Preparation and Optical Properties of V_2O_5 Nanotube Arrays*

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Abstract: *V_2O_5 nanotube arrays in porous anodic alumina (PAA) template were obtained from V_2O_5 sols prepared by melt quenching method. X-ray powder diffraction and selected area electron diffraction investigations demonstrate that V_2O_5 nanotubes are orthorhombic. Results by scanning electron microscopy and transmission electron microscopy results show that V_2O_5 nanotubes with a uniform diameter form highly ordered arrays. The diameter and length of the nanotubes depend on the pore diameter and the thickness of the PAA template used. It is proved that the sol-gel template process is a cost-saving, simple and readily-controlled method to prepare metal oxides nanomaterials. Owing to the quantum size effect, the optical absorption edge of V_2O_5 nanotubes in PAA exhibits a significant blue shift with respect to that of bulk V_2O_5.*

Key words: *V_2O_5; nanotube arrays; porous anodic alumina template; sol-gel; optical properties*

1 Introduction

Vanadium oxides have important applications in many fields, such as cathode material for lithium-ion batteries, catalyst and gas sensor. One-dimensional vanadium oxide nanomaterials show excellent properties because of the larger surface areas and specific shape[1]. Many one-dimensional nanomaterials have been successfully synthesized by using a variety of methods including solvothermal[2], vapor-liquid-solid process[3], chemical vapor deposition[4] and carbon nanotube template synthesis[5], *etc*. Recently template pathway[6] to synthesize nanomaterials has aroused worldwide interest, because the high density, well-ordered nano-structured arrays can be easily fabricated by this method. The nano-structured arrays are well-ordered, and have a high aspect ratio and large surface areas. These advantages make them have great applied prospects in many fields such as data storage[7], nano-structured electrode[8] and field emission displays[9]. The templates mainly are porous anodic alumina, polymer and nanochannel glass templates. Among them, porous anodic alumina (PAA) template has been more widely used for its tunable pore dimensions, narrow pore size distribution, and good mechanical and thermal stability[10,11]. Martin *et al*[1] and Limmer *et al*[12] prepared V_2O_5 nanorod arrays using expensive triisopropoxyvanadium oxide and complex direct electrochemical deposition, respectively, in polycarbonate membranes. In this paper, V_2O_5 nanotube arrays have been obtained via a simple and cost-saving method, which used cheaper and more accessible V_2O_5 as raw material, combining sol-gel chemistry and PAA template. The structure and morphology of these V_2O_5 nanotube arrays were characterized and the optical transmittance spectrum was also investigated.

2 Experimental

2.1 Membrane preparation

The PAA templates were fabricated by a two-step anodization process. Prior to anodization, a high purity (99.999%) aluminium plate was degreased in acetone for 30 min and annealed at 500 ℃ for 4 h. The first anodization was conducted at a constant voltage of 40 V in 0.3 M oxalic acid solution for 4 h. Then the produced alumina layer was removed by wet chemical etching in a mixture of phosphoric acid (6 wt%) and chromic acid (1.5 wt%) at 60 ℃ for 4 h. The remnant aluminium plate was anodized again under the same conditions as used in the first step. Then a saturated $CuCl_2$ solution was utilized to remove the central aluminium substrate. Finally, the barrier layer on the bottom side of the PAA was removed in a 5 wt% phosphoric acid solution at 30 ℃ for 50 min.

2.2 Preparation of V_2O_5 nanotube arrays

V_2O_5 sols were synthesized using a melt quenching method as described before[13]. About 20 g crystalline V_2O_5 power was heated to 800 ℃ in a ceramic crucible and kept for 20 min, thus a molten liquid was obtained. When the molten liquid was quickly poured into distilled water with stirring, a brownish solution was formed. The solution was allowed to heat to the boiling point and then cool to room temperature naturally. After filtration and ag-

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ing for more than 7 days, brownish V_2O_5 sols were obtained.

The alumina template membrane was dipped into the V_2O_5 sols and then removed. The excess sols on the membrane surface were wiped off using a laboratory tissue. The membrane was dried in air for 30 min at room temperature and then placed in a furnace. The temperature was ramped (50 ℃ h^{-1}) to 500 ℃. The membrane was heated at this temperature for 6 h and cooled to room temperature in the furnace. Thus we obtained the arrays of V_2O_5 nanotubes in the pores of the PAA template.

2.3 Characterization of V_2O_5 nanotube arrays

The structure and morphology of V_2O_5 nanotube arrays were characterized by several methods. X-ray powder diffraction (XRD) patterns were obtained on a D/MAX-III powder diffractometer with Cu-Kα radiation (λ = 1.5418 Å) and graphite monochrometer. The diffraction data were recorded for 2θ between 5 and 60°, with a resolution of 0.02°. Scanning electron microscopy (SEM) images were collected on a JSM-5610LV microscope operated at 20 kV. Before SEM observation, several drops of 5 wt% NaOH were dropped on the sample to dissolve the partial membrane. Transmission electron microscopy (TEM) images were obtained through a JEM-100CX Ⅱ microscope. The accelerating voltage of the electron beam was 80 kV, and the camera length was 55 cm. For TEM sample, the PAA template was dissolved in 5 wt% NaOH and a small drop of the solution was placed on the microgrid. UV-Visible transmittance spectrum of the V_2O_5 nanotube arrays in PAA was obtained using an UV-Vis spectrophotometer (UV-1601, Japan).

