

Short communication

Sol–gel template synthesis of highly ordered MnO₂ nanowire arrays

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Abstract

In this paper, anodic aluminum oxide (AAO) templates with uniform pore diameter and periodicity were fabricated using a two-step oxidizing method at a constant current of 1.5 A dm⁻² in a mixed solution of 0.5 M sulfate acid and 5 g L⁻¹ oxalic acid at room temperature, pore-widening was done in 5 wt.% phosphoric acid. Then, arrays of manganese dioxide nanowires were prepared by combining the AAO template and a sol–gel solution containing Mn(CH₃COO)₂ and citric acid. SEM was used to characterize the structure of AAO and MnO₂ nanowires. The results show that uniform length and diameter of MnO₂ nanowires were obtained, and the length and diameter of MnO₂ nanowires are dependent on the pore diameter and the thickness of the applied AAO template. The pore diameter of the AAO was about 70 nm, the diameter of the MnO₂ nanowires was 70 nm and the length of the MnO₂ nanowires was about 500–700 nm. XRD analysis indicate the MnO₂ nanowires was α -MnO₂ polymorph. The results of cyclic voltammetry indicated that the α -MnO₂ nanowires are promising electrode materials for application in supercapacitors, the specific capacity of the electrode was 165 F g⁻¹.

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1. Introduction

Since the successful growth of carbon nanotubes, great interest has been focused on one-dimensional materials, including nanotubes and nanowire, due to their unique structure and properties as well as potential application in electronics, mechanics and optics [1,2]. Various methods have been reported to fabricate nanowires, including arc discharge, laser ablation, catalytic CVD growth, and template synthesis [3], etc. A method, which entails synthesizing the desired material within the pores of a nonporous membrane, is called “template synthesis” [4]. In this case the size and shape of the nanostructures are controlled by the size and shape of the nanotemplates. Different kinds of templates such as anodic porous alumina, polymer and nanochannel glass tem-

plates have been widely investigated [5]. One of the attractive templates is anodic aluminum oxide (AAO) [4]. Anodic aluminum oxide (AAO) films possess very regular and highly anisotropic porous structures with pore diameters ranging from below 10 to 200 nm, pore length from 1 to 50 μ m, and pore densities in the range 10⁹ to 10¹¹ cm⁻², the pores have been found to be uniform and nearly parallel [6]. This offers a promising route to synthesize a high surface area, ordered nanostructure material with high aspect ratio. So porous alumina films formed by anodic oxidation of aluminum have been intensively studied for use as molds to form nanowires or dots [7]. Metal or semiconductor nanowires or dots, for example, Si [8], Ni [9], Au [3] and AlN [10] nanowire arrays have been successfully prepared by using AAO templates. In recent years AAO templates have been intensively studied to form novel nanostructured electrode materials. It is well-known that electrode materials with high surface area show better electrochemical performance than having much lower

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surface areas [11]. Much effort is being made to prepare low-dimensional nanostructured MnO_2 [12]. In this paper, AAO templates were fabricated using a two-step oxidation method firstly, and then, arrays of MnO_2 nanowires were prepared by combining AAO template and sol-gel methods.

2. Experimental

2.1. AAO template preparation

A high-purity aluminum foil (99.5%, 0.01 mm thick) was used as substrate material. Aluminum foil was annealed at 500 °C for 5 h to form texture, then degreased in acetone. Subsequently, it was first anodized at a constant current of 0.15 A cm⁻² in 0.5 M sulfuric and 5 g L⁻¹ oxalic solution for 1 h at room temperature. As a result, an anodic oxide layer was formed. The top part of this layer was disordered, which was removed in a mixture of phosphoric acid and chromic acid. After the removal of the top layer, the textured Al foil was anodized again for 6 h under the same condition as the first. Then the bottom part of the membrane was removed by exposure to phosphoric acid at 30 °C. Finally, the anodized aluminum oxide (AAO) in porous structure was formed and dried at room temperature.

2.2. Preparation of MnO_2 nanowires

Manganese acetate was used as the cationic source, and citric acid and *n*-propyl alcohol as the monomers for forming the polymeric matrix. $\text{Mn}(\text{CH}_3\text{COO})_2$ was dissolved in a mixture of citric acid and *n*-propyl alcohol. The molar ratio of Mn^{2+} and citric acid was 1:2, the preliminary pH of the medium was maintained around 8.5 by the addition of ammonium hydroxide. This solution was heated at 80 °C to induce etherification and distill out excess *n*-propyl alcohol. When the solution changed to a transparent viscous sol, the AAO templates were slowly dipped into the sol for the desired period of time, the AAO templates in which the sol was incorporated into the holes were taken out of the sol when the sol could not flow freely, then the excess sol on the membranes surface was wiped off using a laboratory tissue, followed by drying in air at 80 °C for 2 h. Finally, the dried membranes were heated at 400 °C for 12 h. To obtain bulk MnO_2 nanowires, the heat-treated templates were dissolved

in 3 M NaOH solution and washed with water several times and dried.

