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Short communication

Electrochemical behavior of carbon-nanotube/cobalt oxyhydroxide nanoflake multilayer films

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ABSTRACT

A new type of multilayer films consisting of multi-walled carbon nanotubes (MWCNTs) and cobalt oxyhydroxide nanoflakes (CoOOHNFs) are developed by alternately electrostatic self-assembly and electrodeposition technique, respectively. The successful growth of multilayer films composed of MWCNT and CoOOHNF are confirmed by scanning electron microscopy and X-ray photoelectron spectra. The multilayer film electrode is investigated for use in a supercapacitor with cyclic voltammograms and galvanostatic charge-discharge experiments. Experimental studies reveal that coatings of MWCNT/CoOOHNF on ITO glass present excellent electrochemical capacitance with specific capacitance being 389 F g^{-1}. The overall improved electrochemical behavior is accounted for the unique structure design in the multilayer films in terms of effective micro-porous nanostructure, large specific surface-area and good electrical conductance.

1. Introduction

Electrochemical capacitors (ECs), widely being used as power sources [1], have attracted much attention in current electrochemistry research because of their high energy densities and long cycle lives. The choice of material for use as electrodes is an important factor to improved-electrochemical capacitance because the performances of the ECs are highly dependent upon the nature of the electrode materials, such as compositions, structures and surface areas etc. Commonly, activated carbons with high surface areas were used as electrode materials for the electrochemical double layer capacitors; and transition-metal oxides were used as electrode materials for the pseudo-capacitors related to the redox reaction [2], respectively. Initially, RuO_2 generated great interest due to its high specific capacitance [3], but it has less possibility to be commercialized inmost applications because of its high cost. In attempting to develop economical electrodes, oxides of MnO_2 [4,5], Co_3O_4 [6], NiO_x [7], and SnO_2 [8] have been suggested for use.

Specifically, cobalt-based materials have been considered one of the most promising candidates for use in developing electrodes due to comparatively lower material costs. On the other hand, both their narrow potential-windows and relatively poorer electrochemical capacitances limit their possible usage in various applications. A key strategy to improving the electrochemical properties of such otherwise useful cobalt-based materials is the morphological and/or chemical composition design of cobalt-based materials at the nanometer-scale. Recently, nanostructured cobalt hydroxide $Co(OH)_2$ and cobalt oxyhydroxide (CoOOH) films as electrode materials were fabricated by the chemical-bath deposition [9–11] and electrodeposition methods [3] for the high-performance ECs which exhibited reasonably high pseudo-capacitance derived from the Co^{III}/Co^{II} redox process in aqueous solution. Other innovative methods include the addition of carbon nanotubes (CNTs) into transition-metal oxides (RuO_2, MnO_2, SnO_2-V_2O_5) to prepare multilayer film electrode materials [12–17], and the CNT used as substrates for the deposition of active materials [18,19]. These resultant multilayer film electrodes exhibited enhanced performances for ECs due to the advantages, such as highly accessible surface areas, high chemical stability, and good electrical conductivity [20,21].

The current work demonstrates the design of multilayer films consisting of multi-walled carbon nanotubes (MWCNTs) and cobalt oxyhydroxide nanoflakes (CoOOHNFs). The stepwise preparation firstly involves the electrostatic-assembly of well-dispersed carbon nanotubes on ITO glass followed by potentiostatically depositing CoOOHNF. Overall, this process leads to pronounced

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electrochemical performance and widened potential windows for pseudo-capacitors.

2. Experimental

2.1. Reagents and materials

The reagents and electrolytes, $CoCl_2{\cdot}6H_2O$, Na_2SO_4, NaOH, H_2SO_4, HNO_3, and Poly diallyl dimethyl ammonium (PDDA), were all of analytical grade (Aldrich Chemical Company, Inc.). Water was purified to a resistivity of 18.2 MΩ cm by passing through a Milli-Q water system. Indium-tin oxide (ITO)-coated glass (0.5 mm, 10 Ω cm^{-2}) was purchased from CSG Holding Co., Ltd, of Shenzhen, China. MWCNTs, with diameters 40-60 nm, were obtained from Shenzhen Nanotech Port Co. Ltd.

2.2. Oxidation and dispersion of MWCNT

Oxidation of MWCNT has been described in detail previously [22], Briefly, MWCNTs were oxidized by sonicatation in 20 ml of a mixture of H_2SO_4:HNO_3 (3:1) for 2 h, then washed using an aqueous NaOH solution. The oxidized-MWCNTs were sonicated, rinsed, and centrifuged, three times to obtain well-dispersed MWCNTs with negatively charged surfaces, and partially-oxidized carboxylic groups on the outer walls.

