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Synthesis and enhanced electrochemical supercapacitive properties of manganese oxide nanoflake electrodes

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ABSTRACT

$MnO_{2+\delta}$ (Manganese oxide) nanoflakes were synthesized for use as electrode material in electrochemical supercapacitors. The nanoflakes were produced via RF-magnetron sputtering with various excess oxygen contents (δ), and the electrochemical supercapacitive properties of the $MnO_{2+\delta}$ nanoflakes were investigated as a function of δ with the use of a Na_2SO_4 electrolyte. The excess oxygen (δ) induces the $MnO_{2+\delta}$ nanoflakes to form a thin open structure, and μ-Raman measurements revealed that the $MnO_{2+\delta}$ nanoflakes formed a birnessite phase with a layered structure. X-ray photoelectron spectroscopy was used to obtain quantitative information on both the oxidation state and the chemical composition of the nanoflake electrodes. The crystallinity of the nanoflakes improved when the oxygen partial pressure increased during sputtering. At an optimal δ ~ 0.6, the electrochemical stability and the capacity retention significantly improved, and electrochemical impedance spectroscopy revealed that easy access of Na^+ ions into the nanoflakes at an optimal δ value resulted in a low diffusion resistance, playing a key role in determining the improvement in the supercapacitor characteristics.

1. Introduction

Advances in modern electronics have increased the demand for energy storage, and so it is now urgent to search for sustainable energy storage materials. Supercapacitors have attracted a great amount of attention because they exhibit a high power density, low cost, long cycle life and a high rate capacity. Three types of materials are being considered for use in supercapacitors, including carbon-based materials, TMOs (transition metal oxides), and conducting polymers, and of these, TMOs are of much interest due to their higher energy density, better electrochemical stability, and environmental abundance [1]. TMOs, such as MnO_2, have attracted much attention as pseudocapacitive electrode materials due to their outstanding properties, including low cost, high energy density, natural abundance, and low toxicity [2–5]. However, MnO_2 possesses poor electrical conductivity and a dense morphology that negatively impact the electrochemical performance of the devices. To address this issue, recent studies have investigated the fabrication of free-standing nanostructures of alkali metal manganese oxides – such as nanobelts, nanoflakes, three-dimensional coral like nanostructures, and porously assembled nanosheets – that result in a high surface area and can provide improved electrochemical performance and fast ion and electron transport [1,6–9]. MnO_2 nanoflakes were deposited on C/TiO_2 shell/core nanowire arrays, and these structures exhibited a high specific capacitance of 639 F/g and a high capacity retention of up to 78.7% after 1000 charge/discharge cycles [1], suggesting that the nanoflakes are suitable for use in electrochemical energy applications. Similarly, many efforts have been made to increase the surface area and the electrochemical activity of manganese oxide by using a synthesis of hybrid MnO_2/nanostructured carbon compound electrodes [10–18]. The MnO_2 embedded-CNT/GS electrodes showed specific capacitance of 540.7 F/g, a high rate capability, and good cycling stability after 1000 cycles [19]. The carbon nanotube/MnO_2 nanocomposite ultrathin film electrodes demonstrated a high specific

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capacitance of 940 F/g [20], and the tubular nanostructures of the MnO_2 prepared on the carbon nanofibres exhibited a long cycling life of over 3000 charge/discharge cycles due to the large surface area and the optimized charge transport pathway [21]. Stacked nanosheets composed of Mn_3O_4 solid-state flexible thin film electrodes with a gel electrolyte demonstrated a specific capacitance of 127 F/g with good power and energy density [22]. while the hydrothermally prepared porous cactus-like manganese oxide electrodes showed a specific capacitance of 187.8 F/g at a current density of 0.2 A/g and a higher capacity retention of 92.9% after 1000 cycles [23]. The nanostructured and ultrathin manganese oxide electrode films exhibited good cycle life and capacity retention properties, providing better supercapacitive performance [7,24]. A careful survey of the literature indicated that the surface Faradic reaction in MnO_2 contributes to the pseudocapacitance, so it is desirable to produce ultrathin surface morphologies. Although many efforts have been made to date, certain challenges have yet to be addressed, including the development of a simple and cost effective synthetic route to achieve a controlled synthesis of the MnO_2 nanostructures.

To this end, the main purpose of the present study is to synthesize MnO_2 nanoflake electrode films for use in electrochemical supercapacitors. The nanoflakes were produced via RF (radio frequency) magnetron sputtering, and to the best of our knowledge, the synthesis of the MnO_2 nanoflake electrodes via sputtering has not yet been reported. We demonstrate that changes in the oxygen partial pressure during sputtering can be used to effectively control the chemical and structural properties of the MnO_2 nanoflakes, and such effects on the electrochemical supercapacitive properties of the $MnO_{2+\delta}$ nanoflake electrodes due to excess oxygen content (δ) are herein presented.

