Facile Route to Laterally Graded Nanotemplate

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Preparation of graded materials displaying gradients of desired properties is one of the important issues and less-developed areas in materials chemistry. For the first time we demonstrate facile control of porosity and length in the pores of AAO template in lateral directions by controlled dipping method. To demonstrate the versatility of the proposed method, laterally graded silica nanotubes are also prepared by using the laterally graded AAO templates. The method demonstrated here will open numerous possibilities for obtaining a variety of graded materials with lateral gradients of catalytic, electrochemical, mechanical and optical properties on the nanoscale.

Key Words: Anodic aluminum oxide, Graded nanotemplate, Silica nanotubes

Introduction

Graded materials are a class of relatively novel and promising materials that have emerged from the need to optimize material properties.[1-3] In a homogeneous material, the properties are constant, whereas the properties of a graded material vary continuously with the depth beneath a free surface or in a direction lateral to the surface. Graded materials offer the advantage of advanced functional materials with specific properties, such as porosity,[4] reactivity,[5] composition,[6] and roughness.[7]

Template-based synthesis is a well-known method for producing desired nanostructures in precise and reproducible manners. Anodic aluminum oxide (AAO) is widely used as a host or template in the preparation of nanotubes,[8] nanowires,[9] and nanodots[10] comprising oxides, metals, semiconductors and carbons. Nanostructures based on the AAO template entail a highly-ordered array in high density. Although lateral control of the electrodeposition of a metal into the pores of an AAO template by applying a potential gradient to the Au electrode deposited on one side of the AAO membrane has been reported,[11] to our knowledge lateral control of the template itself has so far not been demonstrated.

This work demonstrated facile control of the porosity and the length of the pores in an AAO template in lateral directions. To demonstrate the versatility of the proposed method, laterally graded silica nanotubes (SNTs), which have been considered as important material for biomedical applications[12,13] were also prepared by using the laterally graded AAO templates.

Experimental Section

The general procedure used to fabricate laterally graded templates is shown in Figure 1. The fabrication of laterally graded templates was realized by controlled dipping of the AAO template during the anodizing or pore-widening process. The process is based on a two-step anodization method.[14] Briefly, an Al sheet of high purity (99.999%) was first anodized at 40 V in a 0.3 M oxalic acid solution at 15 °C for 12 hrs. After chemically etching the AAO film, a length-graded AAO was then obtained by slowly dipping the sample under the same conditions used in the first anodization process (Figure 1a). The dipping rate and time were 5.6 μm/s and 30 min, respectively. For the fabrication of porosity-graded templates, the entire surface of a sample was anodized for 20 min under the same conditions used in the first anodization. Then, the sample was dipped into a 0.5 wt% phosphoric acid solution at 30 °C at the rate of 4.8 μm/s for 35 min. The sample was then withdrawn immediately and washed thoroughly in deionized water. Dipping rates of samples for the fabrication of both length- graded and porosity-graded AAO were controlled by means of a home-made dip coater, driven by a step motor (Southern Palace Trading, 4S56Q-02542SG180).

Before the synthesis of SNTs, the pores of a length-graded template were enlarged by immersing the template in 5 wt% phosphoric acid solution for 35 min, because the original pore diameter was too small to synthesize SNTs. SNTs were synthesized within the pores of a laterally graded AAO by the

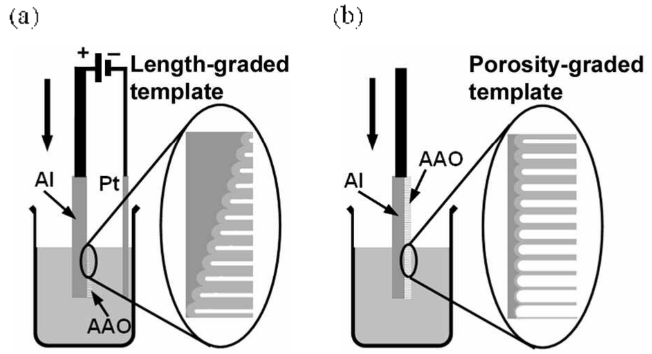

Figure 1. Fabrication schemes for laterally graded AAO templates. After chemically etching the first anodized AAO film, a length-graded AAO (a) was then obtained by slowly dipping the sample under the same conditions used in the first anodization process The dipping rate and time were 5.6 μm/sand 30 min, respectively. For the fabrication of porosity-graded templates (b), the two-step anodized sample was dipped into a pore widening solution at the rate of 4.8 μm/s for 35 min.

