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Electrostatic capacitance of TiO_2 nanowires in a porous alumina template

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Abstract
Titanium oxide (TiO_2) nanowires were prepared for an electrolytic capacitor application by the automatic dipping technique using a porous alumina template. The automatic dipping technique allows us to exactly control the dipping rate so that we can obtain homogenous infiltration of nanowires in the porous alumina membrane, even though the solution is very acidic. From the TEM, SEM and XRD measurements, we confirmed that anatase phase TiO_2 nanowires are highly infiltrated into the porous alumina template. In addition, the electrostatic capacitance of nanowires was measured and compared with a theoretical calculation using an effective thickness (δe). We found that the effective thickness corresponds to the mean radius of nanowires and the experimental measurements were in good agreement with the calculations.

1. Introduction

During the past decades, the synthesis of nanowires with a uniform diameter and an adjustable length has received great attention due to their distinct properties and versatile applications such as interconnectors and active components in fabricating nanoscale devices [1–4]. Among various synthesis routes for monodisperse nanowires with a high aspect ratio (diameter of nanowires/their length), the nanoporous alumina template-assisted method is of great interest due to its easy and inexpensive manufacturing process. So far, the fabrication of nanowires of metals and semiconductors by electrochemical deposition has been extensively demonstrated [5–9]. Highly ordered nanowires of metal oxides such as titanium oxide, indium oxide and zinc oxide, which could usually be prepared by the sol–gel process, have been studied as luminescence sources, chemical sensors, photochemical catalysts, and so on [10–13]. However, the use of a nanoporous alumina template for the preparation of metal oxide nanowires is strictly limited since it is very easily dissolved in a strong acidic solution.

In this study, we will show the preparation of TiO_2 nanowires inside a porous alumina template by a simple dipping method in an acidic solution. In addition, we will discuss the effect of TiO_2 nanowires on electrostatic capacitance compared with a simple thin film of TiO_2.

To the best of our knowledge, there is no report on the electrostatic capacitance of metal oxide nanowires with a high dielectric constant, whereas that of bulk metal oxide has been well studied. For example, titanium oxide has a relatively high dielectric constant, showing 48 for anatase and 110 to 117 for rutile structure [14]. In addition, it was reported by Wihelmsen and Hurlen [15] that anodic oxide films formed on titanium show a dielectric constant of about 60.

2. Experiment

TiO_2 nanowires were infiltrated into commercially available porous alumina membrane (Whatmann, Anodisc 25) with a pore diameter of ca. 200 nm and the depth of 60 μm by two successive processes: dipping and drying. The solution for the preparation of TiO_2 nanowires consists of 5 wt% TiO_2

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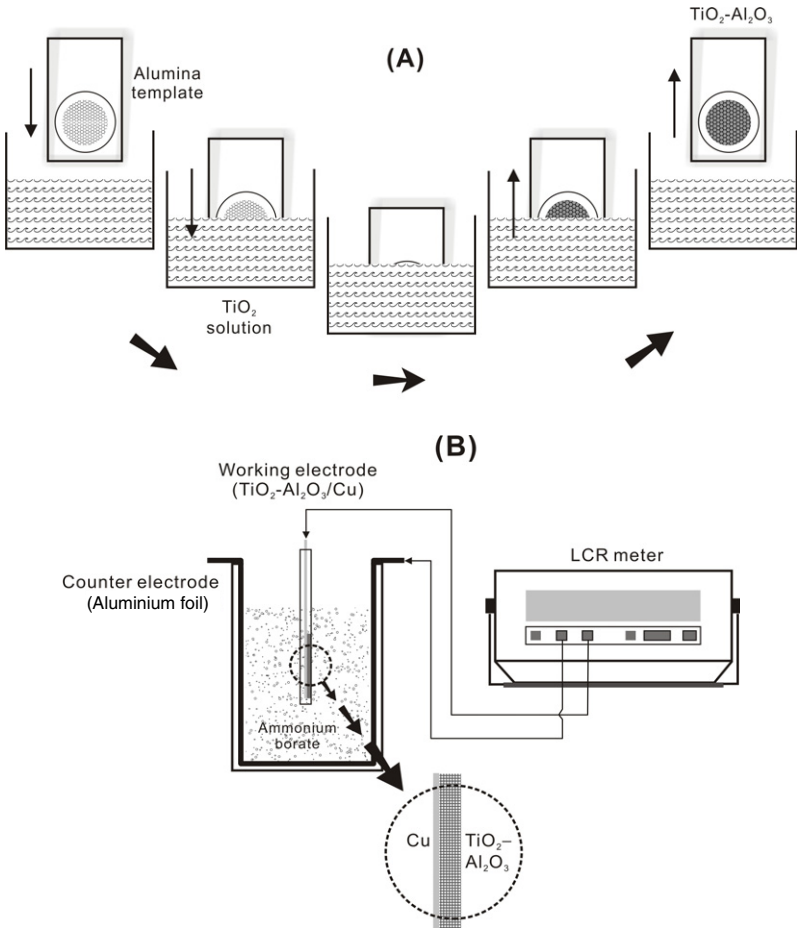

