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Short communication

High-rate supercapacitor utilizing hydrous ruthenium dioxide nanotubes

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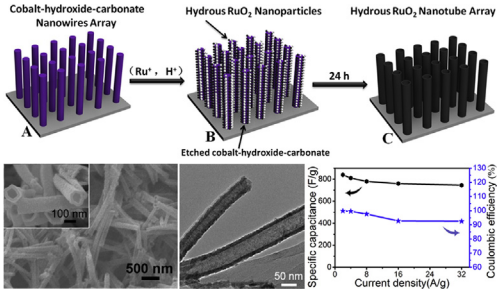
HIGHLIGHTS

- Directly fabricate hydrous ruthenium dioxide nanotubes on a Ti substrate.
- The template can be simultaneously dissolved away at a low temperature.
- The binder-free electrode gives a high-rate performance (745 F g^{-1} at 32 A g^{-1}).

GRAPHICAL ABSTRACT



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ABSTRACT

Three-dimensional criss-crossed hydrous ruthenium dioxide (RuO_2) nanotubes directly on a Ti substrate without any binder are successfully synthesized for the first time via a facile template method at a low temperature of 90 °C. A cobalt-hydroxide-carbonate nanowire array is used as the template and can be completely dissolved away during the formation process of the tubular structure. The synthetic strategy is much more cost-effective and facile than other physical/chemical methods. The obtained material possesses proper crystallinity and water content together with a distinctive structure, resulting in superior electron and ion transmission performance. When the binder-free electrode is used in a supercapacitor, it exhibits a remarkable high-rate performance with a specific capacitance of 745 F g^{-1} at a high current density of 32 A g^{-1}. This represents a retention of 88.7% compared to the value of 840 F g^{-1} at 2 A g^{-1}.

1. Introduction

The advantages of electrochemical supercapacitors (ESs), such as high power density and short charging time, have made them one of the major energy storage devices in the current resource-exhausting society [1–3]. Generally, ESs can be classified into two types: electrical double-layer supercapacitors (EDLCs) that realize energy storage through ion adsorption at electrode interfaces, and Faradaic supercapacitors (FSs) or pseudocapacitors, which mainly depend on fast reversible redox reactions at the surface or near-surface regions of electrodes [2,4,5]. Carbon materials with high specific surface area, good conductivity, and suitable pore sizes are

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promising electrode materials for EDLCs, while redox active and ion/electron transfer profitable transition metal oxides/hydroxides or conducting polymers have always been chosen as the electrode materials for FSs [6–9]. FSs tend to be more advantageous than EDLCs due to their higher energy densities [4,7,8].

Ruthenium oxides and hydrous ruthenium dioxides (RuO_2) in particular are excellent candidate materials for pseudocapacitor electrodes and have been extensively studied [2,4,10–18]. These oxides have many outstanding properties such as multiple highly reversible redox states accessible within their wide potential windows, good electron/proton conductivities, and fairly high specific capacitances [9–18]. The proton and electron transfer rates, which are dominated by the combined water and crystallinity of the material, respectively, directly determine the electrochemical performance of hydrous RuO_2 [11–18]. The design of an appropriate mixed proton/electron-conducting hydrous RuO_2 with a structure that favors storage is an effective way to enhance its capacitive performance. To this end, nanostructured hydrous RuO_2-like nanoparticles, nanotubes, nanotube arrays, and hollow fusiform nanostructures have been reported [13–18]. Among these nanostructures, hollow structures have shown great advantages for enhancing the electrochemical performances of electrode materials; this is attributed to their ability to provide highways for the transmission of electrons and protons, decrease the ion diffusion path distances, and provide large effective surface areas [16–20]. For example, the hydrous RuO_2 nanotubes prepared by Zhang et al. [17] and the nanotube arrays on the graphite [16] obtained by Hu et al. both exhibit excellent performances. In a recent report [18], we demonstrated the effectiveness of a hollow fusiform structure for improving the rate capability of hydrous RuO_2. The application of these materials in ESs is hindered by the tedious fabrication process of traditional slurry-coated electrodes and the need for a binder to construct the electrode [14–19], which can influence its conductivity and lead to abatement in electrochemical performance. Thus, a facile and effective route to construct hollow structures directly on a current collector without a binder will be of great significance for enhancing the energy storage performances of hydrous RuO_2-based ESs.