sol-gel method. First, the AAO template was immersed in a silicon chloride solution for 2 min. Subsequently, the sample was quickly washed several times with hexane and soaked in fresh hexane for 5 min to eliminate any unabsorbed silicon chloride. Then, the AAO was immersed in a 1:1 volume mixture of methanol and hexane, after which it was placed in ethanol for 5 min and dried in an argon flow for 30 min. After the drying process, the sample was soaked in deionized water for 5 min and washed with methanol. Finally the template was dried again under argon. This entire process was performed twice. To peel off the embedded SNTs within the pores, torrseal epoxy (Varian) was used as a support material. First, the torrseal epoxy was coated on the surface of the AAO. Then the AAO containing the SNTs was separated from the Al sheet in a saturated mercury chloride solution. After that, the AAO was etched in a 5 wt% phosphoric acid solution at 30 °C for 90 min. To obtain cross-sectional images of the sample, the torrseal epoxy was cut parallel to the dipping direction. The morphologies of the laterally graded nanotemplate and SNTs were observed by field emission scanning electron microscope (FESEM, Hitachi S-4300).

Results and Discussion

Figure 2a shows a photo of a sample. For cross-section observation, the sample was deliberately bent into a V-shape.

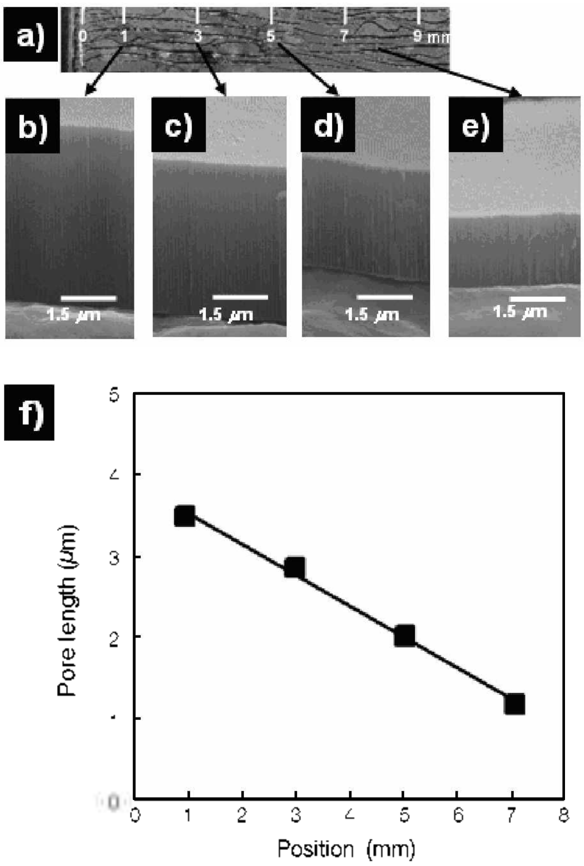

Figure 2. (a) Photo showing the entire surface of a length-graded template. (b-d) FESEM images of cross-sections of the length-graded template taken from the regions indicated by the arrows. (f) plot of position versus pore length in the length-graded template.

resulting in line cracks in the AAO template. Figures 2b-e are the field emission scanning electron microscope images of a length-graded AAO template. The SEM images were taken in different regions from the initial dipping lines along the dipping direction. The pore depths at each position varied gradually from 1.2 to 3.4 μm, as shown in Figure 2f.