2. Experimental section

2.1. Synthesis of manganese oxide nanoflakes

MnO_2 thin films were fabricated at different oxygen partial pressures via RF (radio frequency) magnetron sputtering on ITO (indium-doped tin oxide)-coated conducting glass substrates with sheet resistance of 27 Ωcm^{-2}. A pure manganese metal target (Mn) with 99.99% purity was used for sputtering. The sputtering chamber was initially evacuated to 4.2×10^{-6} Torr, and it was maintained at 10 mTorr by flowing Ar and O_2 gasses. During growth, the Ar to O_2 gas flow rate ratio was set to three different values: 9:1 (i.e. 10% oxygen), 8:2 (20% oxygen), and 7:3 (30% oxygen). The films grown at these ratios are denoted as M1, M2, and M3, respectively. The samples were grown at an applied power of 80 W for 30 min at room temperature. Afterwards, the films were thermally annealed in a nitrogen atmosphere at 400 °C for 2 h with a rising time of 20 min. The thicknesses of the deposited nanoflake thin films were estimated using an alpha-step profiler and were found to be of 234, 197, and 168 nm for the M1, M2, and

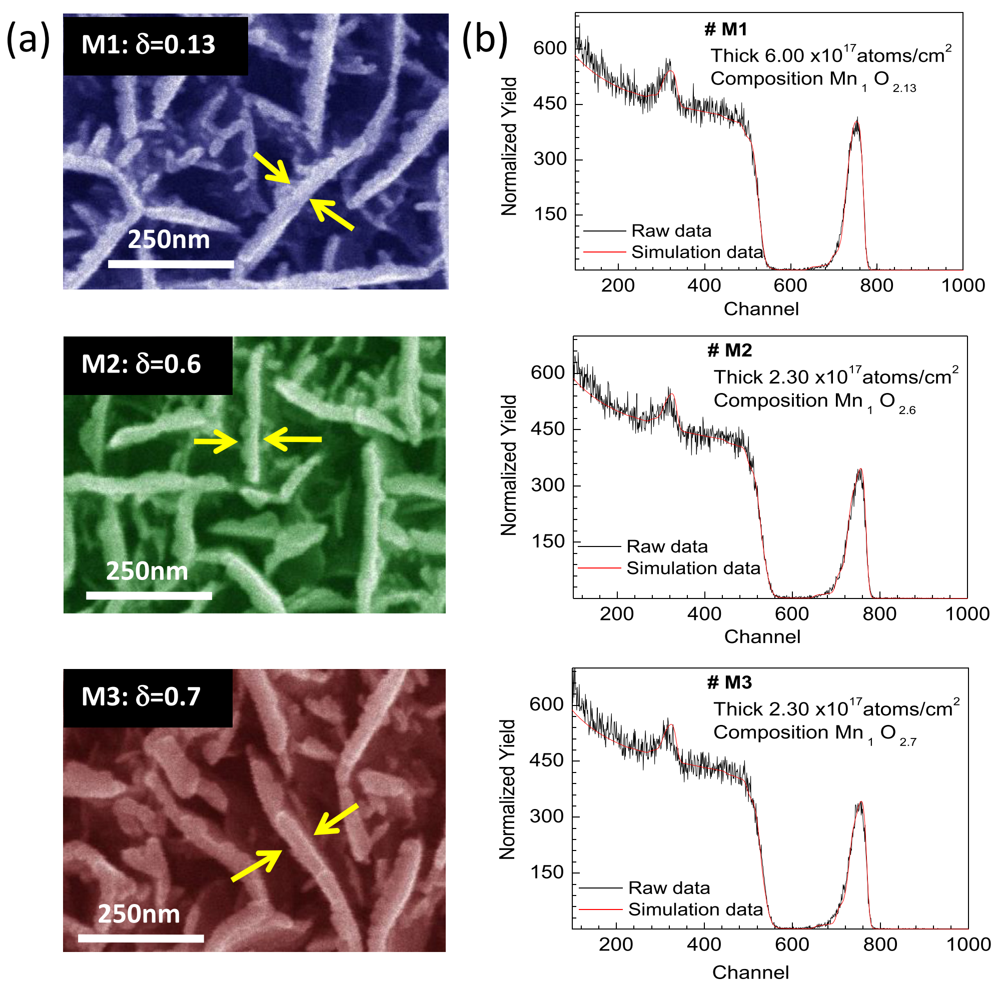

Fig. 1. (a) Plan view of the SEM (scanning electron microscope) images of M1, M2 and M3 samples. (b) Rutherford backscattering spectroscopy measurements of the M1, M2 and M3 samples.