2.3. Preparation of the multilayer films of MWCNT and CoOOHNF

The multilayer films were fabricated on clean-ITO glass slides (the cleaning procedure is described in detail elsewhere [14–16]) via a two-step procedure as shown in Fig. 1. In the first step, the ITO substrate was dipped in a positively-charged PDDA polyelectrolyte solution (1 wt%, pH 11) containing 1.0 M NaCl, and submerged for 15 min, then rinsed with water and dried under a N_2 gas flow [23]. The positively charged PDDA-precoated substrate was subsequently placed horizontally in a solution of dispersed negatively-charged MWCNTs (0.5 mg dm^{-3}) for 30 min, rinsed with water, and dried with N_2 gas to deposit MWCNT layer on the substrate. After electrostatic absorbance of MWCNT layers, CoOOHNF were deposited by potentiostatic deposition from a solution of 0.05 M $CoCl_2$ at a potential of −1.0 V vs. Ag/AgCl, held for 30 min [24]. These two steps resulted in nanostructured multilayer films composed a bi-layer pair of MWCNT and CoOOHNF. The multilayer films with desired multiple layers of repeating MWCNT/CoOOHNF units were fabricated by repeating the electrostatic assembly and potentiostatic deposition for a number of cycles.

2.4. Multilayer film characterization

The topographical features of the films were examined by SEM (JEOL JSM-890). All samples were sputtered with platinum for 3 min before SEM observation to prevent charge accumulation. XPS analysis was performed on a Kratos Axis ULTRA X-ray Photoelectron Spectrometer using a monochromated Al Kα excitation source (1486.6 eV). The quantitative analysis was performed with CASAXPS software.

The mass of each layer (PDDA/MWCNT, or CoOOHNF) were obtained using the electrochemical quartz crystal microbalance (EQCM) technique. The quartz crystals used were commercially available 10 MHz, AT-cut type (diameter, 12.5 mm) consisted of 1000 Å Au with a 50 Å Cr under layer (Beijing Chenjing Electronic Co. Ltd). The frequency changes were measured by a PB-KIT-O1, EQCM-Pico balance measuring system (Technobiochip, S.C.AR.L., Italy). The EQCM device was placed in a static detection chamber with one quartz crystal exposed to a solution volume of 15.0 ml. When the coating deposited on the quartz crystal, the frequency response was stable within ±1.0 Hz over periods of 30 min. Base on the Sauerbrey equation, the mass of the assembly film was calculated by according to the frequency changes and linearly proportional between the frequency and the mass loading of the EQCM.

2.5. Electrochemical measurements

Electrochemical performance of the multilayer film electrodes was evaluated by cyclic voltammetry (CV) and galvanostatic charge-discharge cycles (GC) in a three-electrode electrochemical cell with the Solartron 1480A multistat. Platinum was used as the counter electrode, and Ag/AgCl as the reference electrode. The multilayer films on the ITO substrate as the working electrodes were dried at 120 °C under vacuum for 3 h prior to electrochemical measurements. The 0.1 M Na_2SO_4 electrolyte was degassed by bubbling with N_2 for 30 min to ensure the electrolyte was air-free. CV was measured at a scan rate of 10 mV s^{-1} and GC with a constant current of 1×10^{-5} A, over a cell potential window of 0.1 to 0.9 V.

The specific capacitance is used to evaluate quantitatively the capacitive properties of the multilayer film electrodes and obtained from the GC profiles:

$$SC = \frac{I \cdot \Delta t}{m \cdot \Delta V}$$

where SC is the specific capacitance of the multilayer film electrode (F g^{-1}); I is discharge current (in Fig. 6, $I = 1 \times 10^{-5}$ A); t is discharge time; ΔV is potential window (in this test, $\Delta V = 0.8$ V); m is the mass of the film deposited the PDDA/MWCNT layer or CoOOHNF layer. Base on the results of the EQCM method, the mass of PDDA/MWCNT and CoOOHNF layer are 1.10×10^{-6} and 2.27×10^{-6} g, respectively.

3. Results and discussion

3.1. Film characterization and multi-layer nanostructure

Fig. 2 presents the SEM images of the films of MWCNT and CoOOHNF deposited on the ITO glass substrates. In order to illuminate buildup of the multilayer films, the special surface section, which all of the substrate (ITO glass), MWCNT layer and CoOOHNF layer can be seen, was collected and the SEM image was showed as Fig. 2(A). From Fig. 2(A), it is observed that the MWCNT layer adsorbed on ITO glass slide and the CoOOHNF layer electrodeposited on the MWCNT layer. Fig. 2(B) shows an ITO glass slide deposited with (PDDA/MWCNT) clearly displaying a rough surface with randomly oriented MWCNT ranging from several hundred of nanometer to several micrometers in length. It also can be observed that the surface is densely covered with the CNT layer. Image shown in Fig. 2(C) is the surface morphology of the electrodeposition layer. It is apparent that a network of nanostructured flake is grown vertically on the surface of the CNT layer. The nanoflake

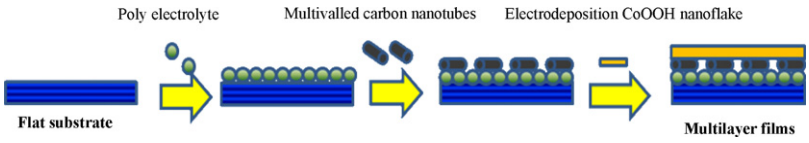

Fig. 1. Schematic illustration of preparation of the multilayer film.