Nano-engineering of three-dimensional core/shell nanotube arrays for high performance supercapacitors
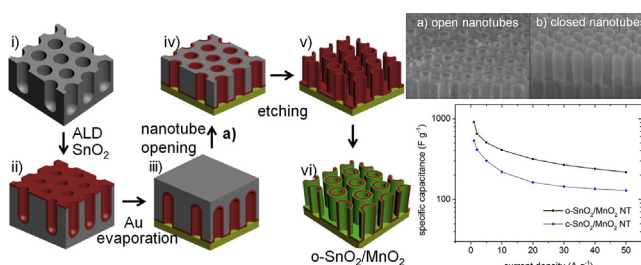
CrossMark

Fabian Grote, Liaoyong Wen, Yong Lei*

Technical University of Ilmenau, Institute of Physics & IMN MacroNano® (ZIK),Prof. Schmidt-Str. 26, 98693 Ilmenau, Germany

HIGHLIGHTS

- Free-standing three-dimensional SnO_2/MnO_2 core/shell nanotubes.
- Demonstration of an innovative template-based fabrication technique with high structural controllability.
- Novel strategy to selectively fabricate open-end and closed-end nanotubes.
- Excellent electrochemical performance compared to other MnO_2-based nanostructures.
- High specific capacitance 910 F g^{-1} at 1 A g^{-1} and a good rate capability.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Large-scale arrays of core/shell nanostructures are highly desirable to enhance the performance of supercapacitors. Here we demonstrate an innovative template-based fabrication technique with high structural controllability, which is capable of synthesizing well-ordered three-dimensional arrays of SnO_2/MnO_2 core/shell nanotubes for electrochemical energy storage in supercapacitor applications. The SnO_2 core is fabricated by atomic layer deposition and provides a highly electrical conductive matrix. Subsequently a thin MnO_2 shell is coated by electrochemical deposition onto the SnO_2 core, which guarantees a short ion diffusion length within the shell. The core/shell structure shows an excellent electrochemical performance with a high specific capacitance of 910 F g^{-1} at 1 A g^{-1} and a good rate capability of remaining 217 F g^{-1} at 50 A g^{-1}. These results shall pave the way to realize aqueous based asymmetric supercapacitors with high specific power and high specific energy.

1. Introduction

Energy storage and energy management are one of the key challenges of mankind in this century in order to meet the requirement of an increasing intermittent energy supply. The demand of energy storage systems include small storage systems for energy harvesting applications [1], medium size applications such as energy storage systems for electrical mobility [2], and large scale systems leveling peaks in power grids [3]. In all these applications supercapacitors play a crucial role and are discussed as a desirable solution to address these emerging challenges. In the past decade various approaches have been attempted to increase the performance of supercapacitors. First, severe effort was made to increasing the electrode surface area by reducing the surface morphology into the nanometer regime and fabricating nano-structured electrodes [4–6]. And second, new electrode materials, such as activated carbons [7,8], and pseudocapacitive materials including conductive polymers [9–11] and metal oxides [4,12–15]

* Corresponding author. Tel.: +49 3677 69 3748.
  E-mail address: yong.lei@tu-ilmenau.de (Y. Lei).

were introduced. [6,16–18] So far two major challenges in the field of supercapacitors exist: (i) highly promising supercapacitor materials such as MnO_2 suffer from high internal resistance ($\sim 10^2$–10^6 Ω cm^{-1}), which limits the electrochemical performance in supercapacitor devices; (ii) it is important to realize a high controllability of all structural parameters to optimize the electrochemical properties of supercapacitors, so as to identify the ideal configuration of high performance devices. In order to solve these challenges, novel functional nanostructures and material compositions (and related fabrication processes) need to be developed. An attractive solution is offered by preparing large-scale arrays of one-dimensional (1D) core/shell nanostructures including nanowires and nanotubes. Such nano-engineered materials combine the unique properties of two materials (*i.e.*, core and shell). Usually, the highly conductive core provides a fast electron transport through the entire electrode and the thin shell ensures a well utilization of the energy storage material and a short ion diffusion. Template-based techniques are efficient methods to prepare large-arrays of 1D nanostructures [19–23], especially for core/shell structures [24,25]. However, the level of controllability of the template-based techniques is partially limited to a few parameters and largely depends on the inherent structural nature of the template itself. Atomic layer deposition (ALD), as an efficient process to prepare conformal films or tubular structures, provides a good solution to further adjust more structural parameters.

Here, we demonstrate an innovative technique to realize highly ordered free-standing three-dimensional (3D) arrays of SnO_2/MnO_2 core/shell nanotubes with precise controllability of many structural parameters. This includes not only diameter, spacing, and length of the core/shell nanostructures originated from the template fabrication process, but also the wall thickness of the core and shell nanotubes. Moreover, advanced core/shell nanostructures including open-end and closed-end nanotubes (donated as o- for open-end and c- for closed-end nanotubes) are achieved, so as to investigate and optimize the electrochemical mechanism for supercapacitor applications. Very importantly, based on the property optimization of the 3D core/shell nanostructures, we obtained an electrochemical performance that is among the highest reported values for MnO_2-based nanostructures.

