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Abstract

Ordered TiO$_2$ nanowire arrays have been successfully fabricated into the nanochannels of a porous anodic alumina membrane by sol–gel electrophoretic deposition. After annealing at 500 °C, the TiO$_2$ nanowire arrays and the individual nanowires were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and x-ray diffraction (XRD). SEM and TEM images show that these nanowires are dense and continuous with a uniform diameter throughout their entire length. XRD and SAED analysis together indicate that these TiO$_2$ nanowires crystallize in the anatase polycrystalline structure. The optical absorption band edge of TiO$_2$ nanowire arrays exhibits a blue shift with respect of that of the bulk TiO$_2$ owing to the quantum size effect.

1. Introduction

In recent years there has been increasing interest in materials with a quasi-one-dimensional nanostructure because of their numerous potential applications in various areas such as material sciences, electronics, optics, magnetism and energy storage. A method called template synthesis provides the possibility of controlling both the size and shape of nanomaterials, and plays an important role in the fabrication of many kinds of nanowire and nanotube arrays [1, 2]. In particular, the highly ordered nanochannels in anodic alumina membranes (AAM) have been widely used to confine the growth of wires and/or tubes since the pioneering work of Martin's group [3, 4].

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Titanium dioxide (TiO_2) has been used extensively as a whitening agent in paints, pigments and cosmetics. Recently, nanosized TiO_2 materials have received much attention as a semiconductor with photocatalyst activities applicable to environmental purification, decomposition of toxic organic pollutants and utilization of solar energy [5–9]. Anatase TiO_2 nanowire and nanotube arrays have also been prepared by a sol–gel template synthesis method [10–14]. However, as was mentioned in a recent report by Limmer *et al* [15], there are some limitations to this technique, such as a weak driving force and low solids content. Sol–gel electrophoresis deposition has been adopted to overcome these limitations, and synthesis of TiO_2 and other complex oxide nanorods with a diameter ~125–200 nm has been achieved using polycarbonate membrane [15, 16]. These workers failed to synthesize nanorods of <50 nm in diameter. In this paper, the fabrication by sol–gel electrophoresis deposition of TiO_2 nanowires with a diameter of about 50 nm embedded in AAM is reported. The optical absorption spectra of these ordered TiO_2 nanowire arrays are investigated.

2. Experimental procedures

AAMs were prepared in a two-step anodizing process [17, 18]. Briefly, initial long-duration oxidation of high-purity aluminium and subsequent complete dissolution of the formed porous alumina leads to patterning of aluminium substrates. The surface retains the regular hexagonal texture, which acts as a mask for the second anodization. After the second anodization, a highly ordered AAM is obtained. Typical anodization parameters used in this work are 0.3 M oxalic acid and 40 V constant voltage. After the remaining aluminium layer was removed in saturated aqueous $HgCl_2$ solution, the AAM was immersed in 6 wt% phosphoric acid to remove the barrier layer on the bottom side. A gold layer was sputter deposited on one side of the hole in the AAM template to provide a conductive contact.

TiO_2 colloidal suspensions for electrophoretic deposition were prepared by first dissolving titanium (IV) isopropoxide in ethanol and stirring for 30 min at room temperature. Then glacial acetic acid was mixed with deionized water and ethanol. The latter solution was added to the former with continuous stirring. A small amount of nitrate acid was added to the sol to adjust the pH to 2–3. The TiO_2 sol thus formed was rather stable at room temperature. For the electrophoretic deposition, a platinum sheet was used as the anode, and an AAM with an Au substrate attached to Cu foil was used as the cathode. TiO_2 nanowire arrays were deposited at a voltage of 2–5 V using a dc power supply. Then the sample was annealed at 500 °C for 24 h in order to crystallize the TiO_2 nanowires.

For observation under a scanning electron microscope (SEM, JEOL JSM-6300), small pieces of AAM with ordered TiO_2 nanowire array samples were dissolved in 5 wt% NaOH solution at 30 °C for 20 min and then lightly washed several times with distilled water to remove the dissolved AAM and the remaining NaOH solution. The morphology of the TiO_2 nanowires was obtained by transmission electron microscopy (TEM, JEM 200CX). The sample for TEM was treated by 5 wt% NaOH solution for 40 min and then ultrasonically dispersed in ethanol. Selected area electron diffraction (SAED) was carried out to investigate the crystalline structure of individual TiO_2 nanowires. The phase structure characterization of TiO_2 nanowire arrays was carried out by x-ray diffraction (XRD, Philips PW 1710 with Cu Kα radiation). The optical absorption spectra were obtained on a Cary-5E spectrophotometer.