Porosity gradients were obtained in an AAO template by the controlled dipping of a preformed AAO template in the pore-widening solution. Before the dipping process, the initial average diameter and length of the pores in the AAO template were 23 nm and 0.9 μm, respectively. Figure 3 shows a porosity-graded AAO template. The images were taken in different regions of the AAO template along the dipping direction, at the distances of 0, 5, 7 and 9 mm from the initial dipping line. The average pore diameter varied gradually from 69.6 nm in the initial dipping region to 32.5 nm at a distance of 9 mm (Figure 3e). In terms of porosity and surface area, it is

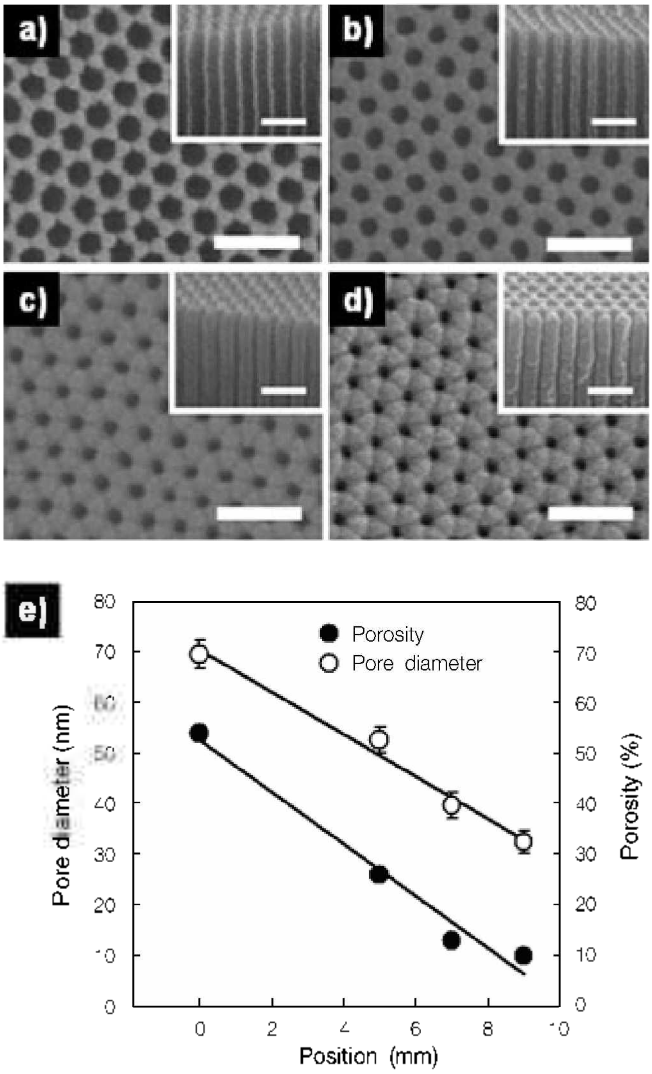

Figure 3. FESEM images of a porosity-graded AAO template, taken from (a) 0 mm, (b) 5 mm, (c) 7 mm, and (d) 9 mm away from the initial dipping line. Insets are the cross-sectional views of the corresponding images. All the scale bars are 250 nm. (e) plot of position versus porosity and pore diameter in the porosity-graded template.

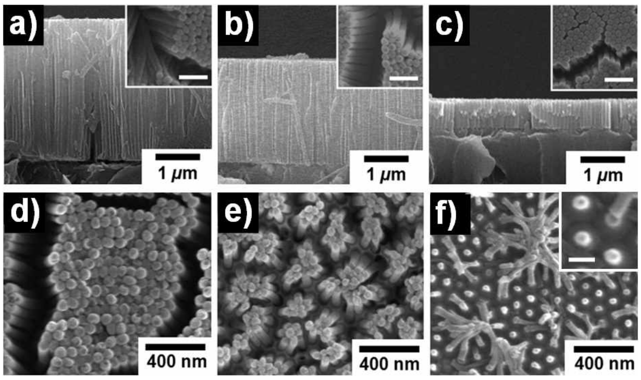

Figure 4. FESEM images in the top row ((a), (b), and (c)) show the as prepared SNTs. These images were taken at different regions of the length-graded AAO template. The white scale bars in the insets of (a), (b), and (c) are 400 nm. The bottom row ((d), (e), and (f)) represents the synthesized SNTs based on the porosity-graded AAO template. The inset in (f) shows a magnified image of the broken SNTs. It clearly shows the tubular structure of SNTs. The scale bar corresponds to 100 nm.