2. Experimental section

2.1. Preparation

Porous anodic aluminum oxide nano-templates were fabricated using a two-step anodization process from 99.999% pure aluminum foils with a second anodization time of 5–15 min followed by a pore widening process in a 5 wt% H_3PO_4 solution for 15 min [26,27]. Such templates were used for the growth of the SnO_2 nanotube arrays by a PicoSun ALD system according to the following procedure. The reaction chamber was heated to 250 °C, and $SnCl_4$ and H_2O were selected as the precursors. First $SnCl_4$ precursor was pulsed for 1 s and purged for 4 s, followed by a 2 s pulse and 8 s purge of H_2O. This procedure was repeated for 500–1500 times depending on the desired wall thickness of SnO_2 nanotubes. After this process, a 100 nm thick layer of gold was evaporated onto the sample by physical vapor deposition to support the SnO_2 nanotube array. Afterward the remaining Al was removed by a saturated solution of $CuCl_2$. In the next step, the template was removed. Hereby different processes for open-end and closed-end nanotube arrays were used. For the fabrication of closed-end nanotubes the entire templates was removed in a 5 wt% NaOH solution for 120 min. In order to successfully fabricate open-end SnO_2 nanotubes, the templates were first partially etched for 20 min to only liberate the nanotubes top parts. Then the top-ends of the nanotubes were removed by

scratching the surface with a sharp scalpel. Thereafter the sample was placed again in a 5 wt% NaOH solution to remove the remaining template. Finally the SnO_2 nanotube array was attached to a stainless steel holder.

The as-prepared open-end and closed-end SnO_2 nanotube arrays were coated by MnO_2 shells. A thin MnO_2 layer was formed by electrochemical deposition in an electrolyte containing 0.1 M $Mn(Ac)_2$ and 0.1 M Na_2SO_4, using 1 V versus a Ag/AgCl reference electrode. A Pt foil was used as a counter electrode. The charge passed was controlled during the deposition process within the range of 130–260 mC. Afterward the samples were cleaned with water and dried.

The entire fabrication process with all steps is shown schematically in the supplementary video.

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.jpowsour.2013.12.029.

2.2. Electrochemical and physical characterizations

All electrochemical measurements were performed in a three electrode cell with a 1 M Na_2SO_4 electrolyte, an Ag/AgCl reference electrode, and a Pt foils as the counter electrode. The CV and charge/discharge curves were measured from 0 to 0.9 V vs Ag/AgCl at scan rates of 2, 5, 10, 20, and 50 mV s^{-1} and current densities of 1, 2, 5, 10, 20, 30, 40, 50 A g^{-1}, respectively. The EIS was performed at 0.1 V with a 10 mV pulse in the frequency range of 100 kHz–0.05 Hz. All measurements were performed on a Bio-Logic VSP electrochemical work station.

The structural characterization was carried out using SEM (Hitachi S-4800) and TEM (Libra 200 FE).

X-ray photoelectron spectroscopy (XPS) was performed under an emission angle of 53° using a monochromated AlKα source and a hemispherical electron analyzer.

3. Results and discussion

3.1. Characterization of the SnO_2/MnO_2 core/shell nanotube array

The fabricated SnO_2/MnO_2 core/shell nanotube arrays are prepared by the ALD process of SnO_2 into a porous anodic aluminum oxide nano-template and a subsequent conformal coating by MnO_2, as illustrated in Scheme 1. Thereby it is possible to selectively control the synthesis of o-SnO_2/MnO_2 (process a in Scheme 1) and c-SnO_2/MnO_2 core/shell nanotubes (process b in Scheme 1). This selectivity is a salient feature of the fabrication process and highly desirable for supercapacitor applications. The possibility of fabricating open-end nanotube arrays enables the access of the total inner and outer surface area of a nanotube for charge storage and thus is superior to closed-end nanotube arrays, which possess a lower accessible surface area.

The morphology of the prepared SnO_2 core nanotubes is analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), as shown in Fig. 1. The SEM image in Fig. 1a clearly shows a highly ordered free-standing array of o-SnO_2 nanotubes (for c-SnO_2 nanotubes see Fig. S1). The outer diameter and the inter-tube distance of the nanotubes are about 60 nm and 105 nm respectively, which are inherited from the structural parameters of the templates. Different lengths of nanotubes between 600 nm and 1800 nm are obtained by using templates with different thicknesses, indicating that the length of nanotubes can be tuned by the template thickness.

The opening process of the SnO_2 nanotubes is shown in Fig. 2. First, the anodic aluminum oxide nano-template is partially etched to liberate the closed nanotube top-ends. Then the liberated closed nanotube top-ends are removed by scratching the samples surface