Short communication

Highly ordered cobalt-manganese oxide (CMO) nanowire array thin film on Ti/Si substrate as an electrode for electrochemical capacitor

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Abstract

Anodic aluminum oxide (AAO) on Ti/Si substrate was successfully synthesized by a two-step electrochemical anodization of the aluminum film on the Ti/Si substrate and then used as template to grow nanowire array. The ordered cobalt-manganese oxide (CMO) nanowires with diameter about 30 nm were directly fabricated on AAO/Ti/Si substrate by direct current (dc) electrodeposition. The microstructure of the nanowire array electrode was investigated by field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM). The electrochemical characterization was performed using cyclic voltammetry in 0.5 M Na_2SO_4 aqueous solution. The ideal capacitive behavior was obtained from the as-prepared sample heat-treated at 100 °C. The specific capacitance of the electrode was 396 F g^{-1}.
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Keywords: CMO nanowire array electrode; AAO/Ti/Si; Electrochemical capacitor

1. Introduction

Electrochemical capacitors are currently receiving considerable amount of attention because of their high power energy storage ability. It is well known that the most widely used active electrode materials are carbon [1,2], conducting polymers [3,4] and both noble [5–7] and transition-metal oxides [8–26]. Among these candidates, MnO_2 and it's ramification, such as CMO have been considered to be the most attractive electrochemical capacitor materials in terms of low cost, abundance and more environmentally friendly than other transition-metal oxide systems [27,28].

Researches indicate that electrochemical characteristics of electrode materials are highly dependent on the grain size, texture, surface area and morphology. The ordered, high surface area structure of electrode materials can enhance electrochemical characteristics. Martin's group has demonstrated that high surface area nanowire array electrodes of SnO_2 and V_2O_5 have significantly improved rate capability compared with thin films of the same material [29–31]. Anodic aluminum oxide template offers a promising route to synthesize a high surface area, ordered nanowire array electrodes because of its advantages. Recently, amorphous manganese oxide nanowire array electrodes with high energy and power density were prepared by anodic aluminum oxide (AAO) template method [32]. But this method is difficult to be used in practical purpose due to the fragility of AAO template.

In our previous work, AAO films were successfully grown on Ti/Si substrate and the first time to be used as template to synthesize high surface area, ordered MnO_2 nanowire array electrode for electrochemical capacitor. This kind of template has a unique property of electrodeposition and can bond well with the deposited materials [33]. The aim of this work is to fabricate CMO nanowire array electrode by depositing mixed oxide into the holes of AAO/Ti/Si substrate. The electrochemical characterization of ordered CMO nanowire array electrode on Ti/Si substrate was performed by cyclic voltammetry in 0.5 mol L^{-1} Na_2SO_4 aqueous solution. The nanowires consist of only electrochemically active material (CMO) and are fairly stable. The results of cyclic voltammetry show that the specific capacitance of the electrode is about 396 F g^{-1} and has promising application in electrochemical capacitor.

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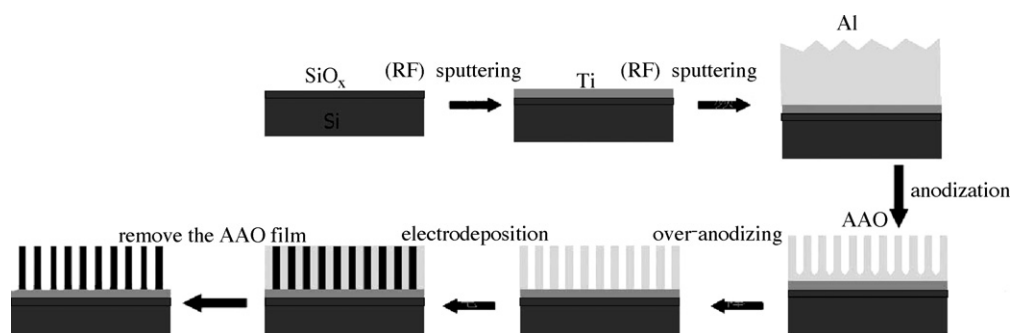
Fig. 1. Scheme of the experiment process.

2. Experiments

2.1. Preparation of AAO/Ti/Si

Herein the highly pure Al film (99.999%, ∼3.0 μm) was deposited on the p-type silicon substrate coated with a Ti (∼300 nm) film by radio frequency (rf) sputtering. The anodization was carried out in 0.3 M oxalic acid solution at 40 V and room temperature for 1 h. After that, the resulting alumina film was etched away in 0.4 M H_3PO_4, 0.2 M $H_2Cr_2O_4$ at 40 °C for 2 h. The remaining aluminum was re-anodized under the same conditions until the Al film was fully oxidized. To remove the barrier layer, the anodization was continuously processed for 30–60 min.

