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The coaxial nanostructure of ruthenium oxide thin films coated onto the vertically grown graphitic nanofibers for electrochemical supercapacitor

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ABSTRACT

In this work, the coaxial nanostructure of ruthenium oxide (RuO_x) thin films coated onto the surface of the vertical graphitic nanofibers (GNFs) was developed and employed as electrodes for electrochemical supercapacitor. The vertically aligned GNFs were directly grown on the fluorine doped tin oxide glass via the chemical vapor deposition, and the RuO_x thin films were prepared by an easy cyclic voltammetric electrochemical deposition. The morphologies and nanostructures of the coaxial-nanostructure RuO_x/GNFs were investigated by the field emission gun scanning electron microscopy and the high-resolution transmission electron microscopy, respectively. Raman spectrum was used to examine the characteristic features of the RuO_x/GNFs. The electrochemical properties were examined by cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectra. The directly grown GNFs not only played the attractive template that offered a large surface area to promote the loading of RuO_x for enhancing electrochemical activity, but also provided a high-speed pathway that promoted charge transport and transfer. The macroporous structure of the vertically coaxial-nanostructure RuO_x/GNFs avoided the self-aggregation, thus allowed the electrolyte can easily diffuse through the open space between them to enhance the electrochemical performance. The electrochemical measurements revealed that the excellent charge storage properties of the RuO_x/GNFs can be obtained, the good electrochemical performance was attributed to the unique macroporous structure and the coaxial nanostructure of RuO_x/GNFs.

1. Introduction

Recently, in order to slow down the climate change problem by global warming, the world devoted to develop the renewable energy and promote the energy utilization efficiency. Among various renewable energy storage devices, the development of excellent performance electrochemical energy storage devices with low cost has attracted huge attention for applications in hybrid electric vehicles, large industrial equipment and microelectronic devices in our life [1–3].

In order to improve the efficiency for electrochemical devices, the requirements of design and election for electrode materials are large specific surface area, high conductivity, excellent chemical and physical stability, good catalytic activities and low cost. Carbon based nanomaterials are the extraordinary strategies to approach the requirements mentioned above [4,5]. In addition, carbon based nanomaterials with functional materials become high performance hybrid nanostructures for energy storage applications in fuel cells [6,7], batteries [8,9], and supercapacitor [10,11]. Among the family of carbon based nanomaterials, the one-dimensional (1D) nanostructure of carbon nanomaterials with good electronic conduction for faster electron transfer can improve electrochemical performance [12]. For example, graphitic nanofibers (GNFs) with high mesoporous area and lots of active sites have many potential applications in green energy [13].

Supercapacitors play an important role in energy storage devices owing to their good stability, high power density, fast charge/discharge rate and long cycling life. Additionally, the electrode materials and their unique structures are important factors in the performance of supercapacitors, such as metal oxide (RuO_2, $Ni(OH)_2$, CoO) with special nanostructures [14–16], or such as graphdiyne nanostructures [17]. Metal oxide especially amorphous ruthenium oxide (RuO_x) has been highly appreciated in supercapacitors due to its high specific capacitance [18,19].

In terms of the above considerations, in this work, we report the synthesis of the coaxial nanostructure of RuO_x/GNFs. We improved the specific capacitance of RuO_x by using the high specific surface area of GNFs. The as-prepared coaxial nanostructure of RuO_x/GNFs exhibits electrochemical performance and good capacitance which may find potential in high-performance supercapacitor applications.

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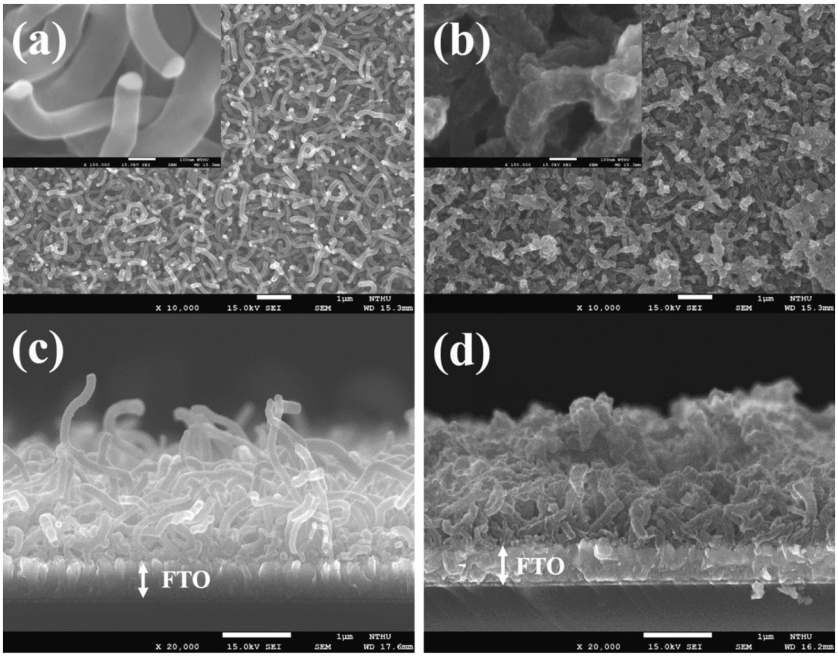

Fig. 1. SEM images of the top view of (a) GNFs and (b) RuO_x/GNFs/FTO, cross-section SEM images of (c) GNFs and (d) RuO_x/GNFs/FTO.

