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Multiwall carbon nanotube supported poly(3,4-ethylenedioxythiophene)/manganese oxide nano-composite electrode for super-capacitors

Raj Kishore Sharma, Lei Zhai*

NanoScience Technology Center and Department of Chemistry, University of Central Florida, 12424 Research Parkway, Suite 400, Orlando, FL 32826, USA

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ABSTRACT

MWCNT-PSS/PEDOT/MnO_2 nano-composite electrodes were fabricated by generating pseudo-capacitive poly(3,4-ethylenedioxythiophene) (PEDOT)/MnO_2 nano-structures on poly(styrene sulfonate) (PSS) dispersed multiwalled carbon nanotubes (MWCNTs). PSS dispersed MWCNTs (MWCNT-PSS) facilitated the growth of PEDOT and MnO_2 into nano-rods with large active surface area and good electrical conductivity. The ternary MWCNT-PSS/PEDOT/MnO_2 nano-composite electrode was studied for the application in super-capacitors, and exhibited excellent capacitive behavior between −0.2 V and 0.8 V (vs. saturated Ag/AgCl electrode) with high reversibility. Specific capacitance of the nano-composite electrode was found as high as 375 F g^{-1}. In contrast, specific capacitance of MWCNT-PSS/MnO_2 and MWCNT-PSS nano-composite electrodes is 175 F g^{-1} and 15 F g^{-1}, respectively. Based on cyclic voltammetric studies and cycle-life tests, the MWCNT-PSS/PEDOT/MnO_2 nano-composite electrode gave a highly stable and reversible performance up to 2000 cycles. Our studies demonstrate that the synergistic combination of MWCNT-PSS, PEDOT and MnO_2 has advantages over the sum of the individual components.

1. Introduction

Electrochemical capacitors (ECs) or super-capacitors are attracting much attention as high power energy storage devices. Super-capacitors are classified into two types based on their charge storage mechanism: electrical double layer capacitors (EDLCs) and pseudo-capacitors. Energy storage in an EDLC is due to the charging of the electrical double layer at electrode and electrolyte interface while a pseudo-capacitor utilizes faradic reactions in addition to double layer charge [1–4]. A conducting electro-active electrode with large surface area accessible to the electrolytic dopant ions holds the key to high performance super-capacitors. To fabricate such electrode, various materials including different types of carbon, conducting polymers, and transition metal oxides have been extensively investigated [5–12]. Graphitic, activated, templated and carbide derived carbons, carbon fabrics, fibers, nanotubes and nano-horns have been tested as highly conducting, open porous, electrochemically stable and cost effective EDLC materials for charge storage [13–16]. However, their performance is limited due to electrostatic nature of charge [3,4]. In order to maximize the electrical double layer (EDL) charge, high surface area (>3000 m^2/g) carbon materials such as acetylene black and activated carbon have been investigated [13], and achieved capacitance up to 300 F g^{-1} [3]. Nevertheless, oxidation of carbon during redox cycling and aging still limits the application of these carbon-based electrodes [17].

On the other hand, metal oxides and conducting polymers constitute pseudo-capacitive electrodes with high capabilities. Unlike EDL, the charge storage in pseudo-capacitive materials is based on the redox transitions of the bulk materials beneath the pore surfaces. Although having high specific capacitance, pseudo-capacitive materials suffer from low mechanical strength, poor electrical conductivity and low porosity which inhibit their application as super-capacitor electrodes. To overcome the challenges of carbon materials and pseudo-capacitive materials, composites containing carbon and pseudo-capacitive materials have been synthesized, and have demonstrated improvement in the electrochemical performance [9,18]. In these composites, carbon has been used as a support material to achieve electrical conductivity, large active surface area and mechanical stability [9,19,20]. Among these carbon materials, carbon nanotubes (CNTs) offer a unique porous network with high electrochemically accessible surface area, excellent electrical conductivity, good mechanical properties and chemical stability [6,10–12]. The effective utilization of CNTs depends strongly on the ability to disperse nanotubes homogeneously in solvents and separate CNT bundles that reduces active surface area and the EDL charge storage [21]. Studies on the preparation of pseudo-capacitive material/CNT binary composites show that the loading of pseudo-capacitive materials on CNTs or assembling the composite on current collectors develops a high contact resistance [22–25]. In order to achieve low contact resistance and high surface area, surface acti-

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* Corresponding author.
E-mail address: lzhai@mail.ucf.edu (L. Zhai).

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vation through dispersion or ordered assembling of CNTs have been investigated [26–35].

Three methods have been extensively applied to disperse CNTs into solvents and polymer matrices [3]: physical blending [4], chemical functionalization [11] and dispersants-assisted dispersion [14,16]. In case of physical blending, the dispersion quality deteriorates with time after the physical agitation such as sonication stops. For chemical modification and functionalization, CNTs are treated with strong oxidizing reagents to form functional groups such as carboxylic acids on the nanotube walls. Although an effective dispersion method, such a treatment inevitably disrupts the nanotube surface structures, leading to decreased electrical conductivity and diminished mechanical strength. In the dispersants-assisted dispersion, a dispersant is mixed with CNTs in solutions and CNTs are mechanically de-bundled by sonication. CNTs are stabilized by the dispersant chemical through non-covalent interactions, maintaining the nanotube structures, electrical conductivity and mechanical properties. Poly(styrene sulfonate) (PSS) is an effective dispersant that involves the non-covalent functionalization of CNTs with negatively charged PSS, and creates active sites on the nanotube surfaces [30].