3 Results and Discussion

3.1 SEM analysis of membrane

The surface image of the PAA template fabricated in oxalic acid is presented in Fig.1(a), which reveals the average pore diameter is approximately 95 nm and the pore density is about 1.1×10^{10} cm^{-2}. The parameters of PAA template can be readily controlled by properly adjusting the condition of anodization. The PAA template obtained has perfect hexagonal pore arrays within domains of microsize. The cross-section of the PAA template is shown in Fig.1(b). It is obvious that the pores are parallel to each other and run through the whole membrane.

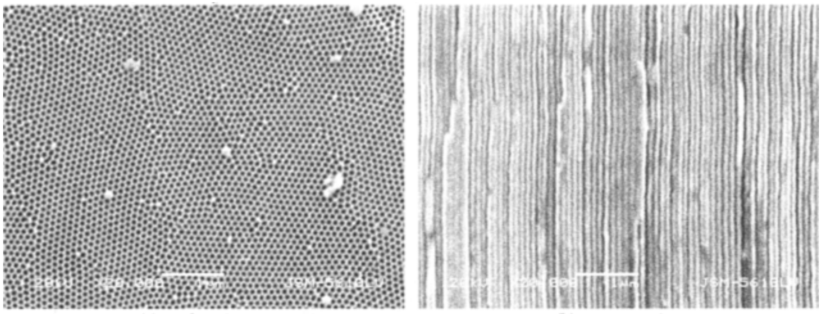

(a) surface image (b) cross-section

Fig.1 SEM images of the PAA template

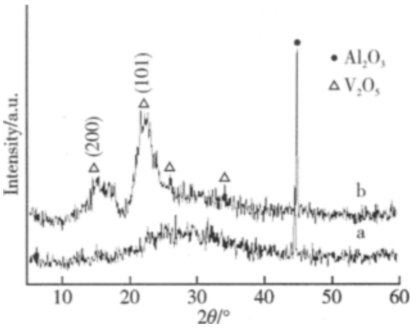


Fig.2 XRD patterns of blank PAA (a) and composite membrane(b)

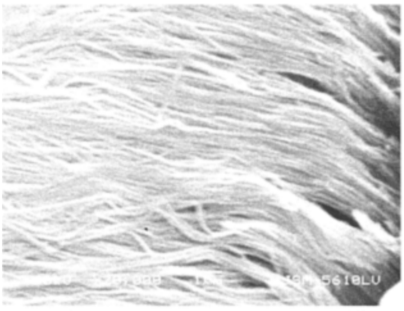
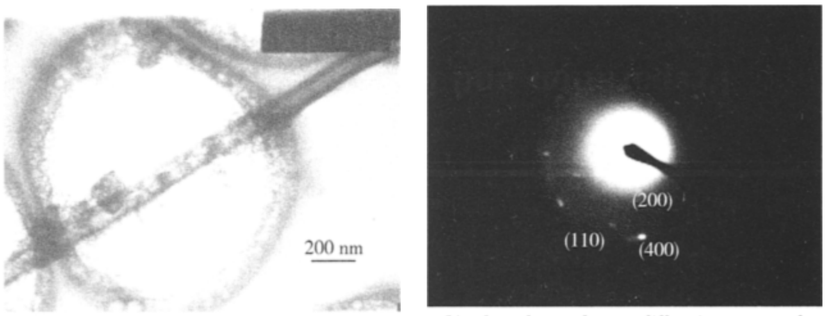


Fig.3 SEM image of the V_2O_5 nanotube arrays



(a) single V_2O_5 nanotube (b) selected area electron diffraction pattern of the single V_2O_5 nanotube

Fig.4 TEM images of the V_2O_5 nanotubes

3.2 XRD analysis

Fig.2 shows XRD patterns of the blank PAA template and the composite membrane obtained by dipping the PAA template into the V_2O_5 sols, respectively. In Fig.2(a), we can see a broad peak at 2θ between 20 and 40°, which is attributed to amorphous PAA. The major peaks of the V_2O_5 are observed in Fig.2(b). The diffraction peaks with 2θ values of 15.34, 21.56, 26.04, 34.08°, correspond to the (200), (101), (110) and (310) diffraction planes of orthorhombic V_2O_5 crystal, respectively, confirming that V_2O_5 enters into the pores of the PAA template. The reason that the diffraction peaks of V_2O_5 are relatively weak may be the influence of! amorphous peak of the PAA template.

3.3 SEM and TEM analysis of V_2O_5 nanotube arrays

Fig.3 shows the SEM image of the V_2O_5 nanotube arrays prepared in the PAA template. It can be seen that the V_2O_5 nanotubes are highly ordered and parallel to each other. They have uniform diameters and look like some brushes. It can be observed that the nanotubes have a high density resulting from the very high porosity of the PAA template. These indicate that well ordered V_2O_5 nanotube arrays can be prepared within the pores of the PAA template.

