



Hierarchical porous cobalt oxide array films prepared by electrodeposition through polystyrene sphere template and their applications for lithium ion batteries

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ARTICLE INFO

Article history:

Received 11 August 2009

Received in revised form 1 October 2009

Accepted 2 November 2009

Available online 10 November 2009

Keywords:

Cobalt oxide

Polystyrene sphere template

Porous film

Lithium ion batteries

ABSTRACT

Hierarchical porous cobalt oxide (Co_3O_4) array films are successfully prepared by electrodeposition through polystyrene sphere monolayer template. The as-prepared Co_3O_4 array films exhibit three typical porous structures from non-close-packed bowl array to close-packed bowl array and hierarchical two layer array structures. These Co_3O_4 array films have a hierarchical porous structure, in which the skeleton is composed of ordered arrays possessing nanoporous walls. A possible growth mechanism of porous Co_3O_4 array films is proposed. As anodes for Li ion batteries, the as-prepared Co_3O_4 array films exhibit quite good cycle life and high capacity. The first discharge capacity for the three Co_3O_4 array films is 1511, 1475, 1463 mAh g^{-1} , respectively, and their initial coulombic efficiencies are as high as 72%. The specific capacity after 50 cycles for the three electrodes is 712, 665 and 640 mAh g^{-1} at 1C rate, corresponding to 80%, 75%, 72% of the theoretical value (890 mAh g^{-1}), respectively.

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1. Introduction

In the past decade, extensive research has been launched into the development of alternative anode materials for Li ion batteries [1–5]. Among the explored systems, transition metal oxides such as NiO, CoO, and Co_3O_4 have attracted great attention due to their noticeable capacity retention, high electrochemical capacity about three times larger than those of graphite and pretty good high rate performance [6–8]. Compared to other transition metal oxides, spinel cobalt oxide (Co_3O_4) is considered as a promising alternative anode material for Li ion batteries because it has shown the highest reversible capacity (890 mAh g^{-1}) and the best cycle performance [6,9–12]. Porous nanostructured Co_3O_4 , with a high surface area and enhanced electrochemical reactivity, is particularly attractive. For example, Co_3O_4 nanoparticles, nanotubes and nanowires have been synthesized and enhanced electrochemical performance for Li ion batteries have been found in these systems [13–16].

Despite numerous porous nanostructured Co_3O_4 materials have been synthesized and applied for Li ion batteries, these researches focused on nanostructured Co_3O_4 power materials [13–19]. In the case of powder materials for Li ion batteries, the active materials need to be mixed with carbon and polymer binders and compressed into pellets. This process risks negating the benefits associated with

the reduced particle size and introduces supplementary, undesirable interfaces. For these reasons, the direct growth of porous nanostructured Co_3O_4 on various substrates, especially on conducting substrates, is an important issue for their applications [20].

In recent years, two-dimensionally (2D) ordered porous array films induced by colloidal monolayer lithography have elicited much interest due to their distinctive structural features and intriguing properties [21–23]. The typical monolayer colloidal crystal template (MCCT) is an ordered monolayer colloidal microsphere array with a hexagonal close-packed alignment on a certain substrate (typically polystyrene or silica spheres as the template) [24,25]. In general, the interstitial spaces between colloidal spheres are infiltrated with another material and subsequent removal of the template by either wet etching or thermal decomposition leads to the formation of ordered porous structure [26,27]. Among the existing synthetic approaches of target materials infiltration into the colloidal template, electrochemical techniques show unique principles and flexibility in the control of the structure and morphology of porous arrays [28]. Electrochemical deposition is believed to be an ideal method for the fabrication of ordered porous arrays with various morphologies, because it occurs from the electrode surface out through the overlying template, different morphologies of the materials can be obtained via the precise choice of deposition bath and deposition conditions.

By far, there are few reports devoted to the synthesis of ordered porous Co_3O_4 array films prepared through the MCCT method and their application for Li ion batteries. Moreover, it is reported that the ordered arrays with a hierarchical pore system would

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bestow the possibility to combine the different functionality provided by each type of porosity [29]. For instance, a structure of interconnected macropores whose walls possess finer pores would present increased mass transport through the former and high specific surface area due to the latter. Therefore, it is interesting to design a porous Co_3O_4 array with a hierarchical porous system, in which the skeleton is composed of ordered macrobowls possessing nanoporous walls. It is believed that this ordered porous Co_3O_4 array will combine the merits of patterned array and nanostructure. Herein, we report a controllable synthesis of porous Co_3O_4 arrays with three different morphologies by the combination of electrodeposition and MCCT method. The morphology evolution of porous Co_3O_4 arrays is realized via adjusting deposition current: 0.5, 1.0 and 1.5 mA cm^{-2} for 300 s, respectively. More interestingly, these Co_3O_4 array films have a hierarchical porous structure, in which the skeleton is composed of ordered arrays possessing nanoporous walls. Furthermore, the as-synthesized porous Co_3O_4 arrays have been applied as anode materials for Li ion batteries, which exhibit superior performance and thus promising application.

2. Experimental

All solvents and chemicals were of reagent quality and were used without further purification. The monodispersed PS spheres with particle sizes of $1 \mu\text{m}$ in diameter were purchased from Alfa Aesar Corporation. They were well dispersed in deionized water and prepared as a suspension with concentration of 2.5 wt.% before fabricating colloidal monolayers.

