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Ternary nanocomposite SWNT/WO_3/PANI thin film electrodes for supercapacitors

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ABSTRACT

We describe a simple and fast process for the fabrication of ternary nanocomposite supercapacitor electrodes. In this work, thin film supercapacitor electrodes made up of binder-free single walled carbon nanotube (SWNT) thin films were deposited onto glass substrates by vacuum filtration followed by stamping method. Next, tungsten oxide (WO_3) and polyaniline (PANI) were electrodeposited on the SWNT thin films. Combination of SWNTs and pseudocapacitive WO_3 and PANI created a synergistic and complementary effect, which enhanced the electrochemical energy storage capacity. A specific capacitance of 28.5 mF/cm^2 was obtained at a current density of 0.13 mA/cm^2. Ternary nanocomposite thin film supercapacitor electrodes showed good capacity retention (76%), limited by the PANI stability, after 2000 cycles.

1. Introduction

Among energy storage devices, supercapacitors (or ultracapacitors) have received a lot of attention due to their high specific power and moderate energy densities. They have wide application areas spanning from electric vehicles, pulse power systems to portable devices [1–3]. Depending on the charge storage mechanism, there are two major groups for supercapacitor electrode active materials. Electrochemical double layer capacitors (EDLCs) store charge electrostatically in double layers, whereas pseudocapacitors store charges on the surface of the electrode active materials as faradaic redox reactions. Carbon based materials are EDLC type, while metal oxides and conducting polymers are pseudocapacitor type materials. EDLC have long-lasting life, while pseudocapacitors have high energy density. Carbon nanotubes are highly appealing candidate materials for supercapacitor electrodes [4–6]. Carbon nanotube thin films are a new class of materials where they are used in an ensemble form [7]. Owing to their high conductivity, permeability (resulting in high power density) and chemical inertness (long cycle lifetime), single walled carbon nanotube (SWNT) thin films are promising candidates for active supercapacitor electrode materials [4,8,9]. For practical device applications, these characteristics together with the fact that carbon typically forms a purely double layer make SWNT thin films unique.

In nanocomposite form, metal oxides and conducting polymers could improve electrochemical and mechanical properties of the supercapacitors [3]. Ruthenium oxide (RuO_2) is the most commonly used and highly pseudocapacitive material; but, its high cost and poisoning nature are the major drawbacks limiting its widespread applications [9]. Therefore, recent research has been focused on the exploration of alternative pseudocapacitive metal oxides and especially cheap metal oxides such as MnO_2, Co_3O_4 and NiO have been investigated [1,2,9,10]. Tungsten oxide (WO_3) is a n-type semiconducting oxide [11], which is readily used in electrochromic devices [12], gas sensors [13], and photocatalysis [14] while its electrochemical properties for supercapacitor devices have been relatively unexplored. Crystalline forms of WO_3 show non-prominent capacitance, while amorphous WO_3 shows high capacitance [15] due to the intercalation of small ions (H^+ and Li^+) [16]. WO_3 and a conducting polymer polyaniline (PANI) are used separately [15,17–19] and together [20–22] to examine their electrochemical potential, as electrode active materials; however, the demonstration of ternary composite electrodes, combining WO_3, PANI and SWNTs have remained elusive. Different methods are available for the synthesis of WO_3; but, synthesis of the WO_3/PANI

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nanocomposite in one step can be simply realized by electrodeposition [20]. Cathodic electrodeposition of WO_3 takes place at low pH values; however, those pH values are not suitable for many current collectors [23]. Moreover, PANI has different oxidation states and the most conductive state among them is the emeraldine salt, which is obtained at low pH values [24,25]. Therefore, formation of WO_3 and PANI nanocomposites on SWNT thin films through one step electrodeposition using cyclic voltammetry is advantageous for fast and large scale fabrication of supercapacitor electrodes. SWNT thin film electrodes can be homogeneously covered by electrodeposited WO_3 and PANI to enhance electrochemical properties with respect to the individual components.

In this work, we have fabricated ternary nanocomposite SWNT/WO_3/PANI thin films based supercapacitor electrodes. High electrical conductivity of SWNT thin films allowed the possibility of the fabrication of supercapacitors without a separate charge collector and enhanced the properties solely arised by the WO_3 and PANI components in a synergistic manner.

2. Experimental details

2.1. Preparation of samples

SWNTs were purchased from Carbon Solutions Inc. (SWNT P3). All other materials used in this work were purchased from Sigma–Aldrich. They were of analytical grade and used without further purification.

SWNT thin films were deposited onto soda lime silicate glass substrates by vacuum filtration and consecutive stamping method [26]. To prepare SWNT thin films, firstly SWNTs were dispersed in 1% sodium dodecyl benzene sulfonate (SDBS) solution by tip-sonication. Then the SWNT solution (SWNT density: 2 mg/ml) was filtrated using mixed cellulose acetate (Merck MCE, pore size: 200 nm) filter membranes via vacuum filtration (flow rate ~ 1 m^3/h). Following the settlement of SWNTs on filter membrane, filtration was repeated with deionized water to remove excess surfactant. Accumulation of SWNTs on the filter membrane controls the film homogeneity. The SWNT mass in the thin film (typically 0.08 mg) was determined by the volume of filtrated SWNT solution. SWNT films on the filter membrane were transferred to soda-lime silicate glass substrates by compressively (under 200 g/cm^2) heating over a hot plate at 80 °C. Following drying, filter membranes were removed by dissolving in acetone. Following deposition, SWNT thin films were treated with nitric acid (HNO_3, 65%) for 3 h to remove metal impurities and filter paper residues. Acid treatment also helps to improve SWNT thin film conductivity [27]. The resulting circular thin films had an area of 2 cm^2. Conductive carbon paint was used to print external contact points.

