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Short communication

Morphology and crystallinity-controlled synthesis of manganese cobalt oxide/manganese dioxides hierarchical nanostructures for high-performance supercapacitors

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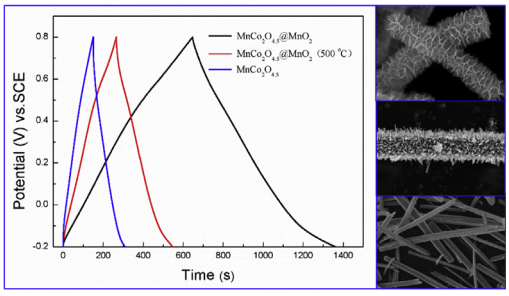
HIGHLIGHTS

- Manganese cobalt oxide@manganese dioxides hierarchical nanostructures.
- Morphology and crystallinity-controlled synthesis.
- High specific capacitance of $MnCo_2O_{4.5}$@δ-MnO_2: 357.5 F g^{-1} at current density of 0.5 A g^{-1}.
- Good cycle stability: 97% capacitance retention after 1000 cycles at a scan rate of 5 A g^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

We demonstrate a novel preparative strategy for the well-controlled $MnCo_2O_{4.5}$@MnO_2 hierarchical nanostructures. Both δ-MnO_2 nanosheets and α-MnO_2 nanorods can uniformly decorate the surface of $MnCo_2O_{4.5}$ nanowires to form core–shell heterostructures. Detailed electrochemical characterization reveals that $MnCo_2O_{4.5}$@δ-MnO_2 pattern exhibits not only high specific capacitance of 357.5 F g^{-1} at a scan rate of 0.5 A g^{-1}, but also good cycle stability (97% capacitance retention after 1000 cycles at a scan rate of 5 A g^{-1}), which make it have a promising application as a supercapacitor electrode material.

1. Introduction

Manganese dioxides (MnO_2) have been studied widely because of their excellent properties and various potential applications such as molecular sieves, catalysts, and especially energy storage [1–3].

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Up to now, MnO_2 with diverse structures and morphologies (such as nanosheets [4], hollow nanospheres [5], nanoflowers [6], nanowires/nanorods [7,8], thin films [9], and nanotubes [10]) and different crystalline phases (such as α [11], β [12], γ [13], and δ [14]) have been fabricated via electrochemical and chemical routes, and their electrochemical properties have been investigated. These studies indicate that the outstanding nanostructures and crystalline phases of the MnO_2 materials have been regarded as critical factors to influence their properties. Thus the precise design of MnO_2 nanostructures with various crystallographic structures has great significance for supercapacitors. However, most of MnO_2-based materials exhibit poor electrical conductivity, volume expansion and severe aggregation during the redox reactions, which could lead to the inadequate utilization and pulverization of the active materials. To overcome these disadvantages, some conducting materials are used as supporting materials to form nanocomposites with MnO_2, such as Cu_2O@MnO_2 [15], Co_3O_4@MnO_2 [16], ZnO@MnO_2 [17], Fe_2O_3@MnO_2 [18] and CuO@MnO_2 [19]. However, the synthetic procedures for these unique MnO_2-based core–shell structures are still relatively complicated since they either need carbon coating or electrochemical deposition process. What's more, these nanostructures may become electrically isolated due to the weak forces and the loose contacts between them. Thus, a novel but simple design and fabrication of MnO_2-based composites with highly-accessible surface areas and fast ion diffusion for supercapacitors still remains a challenge.

An effective approach is the design of heterostructure with the combination of one dimensional nanowire and different crystalline phases of MnO_2. Especially, continuous networks forming by one dimensional core–shell nanowires are being given serious consideration, as they could not only prevent the aggregation and volume change of active materials during the electrochemical reactions, but also provide fully effective electrical contact between the one dimensional nanostructures of the continuous MnO_2 network [20,21].

Herein, we demonstrate a facile and cost-effective approach to design and fabricate hierarchical $MnCo_2O_{4.5}$@MnO_2 core–shell nanowires for high-performance supercapacitors, in which the mesoporous $MnCo_2O_{4.5}$ nanowires served as the "core" and the δ-MnO_2 nanosheets (and/or α-MnO_2 nanorods) as the"shell" layer. The coupling of two metal species (Mn and Co) could render the $MnCo_2O_{4.5}$@MnO_2 with rich redox reactions which are beneficial to electrochemical applications. Besides, the various combinations of the cations and the tunable stoichiometric/non-stoichiometric compositions of the $MnCo_2O_{4.5}$@MnO_2 provide vast opportunities to manipulate the physical/chemical properties. The schematic two-step formation process of the hierarchical $MnCo_2O_{4.5}$@MnO_2 core–shell nanowires is illustrated in Fig. 1. The proposed process is based on hydrothermal reaction where in the initial step $KMnO_4$ is used to obtain the nanostructured layer of δ-MnO_2 nanosheets on the surface of $MnCo_2O_{4.5}$ nanowires. Afterwards, δ-MnO_2 nanosheets are converted to α-MnO_2 nanorods. The electrochemical and supercapacitor properties of as-prepared $MnCo_2O_{4.5}$@MnO_2 are studied, and they exhibit ideal initial capacitive behavior and good cycling stability in a neutral electrolyte system.