Figure 1. Schematic diagram of (A) dipping procedure and (B) electrostatic capacitance measurement using two electrodes.

nanoparticle solution made of 5% tetra ethyl orthosilicate (TEOS) binder and 35% methanol, having ca. pH 1.5 [16].

In detail, the porous alumina template was impregnated into the solution by the automatic dipping technique which allows us to exactly control the dipping rate and the time to soak the template in the solution (see figure 1(A)). Typical dipping rates were 20, 10 and 2 mm min^{-1}. Subsequently, the porous alumina template with the wet titania solution was dried at 80 °C in a vacuum oven under nitrogen atmosphere to remove the solvent and make the structure more compact. Afterwards, the porous alumina template was selectively dissolved in 0.1 M NaOH solution for 10 h in order to obtain TiO_2 nanowires.

The surface morphologies of TiO_2 nanowires were analysed by field emission scanning electron microscopy (FE-SEM, Hitachi S-4300) and transmission electron microscopy (TEM, Phillips CM200). Crystal phases were examined by x-ray diffractometry (XRD, Phillips DY616). Elemental qualitative analysis of prepared TiO_2 nanowires was carried out using energy dispersive x-ray spectroscopy (EDS) coupled with the TEM equipment. Capacitance measurements of the alumina template and TiO_2 filled alumina were performed in two electrode systems, as shown in figure 1(B). In order to measure the capacitance of the Al_2O_3 template and the TiO_2 nanowire–Al_2O_3 template structure, a Cu layer was deposited on one side of the template by a direct current (DC) sputtering technique. The counter-electrode is electrochemically etched high-purity aluminium foil and it was placed at the inner wall of the glass reactor. The electrolyte solution is 80 g l^{-1} ammonium borate and the capacitance was measured at constant frequency of 80 Hz by *LCR* meter (ANDO type AG-4303).

3. Results and discussion

3.1. Preparation of TiO_2 nanowires

In an impregnation process, the dipping rate plays a very important role in fabricating highly dense nanowires embedded in the porous alumina template. For example, if the dipping rate is too fast, the time to contact with a sol solution is too short to make nanowires when it is dried. On the other hand, the porous alumina template would be dissolved if it stayed in an acidic solution for a long time, since the porous alumina is only stable in a solution with the range of pH values between 3 and 10 (in this work, we used a solution with pH 1.5). Therefore, an optimized dipping rate (or time) is an important factor in the process.

As mentioned in the experimental section, three different dipping rates of 20, 10 and 2 mm min^{-1} were performed to obtain homogenously infiltrated TiO_2 nanowires using a porous alumina template. If the dipping rate is 20 mm min^{-1}, the template stays in the solution for only 3 s. As expected, we cannot observe any TiO_2 nanowires formed. Therefore, the

