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Synthesis of $Ru_{0.58}In_{0.42}O_y \cdot nH_2O$ nanoparticles dispersed onto poly(sodium-4-styrene sulfonate)-functionalized multi-walled carbon nanotubes and their application for electrochemical capacitors

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ABSTRACT

In this work, poly(sodium-4-styrene sulfonate) (PSS)-functionalized multi-walled carbon nanotubes (FMWCNTs) were first synthesized *via* a polymer-assisted technique. Then, $Ru_{0.58}In_{0.42}O_y \cdot nH_2O$ nanoparticles (NPs) were mono-dispersed onto the FMWCNTs surfaces under mild hydrothermal condition. Here, PSS with negative charge serves as a bifunctional molecule both for solubilizing and dispersing MWCNTs into aqueous solution and for tethering Ru^{3+} and In^{3+} to facilitate the good dispersion of $Ru_{1-x}In_xO_y \cdot nH_2O$ NPs onto their surfaces. The good dispersion of $Ru_{0.58}In_{0.42}O_y \cdot nH_2O$ NPs onto FMWCNTs makes OH^- ions and electrons easily contact these NPs with abundant electroactive sites, which results in a large specific capacitance (SC) of 319 F g^{-1} for the naocomposites. Moreover, a symmetric electrochemical capacitor (EC) is constructed by using the nanocomposites as electrodes and delivers large specific energy density of 18.1 Wh kg^{-1}, desirable power property of 1302 W kg^{-1}, high electrochemical reversibility and good SC retention of 84.7%.

1. Introduction

Recently, carbon-based electroactive materials for electrochemical capacitors (ECs) have drawn much attention due to their high specific surface area and porous nature [1–4]. Particularly, multi-walled carbon nanotubes (MWCNTs), as one of the attractive carbon materials, have been recognized [5,6] widely for ECs application, considering their unique structural and electronic properties, such as high chemical stability, low mass density, low resistivity, narrow distribution of mesopore sizes, and large surface area to weight ratio as well as the ability to form a three-dimensional conducting matrix. However, their specific capacitances (SCs) are commonly very low. Hence, considerable efforts have been made to improve the SCs of MWCNTs-based electrode materials by various methods, such as chemical activation [7], and modification by using electronic conducting polymers (ECPs) [8–10] and/or transition-metal oxides with typical pseudocapacitive properties [11–16].

Obviously, the combination of an electric double layer system and a pseudocapacitive system could be a better candidate for an EC with higher energy density and power property, because such hybrid can both utilize the fast and reversible pseudocapacitance and the indefinitely reversible double-layer capacitance at the electrode–electrolyte interfaces [5]. However, owing to the poor stability of ECPs [8–10], transition metal oxides owning better electrochemical stability and higher SCs have been extensively studied and expected to offer the enhanced capacitive performance. Among various transition metal oxides, Ru-based oxides doped with homovalent and/or heterovalent substitution (donated as $Ru_xMe_{1-x}O_y$, where Me represents Co [17,18], Ni [19], Sn [20,21], Ti [22], V [23,24], Cr [25,26], Zr [27], Ce [28], *etc.*) have been recognized as the most promising candidates for ECs, due to their larger SCs and better electrochemical stability. Hitherto, the synthesis of Ru-based oxides/MWCNTs nanocomposites with a uniform structure, unfortunately, has been a great challenge yet. Therefore, a facile and effective method to synthesize Ru-based oxides/MWCNTs composites with uniform nanostructure and good electrochemical capacitance is highly desired.

Recently, polymer-assisted technique has been envisaged to be a facile, cost-effective, and general approach to synthesis of metal oxides/MWCNTs nanocomposites [11–13,29]. Poly(sodium-4-styrene sulfonate) (PSS) cannot only solubilize and disperse MWCNTs well into the aqueous solution but also noncovalently functionalize MWCNTs through a polymer-wrapping mechanism [11–13,29–31]. As a consequence, the PSS-functionalized MWCNTs (FMWCNTs)

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would be dispersed well in an aqueous solution and create much more electroactive sites tethering metal ions with positive charge for subsequent formation of metal oxide NPs onto their surfaces. As for the synthesis of metal oxide NPs, mild hydrothermal method has been known as an efficient route and extended to prepare binary and/or ternary transition metal oxide NPs [20–22]. To the best of our knowledge, the synthesis and electrochemical performance of the Ru-based binary oxide NPs dispersed well onto the MWCNTs surfaces have been reported scarcely.