possible to estimate he degree of gradation by simple geometric considerations. If we assume a nearly ideal hexagonal-packing of the pores and a cylindrical pore shape in the AAO template, we can estimate the porosity and surface area to vary from 10 to 54 % and from 0.2 to 0.4 μm^2/pore in the lateral direction of the AAO template, respectively.

To demonstrate the versatility of the proposed method, laterally graded (*i.e.*, length and diameter gradation) SNTs were synthesized within the pores of these laterally-graded AAOs by the sol-gel method.[15] Torrseal epoxy was applied to the upper surface of the template after synthesizing the graded SNTs in the AAO template. After curing, the entire assembly was immersed in a saturated mercury chloride solution to remove the Al sheet. Subsequently, the AAO film was etched in the phosphoric acid. This yielded the desired SNTs arrays on the torrseal epoxy. Figure 4 shows FESEM images of the SNTs grown in the graded template. Figures 4a-c and Figures 4d-f represent FESEM images taken in different regions of the length-graded and diameter-graded SNTs, respectively. As shown in Figures 4a-c, three areas (at distances of 1, 4, and 9 mm from the initial dipping line in the length-graded template) have SNTs with different lengths of 3.3, 2.6, and 0.7 μm, respectively. The FESEM images also confirm the almost perfect filling of the pores in the AAO template by SNTs. Because the dimension of the SNTs is fully dependent on the length-graded template, the measured average lengths of the SNTs in different regions are in good agreement with the plot of the position versus the thickness of the AAO template at each position.

As shown in Figures 4d-f, SNTs with different average diameters were successfully synthesized by using a porosity-graded AAO template. The analyses of three different regions (at distances of 1, 4, and 7 mm from the initial dipping line in the porosity-graded template) showed length-graded SNTs with average diameters of 68.4, 55.5, and 37.1 nm, respectively. As expected, these values are almost the same as the average pore diameters of the porosity-graded AAO template at each position. From Figures 4d-f, it is clear that the exposed SNTs aggregated into bundles after the AAO template was etched. Interestingly, when the SNTs had an average diameter of less than 40 nm (Figure 4f), they had a tendency to be broken. It was also observed that all of the SNTs with an average diameter of less than 30 nm were broken, resulting in the very short SNT arrays on the surface of the torrseal.

The process presented here offers an effective and facile route to the formation of laterally graded templates. While graded AAO templates were prepared in terms of porosity- and length-graded pores, it is expected that other materials such as porous Si[16] and porous metal oxides on various valve metals (Ti,[17] Hf,[18] Zr,[19] Ta,[20] Nb,[21] and W[22]), which are formed by the anodization method, could be directly applied in the proposed strategy for the formation of laterally graded materials. Although we showed the laterally graded SNTs, it should also be noted that a variety of other elements and compounds could be fabricated into the graded AAO template by using electrochemical deposition, chemical vapor deposition, sol-gel method, *etc.*, resulting in laterally graded nanotubes, nanowires, and nanodots. Moreover, such nanostructures could provide highly-ordered arrays in high density without an expensive lithographic technique.

Conclusion

In conclusion, we demonstrate facile control of porosity and length in the pores of AAO template in lateral directions by controlled dipping method. To demonstrate the versatility of the proposed method, laterally graded silica nanotubes are also prepared by using the laterally graded AAO templates. The method demonstrated here will open the way for numerous possibilities for obtaining a variety of graded materials with lateral gradients of catalytic, electrochemical, mechanical and optical properties on the nano scale. Such laterally graded materials could offer interesting properties, and the experimental measurements of properties are currently underway.

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