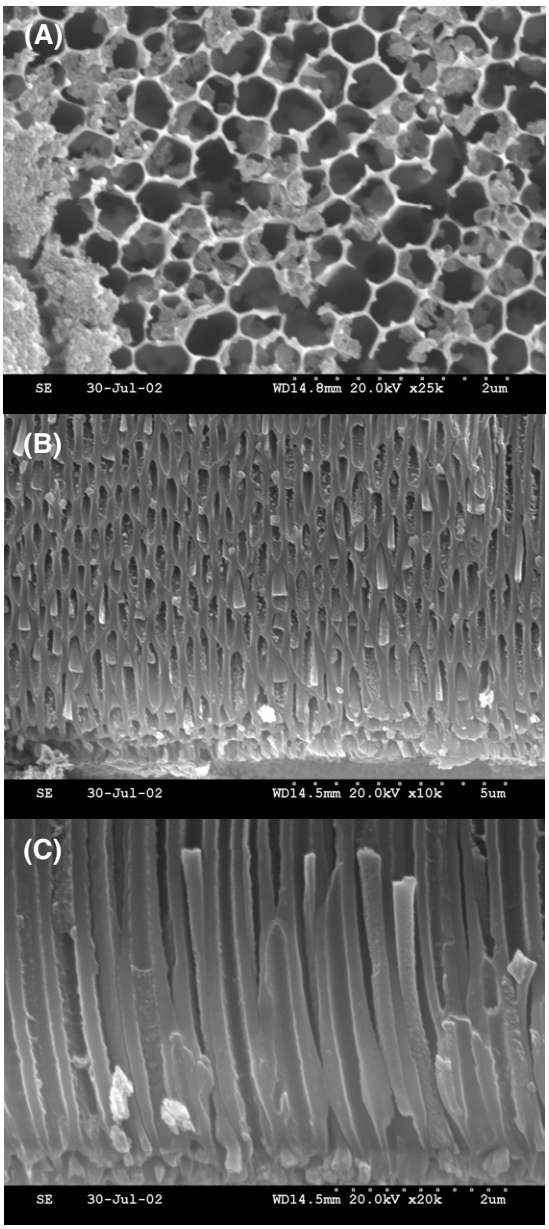

Figure 2. Morphological observations of TiO_2 nanowires in commercial alumina template (TiO_2-AAO I). Dipping rate = 10 mm min^{-1}. (A) is a top view and (B) and (C) are cross-sectional views of TiO_2.

dipping rate was reduced from 20 to 10 mm min^{-1}. Figure 2 shows morphological observations of the sample prepared at the dipping rate of 10 mm min^{-1}. In figure 2(A), TiO_2 agglomerates are observed near Al_2O_3 pores. Figure 2(B) is a cross-sectional view of the alumina template, demonstrating that TiO_2 nanowires are formed inside the alumina template. Even though not all the pores are filled with TiO_2 nanowires, we can observe nanowires with a high aspect ratio and a uniform diameter.

In order to obtain highly infiltrated nanowires, the dipping rate was further reduced from 10 to 2 mm min^{-1}. TiO_2–Al_2O_3 composite prepared at the dipping rate of 2 mm min^{-1} is shown in figure 3. Figures 3(A) and (B) clearly show TiO_2 nanowires with the mean diameter of about 200 nm. In the case of

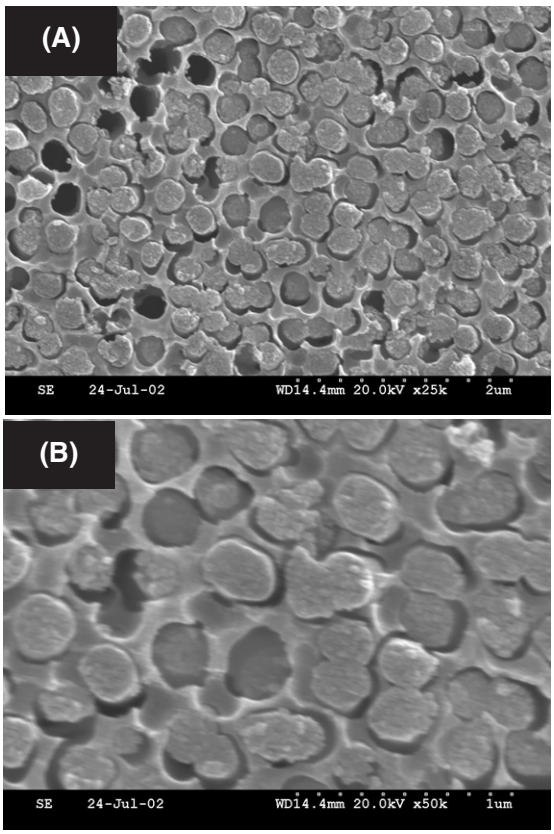

Figure 3. Top view of TiO_2 nanowires in commercial alumina template (TiO_2-AAO II). Dipping rate = 2 mm min^{-1}.

the dipping rate of 2 mm min^{-1}, homogenous infiltration is achieved in most pores since the porous alumina template is soaked in the TiO_2 solution for a longer time. However, it should be mentioned that if the alumina template is dipped in the solution for an extremely long time (for example 1 h) the porous alumina template is dissolved completely and there is no nanowire formation.