2.2. Preparation of nanowire array electrode

The electrolyte used for electrodepositing CMO nanowires was composed of 0.5 M $Mn(CH_3COO)_2$ and 0.5 M $Co(CH_3COO)_2$. Electrodeposition was carried out at room temperature using a three-electrode potentiostatic control and direct current electrodeposition system with a saturated calomel electrode (SCE) as reference electrode, a 1.0 cm × 1.0 cm platinum plate as a counter electrode and the AAO/Ti/Si template as working electrode. The electrodeposition was carried out at 1.4 V for CMO nanowires with a CHI 660 electrochemical analyzer. The electrodeposition was kept running until deposited nanowires overflowed from nanoholes. The overflowed nanowires were mechanically polished with metallographic abrasive paper. The as-prepared sample was immerged in 0.01 M NaOH for 0.5 h to remove the AAO film. And then the brush shapes nanowire array electrode was got. The experiment process is shown in Fig. 1.

2.3. Measurements

A conventional cell with a three-electrode configuration was used throughout this work. The nanowire array electrode was employed as the working electrode and a saturated calomel electrode (SCE) was used as the reference electrode. Electrochemical measurements were performed with a CHI 660 electrochemical analyzer, and the potentials were measured versus the SCE.

The mass of the materials was measured by microbalance (Mettler Toledo, AB 265-S). The morphology of nanowires was characterized by Hitachi 600 transmission electron microscope (TEM). The samples were prepared by scraping the CMO nanowires from the substrate into the vessel and dispersing in ethanol for TEM. The morphology of AAO/Ti/Si and the CMO nanowire array electrode on Ti/Si substrate were examined by field emission scanning electron microscope (FESEM, JEOL JSM-S4800).

3. Results and discussion

3.1. FESEM analysis of AAO film on Ti/Si substrate

After a two-step anodization in 0.3 M oxalic acid solution at room temperature, the resulting template has pores with a fairly narrow size distribution, as shown in Fig. 2. Fig. 2 shows that the porous alumina structure has almost arranged the pore array with the average pore diameter about 30 nm, the interspaces about 60 nm, and pore densities about 10^{10} cm^{-2}. But their arrangement has lower order than AAO on bulk Al probably due to small grain [34] and thin aluminum film [35].

3.2. TEM and FESEM analysis of CMO nanowire array electrode

Fig. 3(a) shows the typical TEM image of CMO nanowires. TEM image reveals that the nanowires obtained on Ti/Si sub-
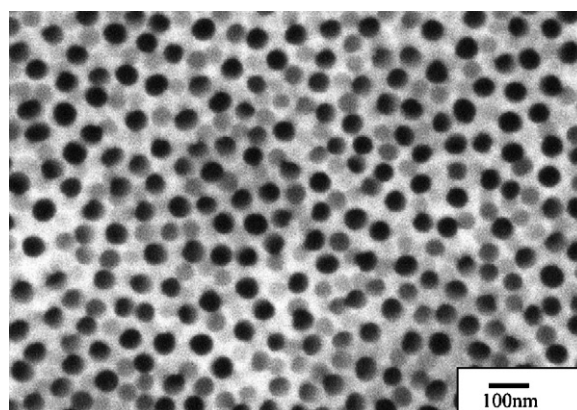

Fig. 2. FESEM image of the surface morphology of an AAO film on Ti/Si substrate after the second anodization.
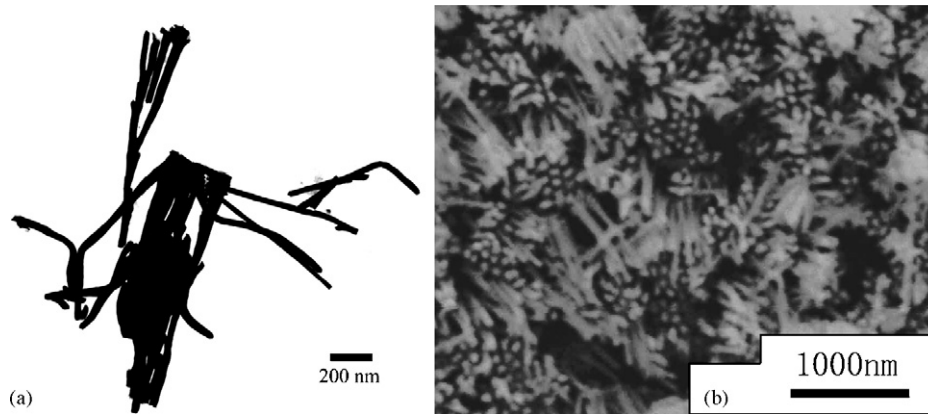
Fig. 3. (a) TEM image of the sample CMO nanowires and (b) FESEM image of the surface morphology of CMO nanowire array electrode.