2. Experimental method

2.1. Fabrication of coaxial-nanostructure RuO_x/GNFs electrode

At first, vertically aligned graphitic nanofibers (GNFs) were directly synthesized on fluorine doped tin oxide (FTO) conductive glass (Hartford, TEC-7, 2.2 mm) via the chemical vapor deposition (CVD) method. The FTO conducting glass was sequentially ultrasonically cleaned with acetone, distilled (DI) water, and ethanol. A 12 nm Ni film was deposited on FTO glass via electron beam evaporation (Cello, Ohmiker-50B, Taiwan) as catalyst for the growth of GNFs. In the process of CVD, the FTO glass coated with Ni catalyst was loaded into the home-made furnace. Then, heated to 550 °C in 20 min at 2666 Pa with 320 standard-state cubic centimeter per minute (sccm) Ar gas introduced into the furnace continuously. A H_2/Ar gas mixture was introduced into the quartz tube for 10 min pretreatment when the temperature reached 550 °C; the gas flow rates were H_2: Ar = 70 sccm: 320 sccm. Then, O_2/C_2H_2/H_2/Ar gas mixtures were introduced into the quartz tube for GNFs growth; the gas flow rates were O_2: C_2H_2: H_2: Ar = 3 sccm: 15 sccm: 70 sccm: 320 sccm. The growth time of GNFs was 20 min and the pressure was controlled at 2666 Pa. After that, the gas mixture was turned off except for Ar gas and the furnace was slowly cooled down to room temperature.

Prior to electrodeposit RuO_x thin films, GNFs/FTO substrate underwent the hydrophilic process by cyclic voltammetry (CV) method as the same as our previous report [20]. The electrolyte used for hydrophilic process was an O_2-saturated 0.5 M H_2SO_4 (J.T.Baker, item #JT-9681-01) aqueous solution. The process for synthesis of hydrous RuO_x was similar as the previous work [21]. In this study, 5 mM $RuCl_3 \cdot xH_2O$ (Uniregion bio-tec, item #UR-IRUT001), 0.01 M HCl (J.T.Baker, item #JT-9535-01), and 0.1 M KCl (SHOWA, item #KZ-3329 T) with initial pH 1.96 were formulated in aqueous solutions as precursors. RuO_x thin films were prepared by the easy CV method with a potential range between −0.2 and 1.0 V_{SCE} at a scan rate of 50 mV s^{-1} for 50 cycles in a three-electrode electrochemical configuration. In order to obtain the coaxial-nanostructure RuO_x/GNFs specimen, the GNFs/FTO served as working electrodes, a Pt mesh was used as the counter electrode, and a saturated calomel electrode (SCE) acted as the reference electrode. Finally, the specimens were cleansed with DI water and dried at 50 °C in the oven. The hydrophilic process for GNFs and the electrochemical deposition of RuO_x thin films were operated via the potentiostat/galvanostat (Eco Chemie, PGSTAT 302 N, Autolab, Netherlands).

2.2. Characterization

The morphologies and microstructures of the prepared specimens were investigated by using the field emission gun scanning electron microscopy (FEG-SEM; JEOL, JSM-7610F, Japan), and the high-resolution transmission electron microscopy (HRTEM; JEOL, JEM-2100F, Japan), respectively. Raman spectroscopy (HORIBA, LABRAM HR 800 UV, Japan) with a 632.8 nm He-Ne laser source was used to characterized the features of the prepared specimens. The cyclic voltammetry (CV), galvanostatic charge-discharge (CD) characteristics and the electrochemical impedance spectra (EIS) were carried out to determine the electrochemical properties. CV and CD were measured by the potentiostat/galvanostat (CH Instruments, 1140B, USA) and performed in a three-electrode electrochemical configuration, which was using a SCE as the reference electrode, a platinum wire as the counter electrode and the specimen as the working electrode. The specimens of FTO, GNFs/FTO, RuO_x/FTO and RuO_x/GNFs/FTO were prepared with the fixed area of 1 cm × 1 cm. The electrolyte used for all electrochemical measurements was a 0.5 M H_2SO_4 aqueous solution, and was saturated by bubbling with Ar gas for 30 min before used. A flow of Ar gas was flushed over the electrolyte during the measurements to ensure continuous Ar saturation. Whereas the EIS measurements were conducted using the potentiostat/galvanostat (PGSTAT 302 N, Autolab, Eco Chemie, Netherlands) with a Frequency Response Analysis (FRA) module, and performed in a two-electrode electrochemical configuration with two identical RuO_x/GNFs electrodes.

3. Results and discussion

3.1. Material characterization

Fig. 1(a) and (b) showed the top-view SEM images of GNFs and RuO_x/GNFs, respectively, insets showed the high magnification SEM images. Fig. 1(c) and (d) showed the cross-section SEM images of GNFs