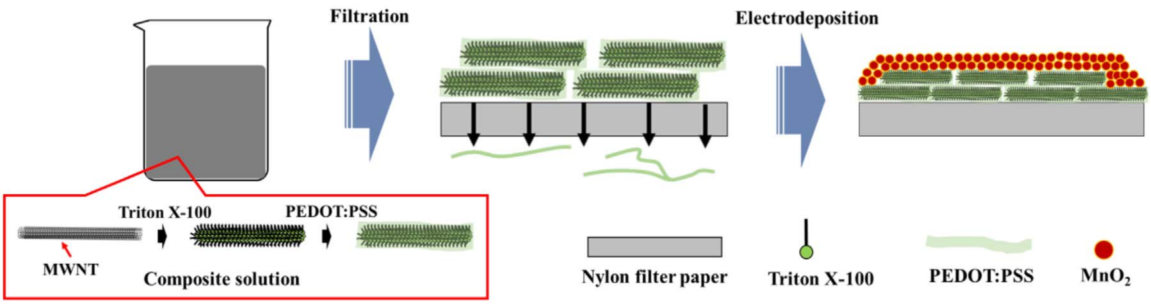

Fig. 1. Schematic illustration of the fabrication process of the flexible PEDOT:PSS wrapped MWNT/MnO_2 composite electrodes.

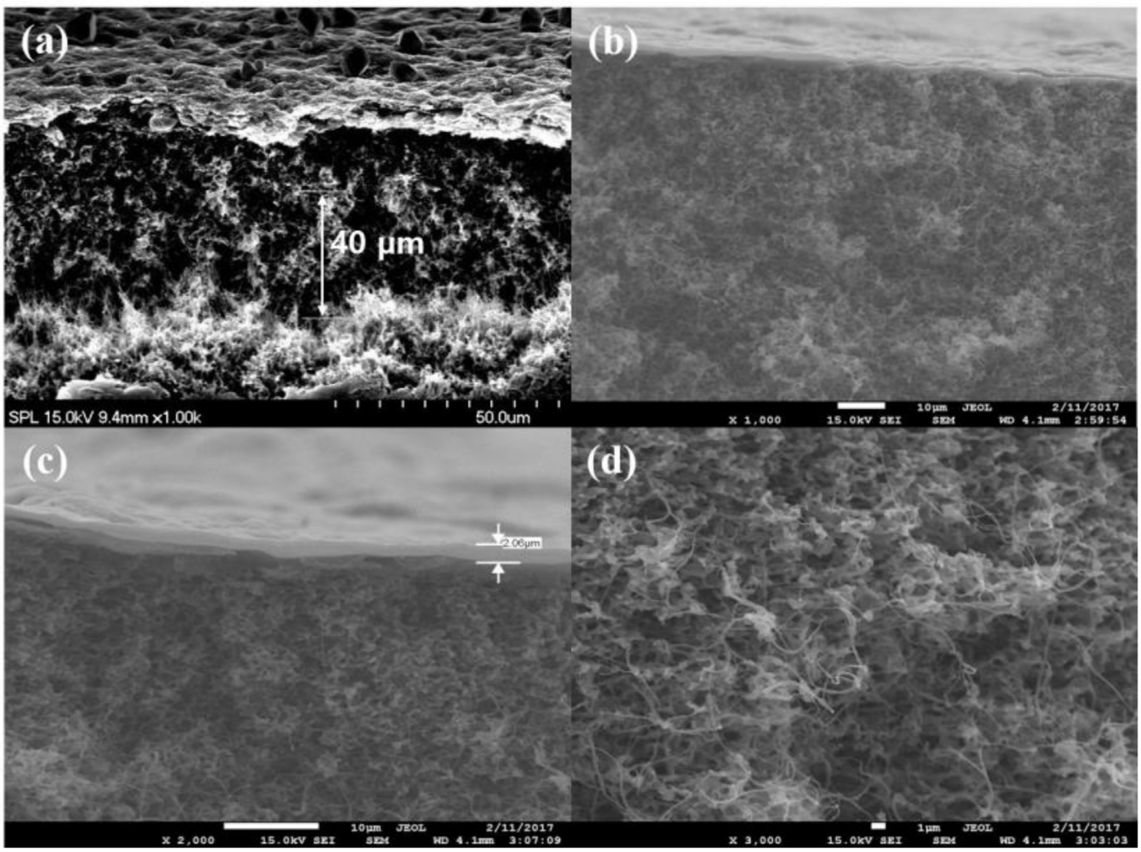

Fig. 2. Cross-section SEM images of (a) PEDOT:PSS wrapped MWNT composite electrode and (b, c, d) PEDOT:PSS wrapped MWNT/MnO_2 composite electrode.

2. Materials and methods

2.1. Fabrication of flexible PEDOT:PSS wrapped MWNT electrode

The flexible PEDOT:PSS wrapped MWNT electrode was fabricated by using a simple vacuum filtration method, as illustrated in Fig. 1.

Firstly, 4 wt% of MWNTs was added and dispersed in 3 wt% Triton X-100 solution. Subsequently, the mixture was energetically ultrasonicated for 1 h to form a homogeneous dispersion. After dispersion, the solution was centrifuged at 10,000 rpm for 30 min, and PEDOT:PSS solution at various 5–50 wt% was added, and kept stirring at room temperature for 24 h to obtain a homogeneously slurry.

Next, the PEDOT:PSS wrapped MWNT composite solution was vacuum-filtered and coated on a nylon membrane filter (Pore size: 0.45 μm, Diameter: 47 mm, Whatman™). An enhanced interfacial adhesion can be formed between nylon membrane filter and the dispersed PEDOT:PSS wrapped MWNT composite [17]. The composite solution was forced through the nylon membrane filter using a razor blade as a squeegee at a 45° angle. The applied pressure was applied to remove the excess composite solution on the filter paper. Finally, the sample was placed in an oven at 120 °C for 30 min and left to cool to room temperature.

2.2. Preparation of PEDOT:PSS wrapped MWNT/MnO_2 composite electrodes

The MnO_2 were electrochemically deposited on the surface of previously prepared PEDOT:PSS wrapped MWNT composite electrode. The electrodeposition solution was consisted of 0.05 M $Mn(CH_3COO)_2$ and 0.1 M Na_2SO_4. The potentiostatic deposition was performed at 0.6 V applied potential for 600–1800 s.

2.3. Characterization

The morphology and structural properties of the sample were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4700). The chemical composition was analyzed by X-ray Photoelectron Spectroscopy (XPS, ULVAC-PHI X-TOOL). Sheet-