WO_3/PANI nanocomposites were electrodeposited onto SWNT thin films by cyclic voltammetry at room temperature conditions [20,24]. A potential range between −0.6 and 0.9 V at a scan rate of 50 mV/s was used for 105 cycles and films were then rinsed with distilled water. The solution used for the deposition of composite films contained sodium tungstate dihydrate ($Na_2WO_4.2H_2O$, 15 mM), sulfuric acid (H_2SO_4, 0.25 M) and aniline monomer (46 μL). During electrodeposition, $Na_2WO_4.2H_2O$ was added to the solution after the 5th cycle, whereas aniline was added after the 55th cycle. The reference and counter electrodes were Ag/AgCl and platinum wire, respectively.

2.2. Characterization

The structure and morphology of the fabricated ternary nanocomposite films were characterized by scanning electron microscopy, (SEM, FEI Nova Nano SEM 430, operated at 10 kV). X-ray photoelectron spectroscopy (XPS) analyses were performed for chemical identification and evaluation of the chemical state of the constituent elements. XPS spectra were collected using a PHI 5000 VersaProbe spectrometer. The qualitative analyses for chemical identification were performed using high-resolution scans of the W (4f) and O (1s) and C (1s) spectral regions. The binding energies (BE) and charge corrections were referenced to the C (1s) line at 284.5 eV. XPS signals were fitted with Gaussian curves. Fourier transform infrared (FT-IR) spectroscopy analyses were performed using a Bruker IFS 66/S model spectrometer. FT-IR spectra of thin films were obtained in the ATR mode. Electrochemical measurements of the supercapacitor electrodes were conducted in a three-electrode configuration using potentiostat/galvanostat system (Gamry Reference 3000). The reference and counter electrodes were Ag/AgCl and platinum wire, respectively. All potentials are relative to the Ag/AgCl. Electrochemical behaviors of the electrodes were studied by cyclic voltammetry (CV), chronopotentiometry (CP), potentiostatic electrochemical impedance spectroscopy (EIS) in a 0.1 M lithium perchlorate ($LiClO_4$) in propylene carbonate (PC) electrolyte solution. A microbalance was used to measure the mass of SWNT/WO_3/PANI and the weight of total active materials in SWNT/WO_3/PANI electrode was measured around 0.4 mg.

3. Results and discussion

The electrodeposition of WO_3 and PANI composites on vacuum filtrated SWNT films was achieved using cyclic voltammetry at a potential window between −0.6 V and 0.9 V at a scan rate of 50 mV/s. Evolution of ternary composite films is shown in Fig. 1(a) with respect to CV cycles. Peaks within the CV curves showed that the thickness of the WO_3 and PANI coating gradually increases on the SWNT film surface. Porous nature of the SWNT films facilitates deposition of WO_3 and PANI in a conformal manner.

Cyclic voltammograms of the obtained films are shown in Fig. 1(b). The cyclic voltammetry measurements revealed that the cathodic electrodeposition of WO_3 layer on SWNT thin films result in a broad peak at negative potential region, as shown in Fig. 1(b). The SWNT/WO_3/PANI nanocomposite film showed complementary peaks corresponding to the redox pairs of WO_3 and PANI. Moreover, the peak positions corresponding to the redox process of WO_3, in the cyclic voltammogram of SWNT/WO_3/PANI were shifted to the higher potentials due to WO_3 and PANI related redox reactions.

Surface morphologies of the SWNT, SWNT/WO_3 and SWNT/WO_3/PANI thin films on glass substrates were investigated through SEM analysis. SEM images of bare SWNT thin films, electrodeposited WO_3 layer on SWNT thin films and ternary nanocomposites (SWNT/WO_3/PANI) are provided in Fig. 2(a)–(d), respectively. Bare SWNTs (Fig. 2(a)) were coated with a thin WO_3 layer during electrodeposition as shown in the SEM images (Fig. 2(a)–(b)). Thin metal oxide coating is necessary for the electrolyte ion intercalation to enhance the surface reactions [28]. PANI not only fills the openings of SWNT/WO_3 composite but also covers the whole surface of the composite films as evidenced in low and high resolution SEM images provided in Fig. 2(c)–(d), respectively. According to cross sectional SEM images (Fig. 2(a) and (c) insets), average thicknesses of the SWNT and SWNT/WO_3/PANI are 500 nm and 900 nm, respectively. Top hybrid WO_3/PANI layer within the ternary nanocomposite film improved the conductivity (as will be further discussed in EIS analysis) and also acted as a blanket to prevent the detachment of the WO_3 nanoparticles. No further annealing treatment was applied, thus the electrodeposited WO_3 layer is supposed to be in amorphous state.

Surface measurements by XPS are carried out for WO_3 in SWNT/WO_3 nanocomposite to verify the chemical composition. Position correction was done with respect to C 1s peak. According to