Ternary composites of MnO_2 and polypyrrole with dispersed CNTs have shown improved performance with CNT good dispersion and material utilization [26]. In a recent study, electrodeposited MnO_2 on CNTs has been shown to improve the electrode performance and rate capability in comparison to the electrodeposited MnO_2 film [33]. The specific capacitance of CNT/MnO_2 electrode based on MnO_2 mass is $\sim$471 F g^{-1}. The MnO_2 utilization in the CNT/MnO_2 electrode (43%) is much higher than that of 12% in electrodeposited MnO_2 films [33]. Gao and co-workers reported that a capacitance of 205 F g^{-1} in 0.5 M Na_2SO_4 (at 2 mV/s) was obtained from a CNT/MnO_2 composite electrode. The high capacitance was obtained by depositing MnO_2 on surface activated CNTs that helped in high usage of MnO_2 [34]. Studies on CNT/MnO_2 [35–38], CNT/polypyrrole [39], CNT/PEDOT [40], and CNT/PSS/PEDOT [41] composite electrodes show that CNT's surface area plays an important role in material utilization, rate capabilities and electrode performance.

In this article, we report the fabrication of PEDOT/MnO_2 pseudo-capacitive nano-structures on PSS dispersed MWCNTs (MWCNT-PSS) and the electrochemical studies of the obtained composites as electrodes in super-capacitors. Our studies demonstrate that the synergistic combination of MWCNT-PSS, PEDOT and MnO_2 have advantages over the sum of the individual components. The combination of PEDOT and MnO_2 enhances their pseudo-capacitive performance by mutual interactions, and the MWCNT-PSS provides a large area support along with double layer capacitor (DLC) storage and an efficient electron transport. The PSS surface functionalities help the growth of nano-structured pseudo-capacitive materials. PEDOT is utilized to bridge the MWCNTs and MnO_2 to improve the electrical conductivity, and significantly enhances the electrochemical performance of the nano-composite electrode.

2. Experimental

2.1. Chemicals and materials

MWCNTs were purchased from Nanolab (Newton, MA) with a diameter of 10–20 nm and length about 5–20 μm. 3,4-Ethylenedioxythiophene (EDOT), poly(4-styrenesulfonic acid) (PSS), sodium peroxydisulfate, iron (III) sulfate, sodium sulfate, manganese acetate, and potassium permanganate were purchased from Sigma–Aldrich (St. Louis, MO). 5 wt% Nafion solution was purchased from Ion Power (New Castle, DE) and deionized water was used in all aqueous solutions.

2.2. Preparation of nano-composite material

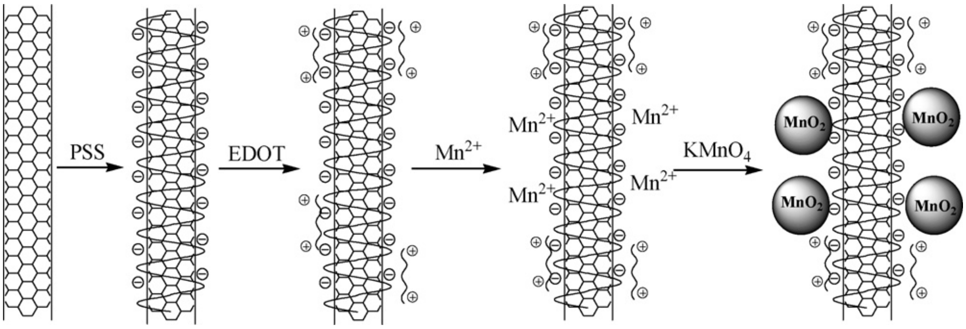
As depicted in Scheme 1, 10 mg MWCNTs were dispersed in 10 ml DI water using 0.3 ml, 18 wt% poly(4-styrenesulfonic acid). During the sonication, PSS wrapped around and formed a protective layer on MWCNT surface, which stabilized the nanotubes in water through static charge repulsion [42]. The negatively charged PSS layer on MWCNT attracted positively charged PEDOT/metal ions, and served as templates for subsequent nano-structure formation. The interaction between the growing nuclei with surface charges ($-SO_3^-$) facilitated the material to grow in nano-structures and retarded the inter-particle agglomeration.

MnO_2 was synthesized on the preformed MWCNT-PSS for the formation of MWCNT-PSS/MnO_2 and co-deposited with PEDOT for MWCNT-PSS/PEDOT/MnO_2 nano-composite formation [25]. Oxidation of Mn^{2+} and reduction of Mn^{7+} occurs to form Mn^{4+}. The resulting Mn^{4+} on interaction with water produces hydrated MnO_2 [9,18,43].

$$3Mn^{2+} + 2Mn^{7+} \rightarrow 5Mn^{4+} \tag{1}$$

$$Mn^{4+} + 2H_2O \rightarrow MnO_2 + 4H^+ \tag{2}$$

In a typical synthesis of hydrated manganese oxide, 50 ml 3.0 mM manganese acetate solution was stirred for 12 h in the presence of MWCNT-PSS and then oxidized using 50 ml 2.0 mM $KMnO_4$ solution under vigorous stirring. The negative charges on PSS layers are expected to bind with the Mn^{2+} ions, and the subsequent oxidation of anchored Mn^{2+} took place on the PSS surface, forming entangled nano-structures (Eqs. (1) and (2)). In case of the co-deposition of PEDOT with MnO_2, additional amount of $KMnO_4$ was used with EDOT monomers and Mn^{2+} ions. Followed by the oxidation with $KMnO_4$, MnO_2 and PEDOT nano-structures were obtained on



Scheme 1. Schematic illustration of synthesizing MnO_2/PEDOT nano-structures on MWCNT-PSS.