In the work, we first synthesized $Ru_{0.58}In_{0.42}O_y{\cdot}nH_2O$/FMWCNTs nanocomposites with uniform structure, where $Ru_{0.58}In_{0.42}O_y{\cdot}nH_2O$ NPs were mono-dispersed onto the FMWCNTs surfaces under mild hydrothermal condition. The unique nanocomposites delivered desirable electrochemical capacitance. And electrochemical performance of a symmetric EC constructed by using the $Ru_{0.58}In_{0.42}O_y{\cdot}nH_2O$/FMWCNTs nanocomposites as electrodes was also investigated in detail.

2. Materials and methods

2.1. Materials

MWCNTs were synthesized by the chemical vapor deposition (CVD) method and purified by refluxing them in nitric acid (HNO_3, 2.6 M) for 12 h before use. All the chemicals used were of analytical grade. $RuCl_3{\cdot}nH_2O$, NaCl, absolute ethanol and $InCl_3{\cdot}4H_2O$ were obtained from Nanjing Chemical Company (Nanjing, China). Poly(sodium-4-styrene sulfonate) (average MW, 70,000) was purchased from Aldrich. Saturated calomel electrode (SCE) was manufactured by Leici (Shanghai, China). All aqueous solutions were freshly prepared by using high-purity water (18 MΩ cm resistance) from an Ampeon 1810-B system (Jiangsu, China).

2.2. Synthesis and characterization of $Ru_{0.58}In_{0.42}O_y{\cdot}nH_2O$/FMWCNTs nanocomposites and PVA–KOH (5 M)–H_2O gel electrolyte

The FMWCNTs could be obtained by the same method as we reported before [9,11–13]. Then, the obtained FMWCNTs were ultrasonicated into 120 mL water with 35 mg $RuCl_3{\cdot}nH_2O$ and certain amount of $InCl_3{\cdot}4H_2O$ with the molar ratio of 3:2 for Ru and In species, which was further ultrasonicated for 0.5 h. After well mixed, the pH of the mixture was adjusted to *ca.* 5. Then the precursor was kept in a Teflon-lined autoclave (150 mL) with a stainless steel shell. After heated to 180 °C, the autoclave was kept at the temperature for 6 h in an oven and then cooled to room temperature naturally. The reaction product was filtered, washed repeatedly and then dried at 80 °C. The alkaline polymer gel electrolyte (PVA–KOH (5 M)–H_2O) was prepared by the solution-casting technique, as we reported previously [32].

The morphology and structure of the nanocomposites were examined by scanning electron microscopy (SEM, LEO 1430VP, Germany) and transmission electron microscope (TEM) (FEI, TECNAI-20) coupled with an energy dispersive X-ray (EDX) analyzer (Link-200, Britain), and by X-ray diffraction (XRD, Max 18 XCE, Japan) using a Cu Kα source.

2.3. Electrochemical tests

Electrodes for electrochemical measurements were prepared by mixed electroactive materials with acetylene black (AB) and polytetrafluoroethylene (PTFE) with the weight ratio of 5:1:0.5. A small amount of water was then added to this composite to form a more homogeneous mixture, which was pressed (12 MPa) onto nickel grid (1 cm^2) serving as a current collector. The typical loading of the electroactive material was 5 mg. The electrochemical performance of the as-prepared $Ru_{0.58}In_{0.42}O_y{\cdot}nH_2O$/FMWCNTs nanocomposites was evaluated in 5 M KOH solution. A platinum plate (1 cm^2) and a SCE were used as the counter and reference electrodes, respectively. Then, a symmetric EC was constructed by using $Ru_{0.58}In_{0.42}O_y{\cdot}nH_2O$/FMWCNTs nanocomposites as electrodes and the alkaline polymer gel electrolyte (PVA–KOH (5 M)–H_2O) as an electrolyte and a spacer [32].

