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Short communication

Order-aligned Mn_3O_4 nanostructures as super high-rate electrodes for rechargeable lithium-ion batteries

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HIGHLIGHTS

- Mn_3O_4 layer was deposited on Cu nanowire arrays via electrochemical method.
- The 3D electrodes show improved performance as anode for Li-ion battery.
- Improved performance was attributed to the advantages of the electrodes' structure.

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ABSTRACT

We demonstrate the synthesis of order-aligned Mn_3O_4 nanostructures by electrochemically depositing Mn_3O_4 on a pre-fabricated Cu nanowire array current collector. When used as an electrode for lithium-ion batteries, it exhibits a capacity up to 637 and 494 mA h g^{-1} after 100 cycles at a current rate of 10 C and 20 C (10 C = 9.4 A g^{-1}), respectively. The excellent cycling performance and superior rate capability can be attributed to the good electrical contact, fast electron transport and good strain accommodation of the order-aligned nanostructured electrodes. The relationship between the thickness of the Mn_3O_4 film and its electrochemical performance has also been investigated.

1. Introduction

Lithium-ion batteries are currently regarded as promising power sources for popular consumer electronics as well as upcoming electric vehicles [1–3]. Although graphite anodes are now widely used in commercial lithium-ion batteries due to high cyclability, their low capacity (372 mA h g^{-1}) can hardly meet the increasing demand for batteries with higher capacity [4]. Therefore, large research efforts have been devoted to search useful alternative materials with large capacity, high rate tolerance, and long cycle life [5–7]. Recently, transition metal oxides (Fe_2O_3, Co_3O_4, NiO, CoO) with high theoretical capacity have attracted more and more attention [8–11]. Among them, Co_3O_4 is most appealed for its high electrochemical capacity and noticeable capacity retention. Various forms of Co_3O_4 electrode materials have been tried, including Co_3O_4 nanowires, nanotubes and nanobelts [9,12,13]. However, Co based materials is confronted with its high-cost problems, which may restrict its commercial application. Compared to Co_3O_4, Mn_3O_4 exhibits a higher theoretical capacity (936 mA h g^{-1}), less toxic and more abundant in natural resources. Moreover, bulk manganese is about 20 times less expensive than cobalt [14]. Nevertheless, two serious problems greatly prohibit the application of manganese-based anode materials in high-performance lithium-ion batteries: (1) poor cyclability arising from the significant volume change during Li insertion/extraction; (2) low rate capability caused by the extremely low electrical conductivity ($\sim 10^{-7}$ to 10^{-8} S cm^{-1}) of Mn_3O_4 material [15]. To loosen the two obstacles, several strategies have been proposed such as doping Mn_3O_4 with Co, using Mn_3O_4/RGO (reduced graphene oxide) composite and nanosized Mn_3O_4 anode materials [14–16]. In most cases, these approaches can only improve the electrochemical performance of Mn_3O_4 anodes to a limited extent.

It is now recognized that an efficient way to improve the electrochemical response of active materials is optimizing electrode structures and significant improvements in battery performance were obtained by using ordered nanostructures grown directly on

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current collector substrates as electrodes [17–20]. It has been demonstrated that this kind of electrodes allows for good electrical contact, fast electron transport and good strain accommodation [17]. Therefore, it is expected that order-aligned Mn_3O_4 nanostructured electrode could lead to an improved electrochemical performance in cyclic stability and rate capability and could be successfully used in the field of three-dimensional microbatteries.

In this paper, we report the synthesis of order-aligned Mn_3O_4 nanostructures by electrochemically depositing Mn_3O_4 on a prefabricated Cu nanowire array current collector. The as-prepared sample was directly used as electrodes of lithium-ion batteries without any ancillary materials, which afforded a high reversible capacity with good rate capability.

2. Experiment section

2.1. Synthesis of Cu nanowire arrays on a Cu substrate

Cu nano-architectured arrays were fabricated by the cathodic electrodeposition with anodized aluminum oxide (AAO) templates with the pore diameters of about 200–300 nm. Before using the cathode foil, the cathode Cu substrates were mechanically polished with 1.0 μm alpha alumina and 0.25 μm gamma alumina polishing slurry; The electrolyte systems were consisted of $CuSO_4 \cdot 5H_2O$ 100 g L^{-1}, $(NH_4)_2SO_4$ 10 g L^{-1}, diethylenetriamine (DETA) 40 g L^{-1}. The details of synthetic strategy were fully described in the previous paper [17].

2.2. Synthesis of order-aligned Mn_3O_4 nanostructures

The order-aligned Mn_3O_4 nanostructures were synthesized via an electrochemical route. The electrochemical cell consisted of a working electrode (Cu nanowire arrays), a carbon rod counter electrode, and an Ag|AgCl reference electrode. A solution with 0.1 M manganese sulfate (Aldrich) and 0.1 M sodium sulfate (Aldrich) was used as the electrolyte. The deposition of Mn_3O_4 was performed under galvanostatic conditions at a constant current of 3 mA cm^{-2} for 90 s. Four types of thickness-controlled Sn thin films were prepared for comparison by depositing for 40, 90, 180 and 300 s, respectively. After the deposition, the samples were heat-treated at 400 °C for 1 h.