The TEM images of the sample after dissolving the PAA template completely are shown in Fig.4.

It can be seen that it possesses a tubular structure from Fig.4(a). Combined with XRD patterns, it can be confirmed that the tubular structure is V_2O_5 nanotube. The thickness of nanotubular wall is about 20 nm. The V_2O_5 nanotube has an uniform diameter of about 95 nm in the entire length. The diameter and the length of the nanotube correspond closely to those of the template applied respectively, which show that the diameter and length of the nanotubes depend on the pore diameter and the thickness of the PAA template. So the dimensions of the nanotubes can be controlled by using PAA templates with different parameters. Fig.4(b) shows selected area electron diffraction (SAED) pattern of the single V_2O_5 nanotube. Because the number of crystalline grains in the selected area is small, there are only some bright dots and no clear circles. The diffraction spots correspond to the (200), (110) and (400) diffraction planes of orthorhombic V_2O_5.

The growth mechanism of V_2O_5 nanotubes is similar to that of TiO_2 nanotubes[14]. The pore walls are negatively charged and the sol particles are positively charged. Thus the sol particles are easy to be adsorbed onto the pore walls of the template. Drying at an elevated temperature shrinks the sol-gel, causing it to conform to the template pores. Therefore, the diameter of V_2O_5 nanotubes is equivalent to the pore diameter of the template. With the increase of the immersing time, the nanotubular walls will gradually become thick and nanowires can be obtained ultimately if the time is long enough.

3.4 Optical properties of V_2O_5 nanotube arrays

Fig.5 shows the transmittance spectrum of the V_2O_5/PAA composite membrane. V_2O_5 nanotube arrays in PAA have a high transmittance (> 50%) over the entire visible light region. The fast decay below 425 nm is due to the absorption of light caused by the excitation of electrons from the valence band to the conduction band of V_2O_5. In order to estimate the band-gap energy, the absorption coefficient a, near the absorption edge, was calculated from the transmittance T and reflectance R data using the simplified relation $T = (1 - R)^2 e^{-ad}/(1 - R^2 e^{-2ad})$, where d is the thickness of the composite membrane[15,16]. The intercept of the tangent to the $(ahv)^{1/2}$ *versus* photon energy hv plot gives an approximation of the band-gap energy of V_2O_5. The plot of $(ahv)^{1/2}$ *versus* hv for the V_2O_5 nanotube arrays in PAA is shown in Fig.6. The band-gap energy estimated from the intercept of the tangent to the plot is about 2.9 eV. This shows that the optical absorption edge of V_2O_5 nanotubes in PAA exhibits a significant blue shift with respect to that of bulk V_2O_5 (2.24 eV)[17]. There are many reports concerned with quantum size effects in low-dimensional semiconductor systems. It is well known that the semiconductor nanoparticle band-gap energy increases with decreasing grain size, which leads to a blue shift of the optical absorption edge. Herein the blue shift could also be ascribed to the quantum size effect.

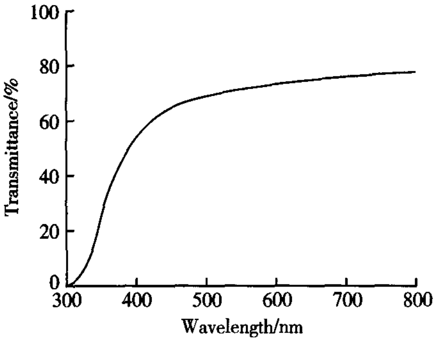


Fig.5 Tranmittance spectrum of the V_2O_5 nanotube arrays in PAA

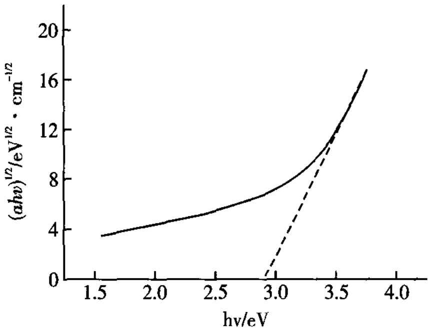


Fig.6 $(ahv)^{1/2}$ *versus* hv for the V_2O_5 nanotube arrays in PAA

4 Conclusions

In summary, highly ordered V_2O_5 nanotube arrays were synthesized in nanochannels of PAA by sol-gel process, followed by being heated at 500 ℃ for 6 h. Investigations of XRD and SAED demonstrate that V_2O_5 nanotubes are orthorhombic. SEM and TEM results show that

V_2O_5 nanotubes with a uniform diameter form highly ordered arrays. The pore walls are negatively charged and the sol particles are positively charged, which causes sol particles to be adsorbed onto the pore walls of the template and result in the formation of V_2O_5 nanotubes. A blue shift of the optical absorption edge of V_2O_5 nanotubes in PAA was observed, which was ascribed to the quantum size effect. This paper proved that the sol-gel template process is a cost-saving, simple and readily-controlled method to prepare metal oxides nanomaterial.

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