3. Results and discussion

The x-ray spectrum of the TiO_2 nanowire arrays is shown in figure 1. The diffraction peaks of (100), (004), (200), (105) and (211) correspond to the anatase TiO_2 phase. In addition, the
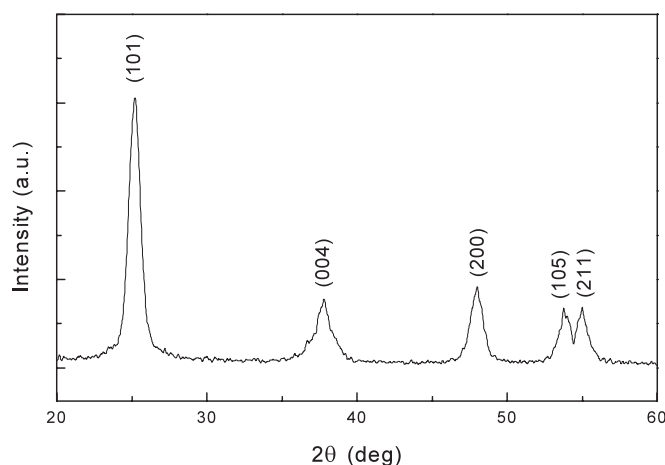
**Figure 1.** XRD spectrum of the fabricated TiO$_2$ nanowires.
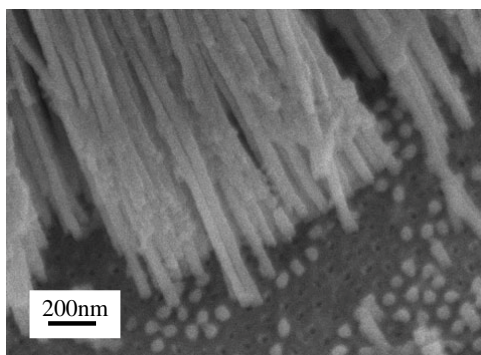
**Figure 2.** A typical SEM image of the fabricated TiO$_2$ nanowires.

peak positions and their relative intensities are consistent with the standard powder diffraction patterns of TiO$_2$, indicating that there is no preferred orientation and that the TiO$_2$ nanowires are polycrystalline. The broadening of TiO$_2$ peaks is due to the small particle size. Further, no obvious peaks for the amorphous AAM were observed.

Figure 2 shows a typical SEM top image of TiO$_2$ nanowire arrays grown in the AAM template by sol–gel electrophoresis deposition and annealed at 500 °C for 24 h. It can be seen that the nanowires are continuous, uniform throughout the entire length of the wires and arranged roughly parallel to one another. The diameter of the TiO$_2$ nanowires is about 50 nm, which is almost equal to the pore size of the template used. Some broken nanowires can be seen, and this can be explained by the differences in thermal expansion coefficients of the membranes and nanowires, distortion of the membranes and the preparation of samples.

The individual TiO$_2$ nanowires were characterized by TEM after the AMM template had been thoroughly dissolved. The TEM image (figure 3) showed that the single TiO$_2$ nanowire was straight, dense and continuous. The crystalline structure of the individual TiO$_2$ nanowire was investigated by SAED experiments, and a detailed diffraction pattern (the inset in figure 3) could be observed, indicating that the TiO$_2$ nanowire was anatase polycrystalline structure, in good agreement with the XRD results.
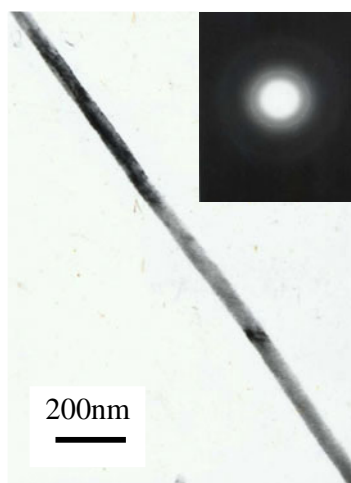
Figure 3. Typical morphology of one of the TiO$_2$ nanowires; the inset shows the SAED results taken from it.
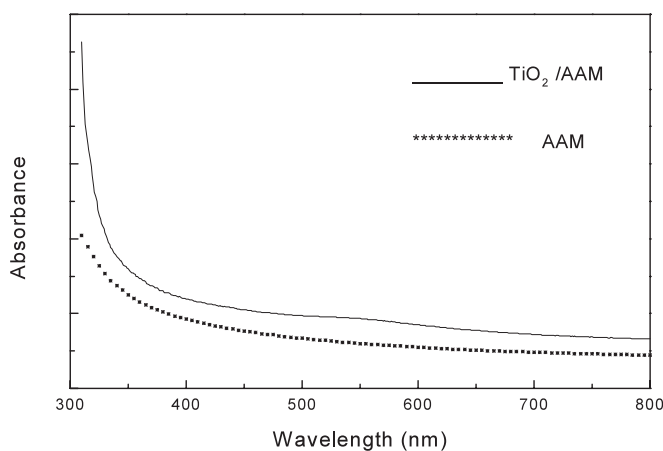
Figure 4. Optical absorption spectra of the TiO$_2$ nanowire arrays in AAM.