2.3. Characterization and electrochemical measurement

The obtained samples were characterized by X-ray powder diffraction (XRD) with a Rigaku D/max-ga X-ray diffractometer with graphite monochromatized Cu K radiation ($\lambda = 1.54178$ Å). The morphology and structure of the obtained samples were examined by scanning electron microscopy (SEM HITACH S4800) with an energy-dispersive X-ray spectrometer (EDX) and transmission electron microscopy (TEM, PHILIPS CM200 and Tecnai G2 F20 S-TWIN, FEI). Electrochemical measurements were performed by coin type cells (CR2025) which were assembled in a glove box (Mbraun, labstar, Germany) under an argon atmosphere by directly using the final-products as the anodes. The counter and reference electrodes were lithium metal foils (15 mm diameter), and the electrolyte solution was 1 M solution of $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume). Finally, the cells were then aged for 12 h before measurements. A galvanostatic cycling test of the assembled cells was carried out on a Land CT2001A system in the potential range of 0.01–3.0 V at a discharge/charge current density of 936 mA g^{-1}. Cyclic voltammetry (CV) was recorded on an Arbin BT 2000 system at a scan rate of 0.1 mV s^{-1}.

The accurate mass of the active material on the Cu nanoarrays current collector was examined using a microbalance. We measured the masses of the substrate with Cu nanowire arrays and the substrate after electrodeposition, respectively. Thus, the total masses of the Mn_3O_4 film could be obtained.

3. Results and discussion

An overview of the synthetic route for order-aligned Mn_3O_4 nanostructures is shown in Fig. 1. Briefly, a typical synthetic procedure involves in two steps: 1) growth of Cu nanowire arrays on a Cu substrate via the cathodic electrochemical deposition in an AAO template; 2) deposition of a Mn_3O_4 layer onto the surface of Cu nanowires. Fig. 2a is the scanning electron microscopy (SEM) image of the Cu nanowire arrays. It can be seen that the Cu nanowires have a relatively uniform size with good alignment. After Mn_3O_4 coating for 90 s (Fig. 2b and c), the diameters of the nanowires slightly increase compared to the bare Cu nanowires, suggesting the formation of Mn_3O_4 layer. The inset magnified SEM images show that the surface of Cu nanowire turns to be rough with many Mn_3O_4 nanoflakes. Fig. 2d is the EDX spectrum of the as-synthesized product. Elements Cu, Mn and O are detected, which may come from the Cu nanoarrays current collector and Mn_3O_4 film, respectively.

The phase and purity of the samples were identified by X-ray diffraction pattern (Fig. 3). Five well-resolved peaks can be indexed to tetragonal phase of Mn_3O_4 (JCPDS card: 18-0803). In addition, the peaks at 43.3°, 50.4°, 74.1° are attributed to the Cu nanowire array current collector. No other crystalline state is observed, indicating high purity and crystallinity of the as-synthesized product. Transmission electron microscope (TEM) was employed to further investigate the morphology and structure of the product. The nanowires were scraped out of the substrate, sonicated in ethanol, and deposited on Au grids for TEM characterization. Fig. 4a and b shows typical TEM images of an individual core-shell

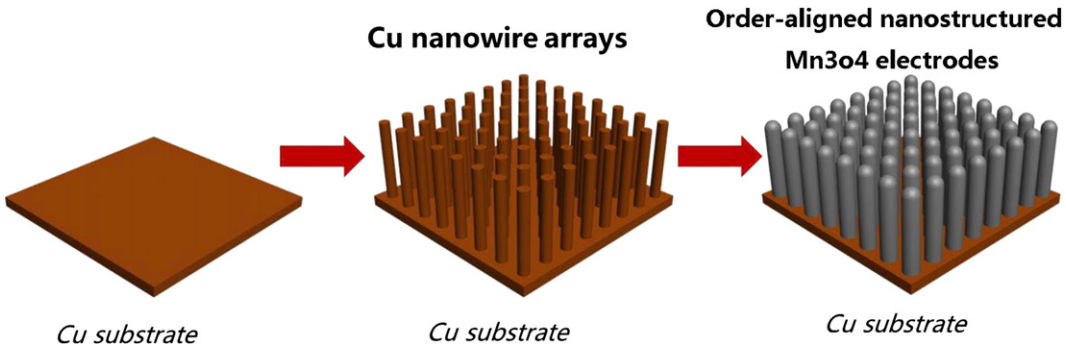

Fig. 1. (a) Schematic illustration for synthesis of the order-aligned nanostructured Mn_3O_4 electrode.