2.3. Characterization methods

The morphology of the as-prepared AAO template and the MnO_2 nanowire arrays was observed using a field emission scanning electron microscope (FE-SEM) (JSM-6700F) and a scanning electron microscope (SEM) (HitachiX-650). X-ray diffraction (XRD) of MnO_2 nanowire arrays was performed on a diffractometer (D/MAX-3C) with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) and a graphite monochromator at 50 kV, 100 mA. The step scanning mode was used with a step of 0.02° and the data were acquired in the 2θ range 10–70°.

2.4. Electrochemical measurement

Electrode A was formed by mixing 80% α - MnO_2 nanowires and 15% acetylene black. Afterwards, the appropriate amount of 5 wt.% of polytetrafluorethylene (PTFE) aqueous suspension (60%) as a binder was added and mixed well to obtain a paste. The paste was pressed into the nickel foam substrate using a spatula, dried at 80 °C for 2 h, and then pressed at 15 MPa for 1 min in order to assure a good electronic contact. Electrode B was prepared by mixing 80% α - MnO_2 powder and 15% acetylene black. The rest of the procedures were the same as in the case for electrode A.

The cyclic voltammetric behavior of the electrodes were measured in a beaker type electrochemical cell equipped with the working electrode, a nickel sheet counter electrode and a standard calomel reference electrode (SCE), by means of electrochemical analyzer systems, CHI600A (CH Instruments, USA). The geometric surface area of the working electrode was 1 cm². The electrolyte was a 2 M $(\text{NH}_4)_2\text{SO}_4$ aqueous solution.

3. Results and discussion

In the anodization process, an electrical circuit is established between the cathode and a thin film of aluminum, which serves as the anode, the anode reaction of aluminum in the presence of acid is as follows:

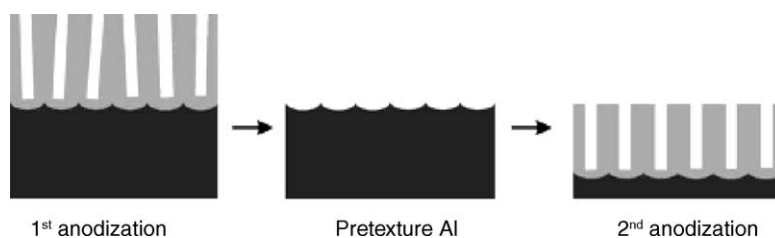
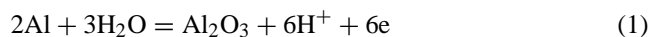


Fig. 1. Schematic of the two-step anodization process. The first anodization step pret textures the Al surface in a highly ordered manner which is retained during the second anodization.

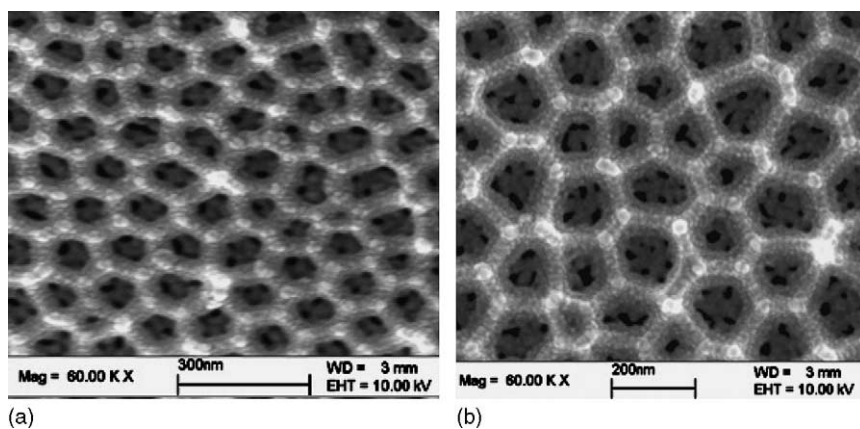
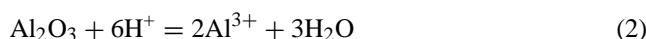


Fig. 2. FE-SEM images of: (a) AAO template A after pore-widening for 20 min, and (b) AAO after pore-widening for 40 min.