strate are of regular size and continuous. All of them have uniform diameter of about 30 nm, which basically equals to that of the pores of the AAO template used in the experiment. The length of nanowires is about 1 μm, which is identical to the thickness of the AAO template on Ti/Si substrate. The FESEM image in Fig. 3(b) shows the surface view of CMO nanowire array electrode. From Fig. 3(b), we can find that many freestanding nanowires which provide high surface area protrude from the Ti/Si substrate. There are also some clusters in the FESEM image in Fig. 3(b). The clusters could result from the situation in which the nanowires are uncovered from the framework of the porous anodic alumina template but freestanding incompletely. When the porous anodic alumina template is dissolved away, the nanowires embedded in the template are released gradually and inclined to agglutinate together to minimize the system free energy. Fig. 3(b) also shows that the nanowires are abundant, uniform and well ordered in the large area. From Fig. 3(b), it can be estimated that the pore filling rate is above 90%, and some nanowires are lost from the electrode surface. Considering the diameter, filling rate and the length of the nanowires, it is easy to calculate that the nanowire array electrode have $10\,cm^2$ of CMO area per cm^2 of substrate electrode area.

3.3. EDS and XRD analysis of the CMO nanowire array electrode

EDS analysis of the CMO nanowire array electrode in Fig. 4 confirms a nearly 7:1 atomic ratio of Mn to Co. Fig. 5 illustrates the XRD pattern of the sample heat-treated at 100 °C. The main peaks of the a-MnO_2 and Co_3O_4 [39] can be roughly identifie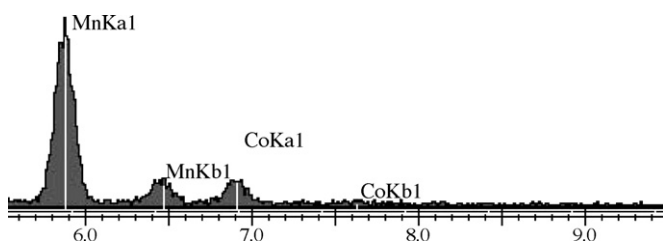d in Fig. 5. However, the amorphous nature of the samples is confirmed by the XRD spectrum, which shows broad and low intense peaks related to a poorly crystallized compound.

3.4. Electrochemical properties of CMO nanowire array electrode

CV is considered to be an ideal tool to indicate the capacitive behavior of any material [28]. A large magnitude of current and a rectangular type of voltammogram, symmetric in anodic and cathodic directions, are the indications of ideal capacitive nature of any material. Fig. 6 shows the typical CVs of CMO nanowire array electrode and MnO_2 nanowire array electrode in 0.5 M Na_2SO_4 electrolyte. It can be seen that the voltage window of cobalt oxide is increased from 0.6 to 1.0 V [36–38] by forming a mixed oxide with MnO_2. The CV curve is rectangular in shape and exhibits mirror-image characteristics which indicate ideal capacitive behavior of the CMO nanowire array electrode. Cyclic voltammogram is also recorded in the same electrolyte with bare Ti/Si electrode, which indicates that no capacitive behavior with negligible current values compared to that shown in Fig. 6. It is generally known that the charge stored at a double-layer is rather low and a large magnitude of current in CV could not be attributed to double-layer process.
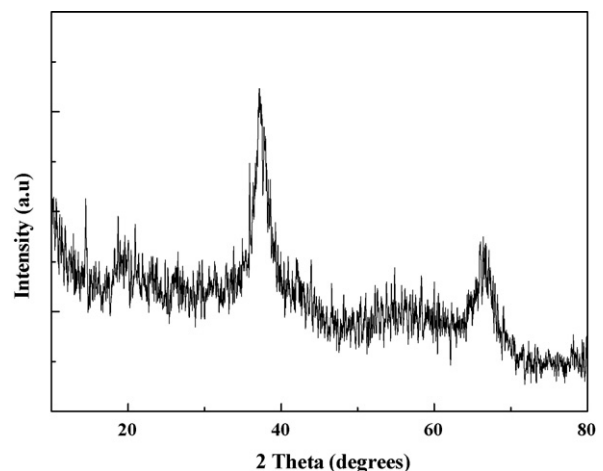

Fig. 4. EDS pattern of CMO nanowire array electrode.