One of the straightforward schemes to prepare hollow structures is the template method [20,21]. This method has shown great advantages in fabricating hydrous RuO_2 hollow structures, and the often-adopted low reaction temperature can preserve the combined water contents of products [15–17]. In this work, by employing a simple template method along with a cobalt-hydroxide-carbonate nanowire array on a titanium substrate as the template [22], we successfully obtain three-dimensional (3-D) criss-crossed tubular hydrous RuO_2 on a Ti substrate at a low temperature of 90 °C for the first time. In addition, the cobalt-hydroxide-carbonate nanowire array can be dissolved away in situ during the tubular structure formation process; thus, there is no need for any subsequent template removal step. When the product is applied as a binder-free electrode, the directly built 3-D hydrous RuO_2 nanotubes on the Ti substrate show excellent electrochemical behavior. The rate performance is remarkable, with only an 11.3% capacity loss upon increasing the charge/discharge current density from 2 (840 F g^{-1}) to 32 A g^{-1} (745 F g^{-1}). This level of performance has rarely been reported for hydrous RuO_2-based pseudocapacitive materials [14–18,23].

2. Experimental section

2.1. Synthesis

All reagents were analytical grade and utilized without further purification. First, a cobalt-hydroxide-carbonate nanowire array on a Ti substrate was synthesized via a hydrothermal process according to our previous work [22]. Subsequently, the as-prepared cobalt-hydroxide-carbonate nanowires were used as the template to obtain hydrous RuO_2 nanotubes. Typically, 0.025 g $RuCl_3 \cdot xH_2O$ and 0.0546 g NH_4Cl were dissolved in 60 mL of distilled water and stirred at room temperature for 30 min. The cobalt-hydroxide-carbonate nanowire array on the Ti substrate (~ 1.3 × 3 cm^2) was then placed into the mixture and kept at 90 °C under water bath conditions for 24 h. The resulting product was washed several times with distilled water and dried in an electric oven at 60 °C.

2.2. Characterization

The obtained products were characterized by X-ray diffraction (XRD; X'Pert PRO MRD, PANalytical, Netherlands), scanning electron microscopy (SEM; JEOL, JSM-6700F) and transmission electron microscopy (TEM; JEM-2100 (HR), 200 kV). Energy dispersive X-ray spectroscopy (EDS) was carried out on an instrument equipped with a QUANT200 scanning electron microscope. Thermal gravimetric analysis (TGA) was performed on an STA 449F3 (NETZSCH).

2.3. Electrochemical testing

The electrochemical measurements including cyclic voltammetry (CV) and galvanostatic charge/discharge were performed on an electrochemical workstation (CHI 440A, Shanghai CH Instrument, China) with a three-electrode system in 1 M H_2SO_4 aqueous solution at room temperature. A platinum slice electrode was used as the counter electrode, and a saturated calomel electrode (SCE) served as the reference electrode. The obtained product was measured directly as the working electrode with a Ti substrate as the current collector. The amount of active material of the electrode was measured by the mass change of the Ti substrate before and after the hydrous RuO_2 was fabricated.

3. Results and discussion

Fig. 1 schematically presents the synthetic route of hydrous RuO_2 nanotubes on a Ti substrate with the following reaction mechanism [22,24]:

$$Co^{2+} + 0.5(2-x)Co_3^{2-} + nH_2O + xOH^- \rightarrow Co(OH)_x(CO_3)_{0.5(2-x)} \cdot nH_2O \quad (1)$$

$$RuCl_3 + 3H_2O \rightarrow Ru(OH)_3^+ + 3HCl \quad (2)$$

$$Ru(OH)_3^+ + NH_4Cl \leftrightarrow (NH_3)Ru(OH)_3^+ + HCl \quad (3)$$

$$(NH_3)Ru(OH)_3^+ + nH_2O \rightarrow RuO_2 \cdot nH_2O\downarrow + NH_4OH + H^+ \quad (4)$$

$$Co(OH)_x(CO_3)_{0.5(2-x)} \cdot nH_2O + 2H^+ \rightarrow Co^{2+} + (1 + n + 0.5x)H_2O + (1 - 0.5x)CO_2 \quad (5)$$

The template of cobalt-hydroxide-carbonate nanowires on a Ti substrate (Fig. 1A) prepared by the easily controlled hydrothermal reaction in Equation (1) according to our previous work is soluble in acids and meets the principle requirements for the template used in this strategy [25]. When the template is immersed in precursor solution, the production of hydrous RuO_2 and the etching of the template in Equations (2)–(5) occur simultaneously (Fig. 1B). The intense consumption of H^+ during the dissolution of the template