During the anodization, initially a planar barrier film forms followed by pore development leading to the formation of the relatively regular porous anodic film, which grows with time. A two-step anodization process, illustrated in Fig. 1, can improve the pore regularity under particular conditions. In this process, after stripping away the thick aluminum oxide film obtained from the first anodization, a porous oxide membrane possessing these qualities, which has a highly oriented porous structure with very uniform and nearly parallel nanopores can be organized in an almost precise hexagonal structure obtained by a subsequent re-anodization under the same condition as the first.

Fig. 2a and b show the FE-SEM images of AAO template A and B, respectively. The results show distinctly that an ordered honeycomb structure with uniformity in pore diameter and spacing can be fabricated with this method. It is clearly seen that the mouth of the pores is widened like a funnel. In Fig. 2a, the pore diameter is 70 nm and pore spacing is 80 nm for AAO template A where the pore-widening time was 20 min, while AAO template B after pore-widening 40 min in phosphoric acid has a pore size of 90 nm in diam-

eter as shown in Fig. 2b. It indicates that the pore diameter increases with increasing pore-widening time, while the pore spacing is almost unchanged. The increase of pore diameter after immersing in phosphoric acid might be due to the etching effect of phosphoric acid that results in the thinning of the outer and inner surface of AAO [13]. This provides a convenient route to prepare the AAO template of any desired pore diameter, then, any diameter nanowire can be synthesized in its pores.

Fig. 3a and b show SEM micrographs of MnO_2 fabricated using AAO template A and B, respectively. The nanowires or nanorods with the uniform diameter and length can be observed in the images. These figures show that the diameter of MnO_2 nanowires is basically equal to that of pores of the AAO used. MnO_2 nanowires can be seen clearly from Fig. 3a, the diameter is approximately 70 nm. Length of the nanowires is in the range of 500–700 nm. It can be seen from Fig. 3b that the nanomaterial is in the form of nanorods rather than nanowires, and there are some nanoparticles in it, because after a longer pore-widening time the pore size of the AAO template becomes larger and the thickness becomes smaller, so the average diameter of the nanorods is slightly larger than the nanowires fabricated using AAO template A, which

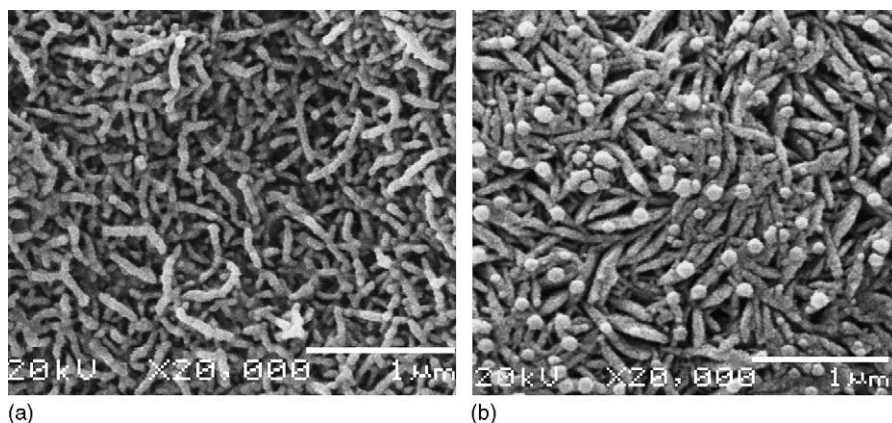


Fig. 3. SEM images of MnO_2 fabricated using AAO template A (a) and template B (b).

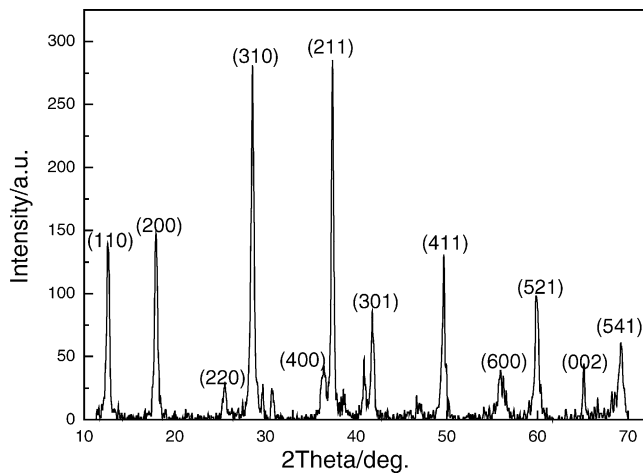


Fig. 4. X-ray diffraction pattern of MnO₂ nanowires.

is about 90 nm, and the length is shorter than that of Fig. 3a. Longer nanowires might be obtained by using AAO with deeper holes.