Fig. 5. XRD pattern of CMO nanowire array electrode heated-treated at 100 °C.
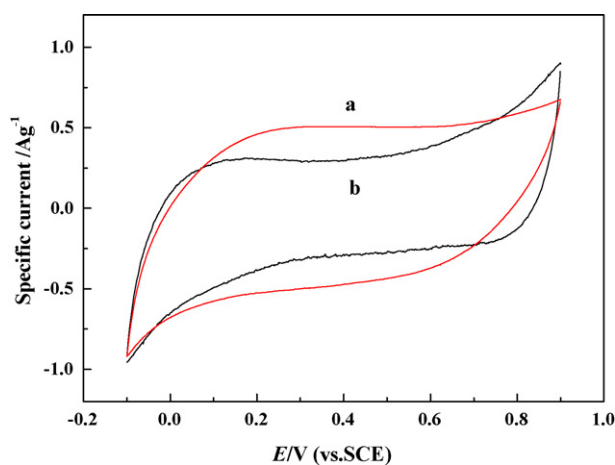
Fig. 6. Cyclic voltammograms of: (a) CMO and (b) MnO_2 nanowire array electrode at a scan rate of $2\,mV\,s^{-1}$ in $0.5\,M\,Na_2SO_4$ electrolyte.

Typical cyclic voltammograms of the samples heat-treated at different temperature for 2 h measured in $0.5\,M\,Na_2SO_4$ at $2\,mV\,s^{-1}$ scan rate are shown, respectively, as curves (a), (b) and (c) in Fig. 7. Within the potential range of -0.1 to 0.9 versus SCE, the capacitive-like and symmetric I/E responses of the CV curves indicate that the oxides through different temperature treatment exhibit electrochemical characteristics suitable for pseudo capacitor application. But, only the sample obtained at $100\,^{\circ}C$ has the ideal regular rectangular, as shown in curve (b). It is ascribe to the variation of crystalline water content as depicted in literature [24]. The specific capacitance of the sample heat-treated at $100\,^{\circ}C$ is $396\,F\,g^{-1}$, which can be estimated from the cyclic voltammogram according to the following equation [39]:

$$C_{cv} = Q \times \Delta E^{-1} \times m^{-1}$$

where C_{cv} is the specific capacitance $(F\,g^{-1})$, Q the charge (C), ΔE the potential window (V) and m is the mass of active material (g). The above results demonstrate that the CMO nanowire array electrode can be as an excellent electrode for electrochemical capacitor.
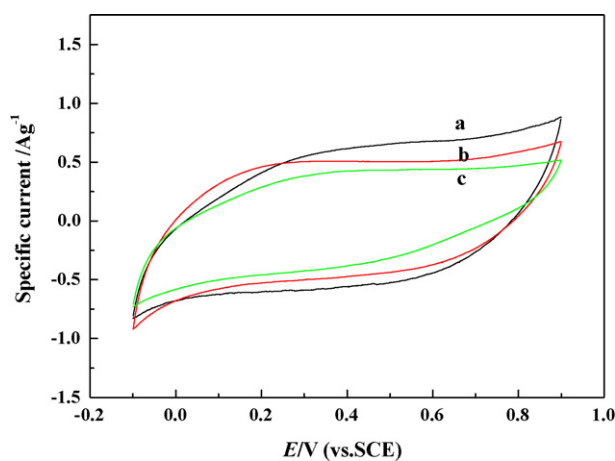

Fig. 7. CV curves of the samples heated-treated at different temperature for 2 h at $2\,mV\,s^{-1}$ scan rate: (a) as-prepared, (b) heated-treated at $100\,^{\circ}C$ and (c) heated-treated at $200\,^{\circ}C$.

4. Conclusion

In this work, CMO (Mn:Co $\approx 7{:}1$) nanowire array was electrodeposited in AAO template on Ti/Si substrate. The AAO/Ti/Si substrate had unique electrodeposition properties and could bond well with the deposited materials. Because the method making electrode was electrodeposition, the loss of material in the experimental process was much less than the traditional method. The CMO nanowire array electrode heat-treated at $100\,^{\circ}C$ showed ideal capacitive behavior and the specific capacitance was up to $396\,F\,g^{-1}$. So, it has promising application in electrochemical capacitor.

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