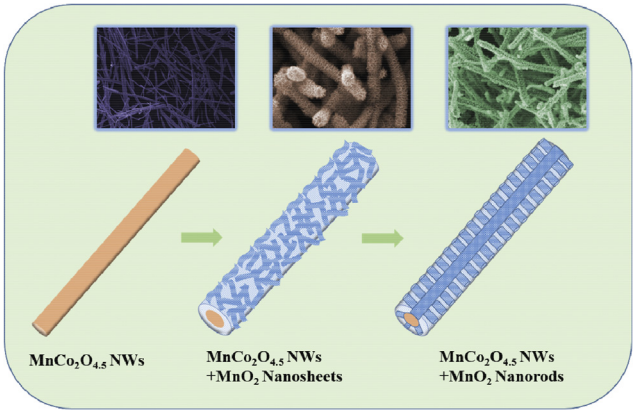

Fig. 1. Schematic illustration of the growth mechanism of the $MnCo_2O_{4.5}$@MnO_2.

2. Experimental section

2.1. Synthesis of $MnCo_2O_{4.5}$ nanowires

All the reagents were of analytical-reagent grade, and used without further purification. In a typical synthesis, 8 mmol of cobalt (II) sulfate heptahydrate ($CoSO_4 \cdot 7H_2O$) and 4 mmol of manganese (II) sulfate hydrate ($MnSO_4 \cdot H_20$) were dissolved in 160 mL of a mixed solution of ethylene glycol and H_2O (v:v = 3:1) at room temperature with magnetic stirring to form a clear pink solution I. And 12 mmol oxalic acid were dissolved in 160 mL of a mixed solution of ethylene glycol and H_2O (v:v = 3:1) to form the solution II. Afterwards, solution II were dropwisely added into solution I and stirred for one hour. The mixture was transferred to a Teflon-lined stainless steel autoclave, and put in an electric oven at 130 °C for 24 h. Subsequently, the sample was washed with distilled water and ethanol, and dried at 60 °C overnight. Finally, the precursors were converted to $MnCo_2O_{4.5}$ after calcination in air at 600 °C for 2 h.

2.2. Synthesis of $MnCo_2O_{4.5}$@δ-MnO_2 and $MnCo_2O_{4.5}$@α-MnO_2

In a typically synthesis, $MnCo_2O_{4.5}$ (30 mg) were dispersed in $KMnO_4$ solution (0.01 M; 30 mL) by ultrasonic vibration for 10 min. Afterwards, the mixed solution was transferred to a 50 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and put in an electric oven at 160 °C for 24 h and then cooled to room temperature naturally. The black resultants were washed with distilled water and dried at 60 °C for 12 h in a vacuum oven. These products were labeled as $MnCo_2O_{4.5}$@δ-MnO_2.

For the preparation of $MnCo_2O_{4.5}$@α-MnO_2, the corresponding $MnCo_2O_{4.5}$@δ-MnO_2 samples were calcined at 500 °C in air for 4 h.

2.3. Materials characterization

The crystallographic information and chemical composition of as-prepared products were established by powder X-ray diffraction (XRD, D/max 2500, Cu Kα). The morphological investigations of the $MnCo_2O_{4.5}$ nanowires and $MnCo_2O_{4.5}$@MnO_2 were carried out with focused ion beam (Zeiss Auriga FIB/SEM) and transmission electron microscopy (TEM, ZEISS LIBRA 200). Nitrogen adsorption–desorption isotherms were measured at 77 K with micrometritics ASAP 2020 sorptometer. The specific surface area was calculated with the Brunauer–Emmett–Teller (BET) equation, and the pore size distributions were calculated from the adsorption curve by the Barrett–Joyner–Halenda (BJH) method.

2.4. Electrochemical measurement

The electrochemical properties of the electrodes were carried out using an electrochemical workstation (CHI 660E) with three-electrode configuration in a 1 M Na_2SO_4 aqueous solution. The working electrode consisted of nickel foam as a current collector and a mixture of active materials, acetylene black and polyvinylidene difluoride (PVDF) with a weight ratio of 7:2:1. Platinum