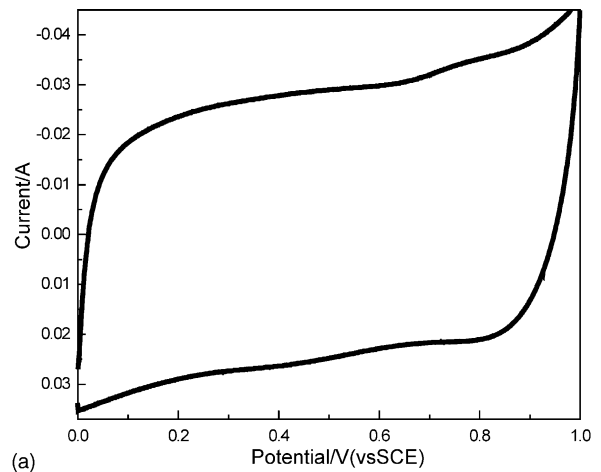
A typical XRD pattern of the MnO₂ nanowires is shown in Fig. 4. The diffraction peaks correspond to the (1 1 0), (2 0 0), (2 2 0), (3 1 0), (4 0 0) and (2 1 1) planes, respectively. All the reflections on the XRD pattern are similar to that of Mn_{0.98}O₂ and can be indexed based on a hollandite type α -MnO₂ structure with a tetragonal cell according to the literature [11,14].

Typical cyclic voltammograms (CV) for electrode A and B are shown in Fig. 5a and b, respectively. The potential varied between 0 and 1.0 V versus SCE taken at a sweep rate of 10 mV s⁻¹. The curve shows no peaks, which indicates that the electrodes are charged and discharged at a constant rate over the complete cycle. But the capacitive behavior of electrode A was obviously better than that of electrode B, the CV curve of electrode A is much closer to an ideal rectangle, which shows a mirror image with respect to the zero-current line and a rapid current response on voltage reversal at each end potential. Because α -MnO₂ nanowires possess special pseudo-one-dimension, high surface area and high aspect ratio dimensions, the interface between the active material and electrolyte increases and conductivity increases. The specific capacitance of the electrodes can be estimated from the voltammetric charge surrounded by the CV curves according to Eq. (1) [15]

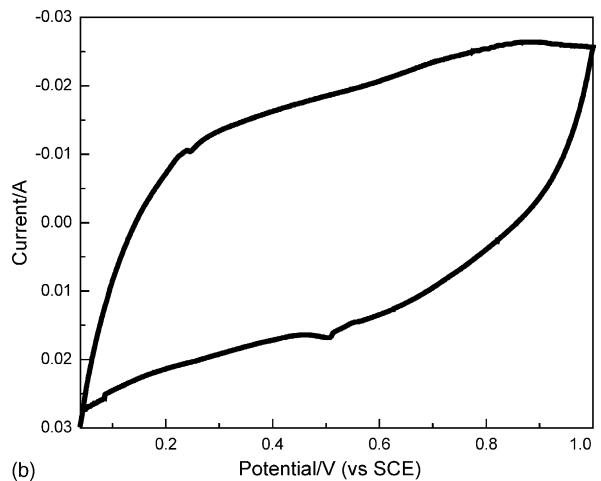
$$C_{\text{st}} = \frac{q_a + |q_c|}{2W\Delta V}, \quad q = It \quad (3)$$

$$C_{\text{st}} = \frac{I_a + |I_c|}{2W(dV/dt)} \quad (4)$$

where I_a , I_c , W and dV/dt are the current of anodic and cathodic voltammetric curves on positive and negative sweeps, mass of the composite, and the sweep rate, respectively. The specific capacitance of electrode A was 165 F g⁻¹, which is much more than electrode B (108 F g⁻¹).



(a)



(b)

Fig. 5. CV curves for different electrodes in 2 M (NH₄)₂SO₄ aqueous solution at 10 mV s⁻¹: (a) electrode A; (b) electrode B.

4. Conclusion

Anodic aluminum oxide (AAO) templates with uniform pore diameter and periodicity were fabricated using a two-step oxidation method. Then, a sol-gel template process successfully synthesized MnO₂ nanowire arrays. The microstructure of the AAO template and nanowires were characterized by FE-SEM and SEM. The diameter of MnO₂ nanowires was basically equal to that of pores of the AAO used. The diameter was approximately 70 nm and length of the nanowires was in the range of 500–700 nm. XRD analysis indicated that MnO₂ nanowires were α -MnO₂ polymorph. The results of cyclic voltammetry indicated that α -MnO₂ nanowires are promising electrode materials for supercapacitor applications. The specific capacity of the electrode was 165 F g⁻¹.

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