Figure 4 shows TEM image of TiO_2–Al_2O_3 structure. The bright areas indicate TiO_2 nanowires in the porous alumina template. In order to confirm the structural doubt, the EDX analysis of TiO_2 nanowires was performed. Interestingly, there are four elements (Al, Si, Ti and O) detected. We can assume that the silicon peak is originated from the silicon component in the TiO_2 solution. Al element can be explained as follows: the low solution pH (1.5) induces a partial dissolution of the porous alumina template and it makes a complex structure with the TiO_2 particles.

The crystal phase of TiO_2 nanowires was revealed as polycrystalline anatase phase by the XRD analysis (see figure 5). We found that the crystal phase is mainly determined by the annealing temperature, not depending on the dipping rate, even though the dissolution of alumina slightly increases as the dipping rate decreases.

3.2. Electrostatic capacitance

The electrolytic capacitor generally consists of foils separated by thin layers of an insulating medium. Its capacitance is

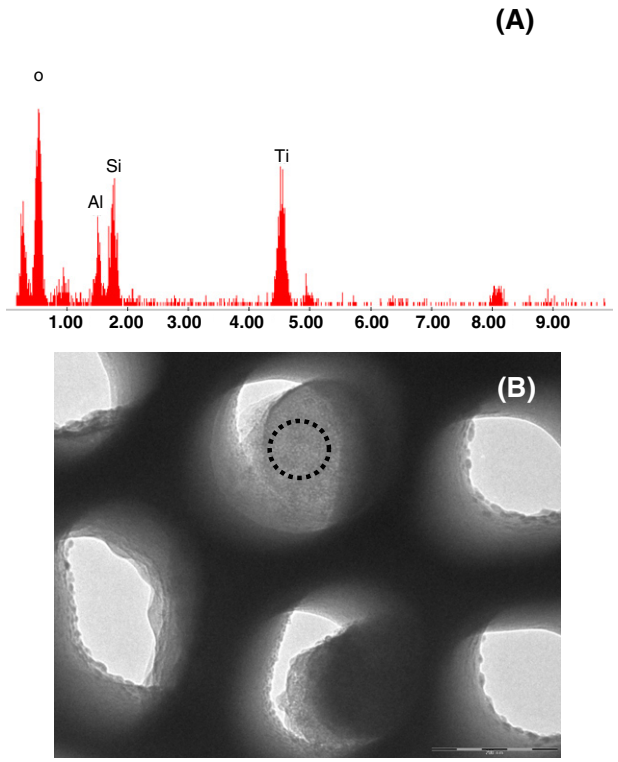

Figure 4. EDX analysis and TEM image of TiO_2 nanowires in porous alumina.
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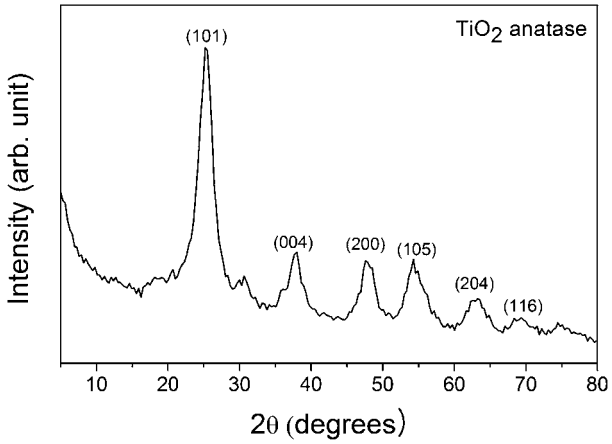

Figure 5. X-ray diffractometry (XRD) analysis of TiO_2 nanowires. It shows that the crystal phase is polycrystalline anatase structure.

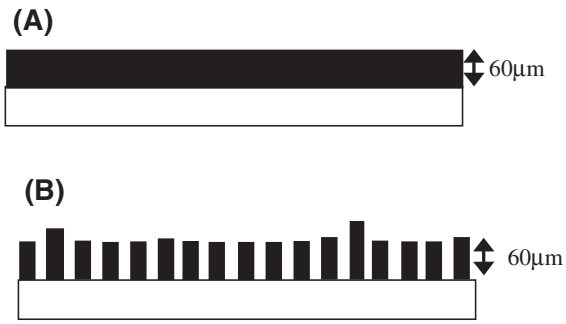

Figure 6. Schematic diagram of (a) TiO_2 thin film capacitor and (b) TiO_2 nanowire capacitor.

determined by both electrode surface area and the thickness of dielectric layer and the permittivity of dielectric material.

$$C = \varepsilon\varepsilon_0 A/\delta \tag{1}$$

where ε_0 is the vacuum permittivity, ε is the relative dielectric constant of the oxide film, A is the surface area, and δ is the film thickness.