By using sol–gel electrophoretic deposition, TiO$_2$ nanowires can be conveniently fabricated within the nanochannels of the AAM. However, an explanation of the mechanism of nanowire growth still remains speculative. Sol–gel electrophoretic deposition is a combination of two processes: electrophoresis and deposition. A dc field causes the charged particles in a suspension to move toward, and deposit on, the oppositely charged electrode [19]. The situation becomes more complex due to the presence of the AAM. The size and surface state of the charged particles in the suspension are two important factors in determining the processing of electrophoretic deposition. In addition, the precursor concentration, the applied voltage and the pore diameter of the AAM also have an important influence on the deposition process. Determining the exact nature of the deposition process will require further detailed study.

Optical absorption spectra were obtained on a Cary-5E spectrophotometer at room temperature. Figure 4 shows the optical absorption spectra of the blank AAM and the TiO$_2$/AAM assembly system annealed at 500 °C. It can be seen that the spectrum of the
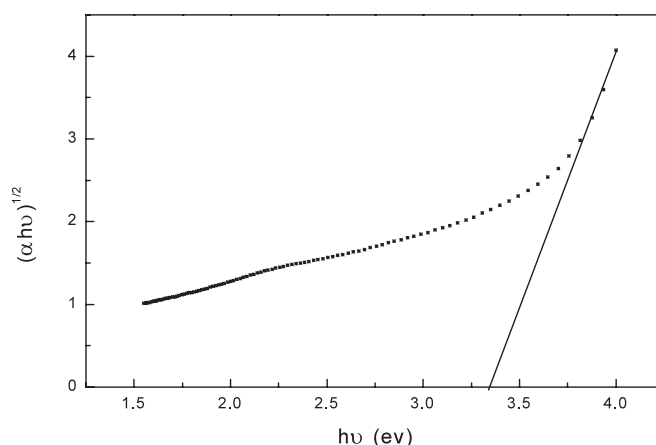
Figure 5. $(\alpha h\nu)^{1/2}$ versus $h\nu$ plot for the TiO$_2$ nanowire arrays in AAM.

annealed TiO$_2$/AAM assembly system is quite different from that of the blank AAM. It is known that the relationship between absorption coefficient α near the absorption edge and the optical bandgap E_g for indirect interband transitions obeys the following formula [20, 21]:

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g)$$

A is the parameter that depends on the interband transition probability, and $h\nu$ is the energy of incident light. Hence, the optical bandgap for the absorption edge can be obtained by extrapolating the linear portion of the plot $(\alpha h\nu)^{1/2}$ versus $h\nu$ to $\alpha = 0$. Figure 5 shows $(\alpha h\nu)^{1/2}$ versus $h\nu$ plots for the sample annealed at 500 °C. For all samples, the optical absorption in the edge region can be well fitted by the relation $(\alpha h\nu)^{1/2} \sim h\nu - E_g$, which shows that TiO$_2$ nanowires embedded in AAM have an indirect bandgap. The bandgap of TiO$_2$ nanowires in AAM is about 3.35 eV for samples annealed at 500 °C. This shows that the optical band edge of the TiO$_2$ nanowires embedded in AAM exhibits a marked blue shift with respect to that of bulk anatase TiO$_2$ (3.2 eV). There are many reports concerned with quantum size effects in low-dimensional semiconductor systems. It is well known that the semiconductor nanoparticle energy gap increases with decreasing grain size, which leads to a blue shift of the optical absorption edge and has been observed in many semiconductor nanoparticle systems [21–24]. Here the blue shift could also be attributed to the quantum size effect. In figures 4 and 5, a small absorption band is observed around 540 nm (2.3 eV), but the exact origin of this absorption is still unclear.

4. Conclusions

In summary, ordered anatase polycrystalline TiO$_2$ nanowire arrays embedded in AAM were prepared using sol–gel electrophoretic deposition. The TiO$_2$ nanowires (diameter ~50 nm) were dense, continuous and uniform throughout the entire length of the wires. A blue shift of the optical bandgap of the TiO$_2$/AAM was observed and was mainly attributed to the quantum size effect.

Acknowledgment

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