Electrochemical performance was evaluated by cyclic voltammetry (CV) performed by CHI660C electrochemical workstation system. Galvanostatic charge/discharge, leak current and self-discharge tests were carried out with a BT2042 battery tester.

3. Results and discussion

3.1. The characteristics of $Ru_{0.58}In_{0.42}O_y{\cdot}nH_2O$/FMWCNTs nanocomposites

Fig. 1 displays the wide-angle XRD pattern of $Ru_{0.58}In_{0.42}O_y{\cdot}nH_2O$/FMWCNTs nanocomposites. As indicated by the solid black circles, the diffraction peak at $2\theta = 26.5°$ is identified for the (0 0 2) plane reflection of FMWCNTs [33,34]. Other two obvious peaks with lower intensities at $2\theta = 35.1°$ and 54.4° are ascribed to (1 0 1) and (2 1 1) crystal faces of $RuO_2{\cdot}nH_2O$ phase, respectively. Notably, the broad diffraction peaks with lower intensity should result from the relative poor crystalline quality and/or nanometer-scale size of the as-prepared hydrous Ru–In binary oxides NPs. The EDX data presented in the inset reveals the existence of In species in the binary oxides. And the molar ratio of Ru and In species is 0.58–0.42, which is almost the same as that in the precursor solution. Of note, the typical diffraction peaks of InO_x have not been found in Fig. 1. Therefore, the Ru–In binary oxides is a solid solution and donated as $Ru_{0.58}In_{0.42}O_y{\cdot}nH_2O$. The presence of S element reveals the vestige of the PSS in the nanocomposites. The amount of PSS in the nanocomposites can be estimated as *ca.* 1 wt.% based on the presented EDX data.

The SEM images of the $Ru_{0.58}In_{0.42}O_y{\cdot}nH_2O$/FMWCNTs nanocomposites are presented in Fig. 2. From the lower-magnification image (Fig. 2a), the good three-dimensional mesoporous structure with its pores unblocked by the $Ru_{0.58}In_{0.42}O_y{\cdot}nH_2O$ NPs still can be found. Moreover, the obvious coexistence of island-like aggregations of $Ru_{0.58}In_{0.42}O_y{\cdot}nH_2O$ NPs and the bare MWCNTs cannot be seen from the higher-magnification image (Fig. 2b), that is, the $Ru_{0.58}In_{0.42}O_y{\cdot}nH_2O$ NPs are dispersed well onto the FMWCNTs

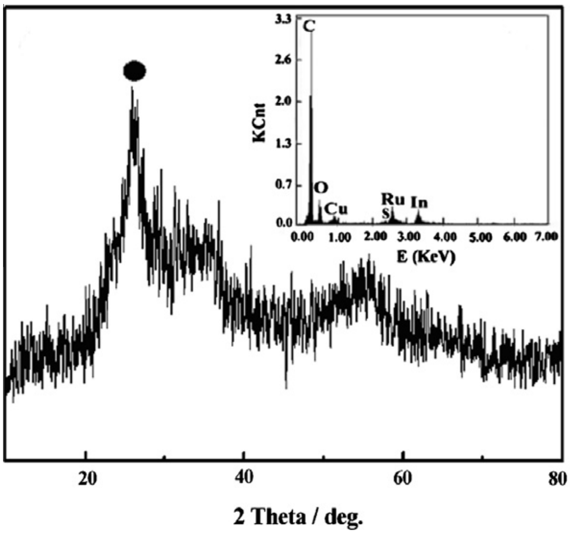

Fig. 1. XRD pattern and EDX (the inset) of $Ru_{0.58}In_{0.42}O_y{\cdot}nH_2O$/FMWCNTs nanocomposites.