In order to increase the electrostatic capacitance of the capacitor, it is necessary to increase the surface area (A) of the electrodes, to decrease the gap (δ) between the electrodes, or to provide an insulator with a high dielectric constant (ε) between the electrodes. In a conventional aluminium-based capacitor, the surface area could be increased by a factor of 1000 by electrochemical etching of aluminium. Aluminium is electrochemically dissolved at pitting sites of aluminium oxide film when it is exposed to aggressive anions such as Cl^-. As a result of metal dissolution, the aluminium becomes rough, with higher surface area [17–20].

In a capacitor based on nanowires with a high aspect ratio, we expect that the interface area between the electrolyte and the dielectric metal oxide ($A_{e/o}$) can be increased, whereas that between the dielectric metal oxide and the metal ($A_{o/m}$) is almost the same or less. In this study, the effect of the unbalanced surface areas on the capacitance is investigated.

Assuming that the titanium oxide is the anatase phase with the relative dielectric constant of 48 and the thickness of 60 μm as shown in figure 6(A), we can calculate that the electrolytic capacitance of the film is around 7.0×10^{-4} μF cm^{-2} from equation (1). However, the measured capacitance of the TiO_2 nanowires in the porous alumina is about 143 μF cm^{-2}, which is 3.5×10^5 times higher than the calculation based on the simple thin film. In fact, the real geometry of our sample is complicated, as shown in figure 6(B). The surface areas of $A_{e/o}$ and $A_{o/m}$ are enlarged by a factor of 174 and 0.5, respectively, compared with those in figure 6(A), if we suppose that the density of pores in the porous alumina with the pore diameter of 200 nm is 4.6×10^8 cm^{-2} [21]. Now, an effective thickness (δe) is derived for the calculation of the capacitance based on nanowires with the high aspect ratio since the films discontinue in the case of nanowires.

Equation (1) can be rationalized as

$$C/A = (\varepsilon\varepsilon_0/\delta e) \times F \tag{2}$$

where F is the surface enlargement factor, e.g., unity for figure 6(A). In addition, we assume that F is 174 in figure 6(B), since $A_{e/o} \gg A_{o/m}$.

Equation (2) would be described as

$$\delta e \text{ (cm)} = (\varepsilon\varepsilon_0 \times F)/C_A \tag{3}$$

where C_A ($=C/A$) is the capacitance per unit area (cm^2).

The C_A of TiO_2 nanowires can be roughly estimated as around 93 μF cm^{-2}, that is the deduction of 50 μF cm^{-2} (porous alumina template with the Cu electrode only, measured

value) from 143 μF cm^{-2} (TiO_2 nanowires/porous alumina composite with the Cu electrode, measured value).

From equation (3), δe of the nanowire capacitor is about 90 nm, which corresponds to the mean radius of nanowires ($r \approx 100$ nm). Since the core of the nanowires is the farthest away from the electrolyte, it is reasonable to assume that the radius of the nanowires is the effective thickness, δe, for the calculation of capacitance based on nanowires. We believe that the small difference between the calculated δe and the actual radius r is due to the facts that the nanowires are not a perfectly circular shape and that there is a deviation of the density of nanowires. Even though a carefully theoretical study is needed to deeply understand the capacitance of nanowires, we believe that this study shows the basis for the development of a nanowire capacitor.

4. Conclusion

In summary, highly ordered TiO_2 nanowires were infiltrated into a porous alumina template by a simple dipping technique. Since the solution was very acidic, the dipping rate was the critical factor to obtain the homogenous infiltration of TiO_2 nanowires. We found that the optimized dipping rate is 2 mm min^{-1} and the prepared TiO_2 nanowires are polycrystalline anatase phase, which is determined not by the dipping rate but by the annealing process. The electrostatic capacitance of the nanowires was measured and compared with a theoretical calculation. Considering the effective thickness (δe) of nanowire structured TiO_2, the capacitance calculation of TiO_2 nanowires supported experimental measurement. We expect that this paper will be a reference for the development of nano-scale dielectric capacitance systems.

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