We have successfully electrodeposited porous Co_3O_4 array films on indium tin oxide (ITO) and nickel foil substrates through the MCCT method. There was no apparent difference in the coating morphology for different substrates. Thus, the method presented here was very robust and might lead to broad applications. As an illustrative case for morphology, we chose ITO as a substrate. Additionally, the samples for electrochemical measurements of Li ion batteries were prepared on nickel foil substrates.

2.1. Assembly of monolayer PS sphere template

The first step was to prepare an ordered monolayer PS spheres by self-assembly. Firstly, a small amount of PS suspension was dropped onto the surface of the clean indium tin oxide (ITO) substrate with a size of $1.5 \text{ cm} \times 1.5 \text{ cm}$. After holding the substrate stationary for 1 min to obtain good dispersion of the suspension, the substrate was then slowly immersed into deionized water. Once the suspension contacted the water's surface, a monolayer of PS spheres was observed on the surface of the water and on the surface of the ITO substrate. To prevent any further additions to the substrate, it was kept immersed. Then, a few drops of 2% dodecyl sodium sulfate solution were added to the water to change the surface tension. As a result, the PS spheres that remained suspended on the surface of the water were pushed aside due to the change in the surface tension. Then the substrate was lifted up through the clear area, making sure that no additional PS spheres were deposited on the monolayer during this process and followed by heating at 110°C in an oven for 5 min to bond the monolayer with the ITO substrate.

2.2. Preparation and characterization of porous Co_3O_4 array films

The electrodeposition was performed in a standard three-electrode glass cell at 20°C , the above template electrode as working electrode, saturated calomel electrode (SCE) as reference electrode and a Pt foil as counter-electrode. The precursor films were electrodeposited from aqueous solution containing $0.9 \text{ M Co}(\text{NO}_3)_2$ and 0.075 M NaNO_3 using a Chenhua CHI660C

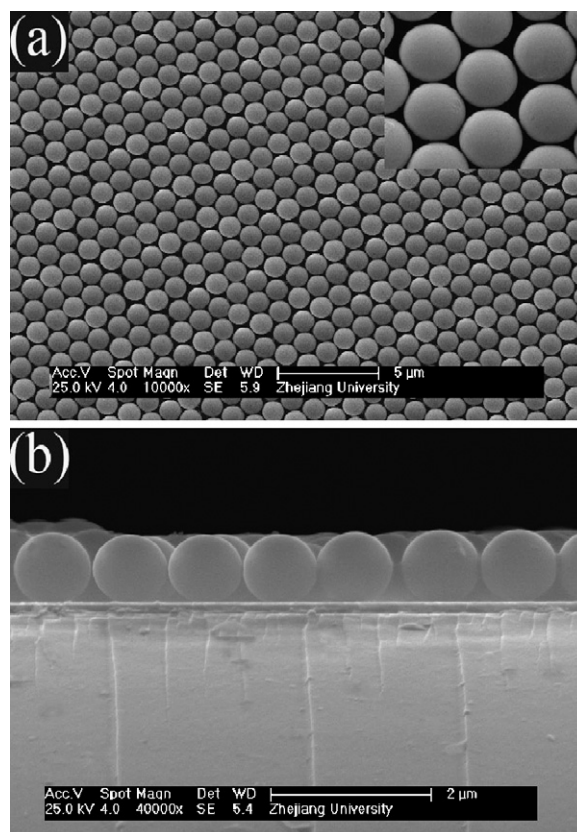


Fig. 1. SEM micrographs of (a and b) top and side views of the self-assembled PS sphere template.

model Electrochemical Workstation (Shanghai). The electrodeposition experiments were carried out at a constant cathodic current of 0.5, 1.0 and 1.5 mA cm^{-2} for 300 s, respectively. The coulombic efficiency for the electrodeposition of $\text{Co}(\text{OH})_2$ is about 98% at 0.5 mA cm^{-2} , 95% at 1 mA cm^{-2} and 90% at 1.5 mA cm^{-2} , respectively. Afterwards, the samples were immersed in toluene for 24 h to remove the PS sphere template. Finally, the as-prepared samples were dried at 85°C , and then annealed at 350°C for 1.5 h in flowing argon.

The powder from the as-deposited precursor film was analyzed by thermogravimetry (TG) and differential thermal analysis (DTA) under N_2 atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$ in a temperature range of $25\text{--}520^\circ\text{C}$. The obtained samples were characterized by X-ray diffraction (XRD) using a Rigaku D/max-GA X-ray diffractometer with graphite monochromatized $\text{Cu K}\alpha$ radiation ($k=1.54178 \text{ \AA}$). The images and structures of the sample were obtained by field emission scanning electron microscopy (FESEM, FEI SIRION), transmission electron microscopy (TEM, JEM 200 CX 160 kV), high-resolution transmission electron microscope (HRTEM, JEOL JEM-2010F) and Fourier transform infrared (FTIR) measurements (PerkinElmer System 2000 FTIR interferometer). The specific surface areas of the samples were determined by BET (Brunauer–Emmett–Teller) measurements using a NOVA-1000e surface area analyzer.

2.3. Electrochemical measurements

Test cells were assembled in an argon-filled glove box using the nickel-supported Co_3O_4 array films as working electrode, Li foil as counter-electrode, polypropylene film as separator, and an electrolyte of 1 M LiPF_6 in a 50:50 (w/w) mixture of ethylene carbonate and diethyl carbonate. The loading weight for Co_3O_4

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