Efficient Preparation Process for TiO₂ Through-Hole Membranes with Ordered Hole Arrangements

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Ordered TiO₂ through-hole membranes were obtained effectively by the repeated use of a Ti substrate with ordered concaves. A combined process involving the formation of two-layer structures with different solubilities through an intermediate heat-treatment, and selective dissolution of the bottom part of the oxide allows the repeated use of the Ti substrate with an ordered array of concaves, which act as initiation sites for hole development during the subsequent anodization. For the repeated use of the Ti substrate with ordered concaves, the oxide layer must be removed selectively without the dissolution of the Ti substrate. A mixed solution of HF and CrO₃ was found to be effective for selective dissolution. Ordered TiO₂ through-hole membranes obtained by this process can be used in various applications requiring an ordered hole arrangement.

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Anodic porous TiO₂, which is formed by the anodization of Ti in an electrolyte containing fluoride ions, has attracted considerable interest because of its applicability to various functional devices, such as photocatalysts, solar cells, and photonic crystals.^{1–6} One important feature of anodic porous TiO₂ is its structural controllability based on the anodization conditions.^{1,7} The hole period and hole size are dependent on the applied voltage, while the hole depth is determined by the anodization period. Another important advantage of anodic porous TiO₂ is its capability of forming self-ordered structures. Under appropriate anodizing conditions, a self-ordered hole arrangement can be obtained in this material.^{1,8} When anodic porous TiO₂ is applied to specific fields, the formation of a through-hole membrane is required.^{9–12} For example, a TiO₂ through-hole membrane can be applied for flow-through-type photocatalysis because it allows the flow of liquids. Until now, several processes have been reported for the preparation of through-hole membranes of TiO₂. Basically, a TiO₂ through-hole membrane can be formed by dissolving or detaching a Ti substrate, then removing the removal of the bottom part of the oxide using an etchant after anodization.^{13,14}

To facilitate the formation of the TiO₂ through-hole membranes, the adoption of two-layer structures, in which the bottom layer has higher solubility of the etchant than the upper layer, has been investigated. The formation of two-layer structures has been carried out through a two-step anodization composed of a first anodization at a high anodizing voltage and a subsequent anodization at a reduced voltage.^{15–18} The bottom layer formed at the reduced voltage has a porous structure with a reduced hole interval, and as a result has higher solubility of the etchant. Two-layer structures with a readily soluble bottom layer can also be formed through a two-step anodization with an intermediate heat-treatment.⁹ The heat-treatment after the first anodization reduces the solubility of the first anodized layer owing to crystallization and allows the selective dissolution of the second anodized bottom layer. However, in the previously reported process, the effective preparation of a TiO₂ through-hole membrane having an ordered hole arrangement has not been considered. For the preparation of a TiO₂ through-hole membrane having an ordered hole arrangement, a two-step anodization process is effective.^{19,20} In this process, after a first anodization to form a self-ordered structure, the TiO₂ is selectively removed. This process generates an ordered array of concaves, corresponding to the ordered hole arrangement of the first oxide layer. A second anodization generates an ordered hole arrangement from the surface because the concaves act as initiation sites for

hole development during the initial stage of the second anodization. To obtain an ordered TiO₂ through-hole membrane effectively, this process must be carried out repeatedly.

In the present report, we describe a new process for the efficient preparation of TiO₂ through-hole membranes with an ordered hole arrangement by the repeated use of a Ti substrate with ordered concaves. In this process, two-layer structures with different solubilities through an intermediate heat-treatment, and selective dissolution of the bottom part of the oxide allows the repeated use of the Ti substrate with an ordered array of concaves along with the formation of through-hole membranes. For the repeated use of the Ti substrate with ordered concaves, the oxide layer must be removed selectively without the dissolution of the Ti substrate. Through an investigation of the most appropriate etchant, a mixed solution of HF and CrO₃ was found to be effective for selective dissolution of the oxide. This is the first report on the repeated preparation of a TiO₂ through-hole membrane with an ordered hole arrangement from a single Ti substrate. TiO₂ through-hole membranes prepared by this process are expected to be applied to various application fields that require highly ordered through-hole architectures.

Experimental

Figure 1 shows a schematic drawing of the preparation process for ordered TiO₂ through-hole membranes. A Ti sheet (99.5% purity) was chemically polished using a commercially available polishing agent (TVP-08, Ryoko Chemical Co., Ltd.) at 50°C for 30 s. In generally, the dissolution of a fluoride-rich layer at the hexagonal cell boundaries of anodic porous TiO₂ during the anodization is affected by the water concentration of an electrolyte.²¹ To obtain a hole array structure rather than a tube array structure, an electrolyte with no added water was used for the anodization. Before the main anodization, 0.38 wt% NH₄F ethylene glycol solution used as an electrolyte for main anodization was aged by pre-anodization of blank Ti substrate under a constant voltage of 60 V at 20°C for 15 h. This aging step was important for the preparation of ordered anodic porous TiO₂. The anodization of Ti was performed in the aged electrolyte at 20°C under a constant voltage of 80 V for 1 h. The oxide layer formed by the first anodization was removed mechanically using adhesive tape to obtain a Ti sheet with an ordered concave array on its surface. The pretreated Ti sheet was anodized under the same conditions as the first anodization for 10 min. After the anodization, the sample was heat-treated at 350°C for 1 h to reduce the solubility and crystallinity of TiO₂. For the preparation of two-layered porous TiO₂ with different solubilities, the sample was anodized again under the same conditions for 10 min. Ordered TiO₂

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Figure 1. Schematic drawing of the fabrication process for ordered TiO_2 through-hole membranes.

through-hole membranes were prepared by selective dissolution of the lower part of the two-layered porous TiO_2 using a mixed solution of 0.07 M HF and 0.17 M CrO_3 at 20°C for 2 h. The residual Ti sheet was used repeatedly for the preparation of ordered TiO_2 through-hole membranes. The obtained samples were characterized using scanning electron microscopy (SEM; JSM-6700F, JEOL) and X-ray diffraction (XRD; SmartLab, Rigaku).

Results and Discussion

Figure 2 shows surface SEM images of the anodic porous TiO_2 with (a) ordered and (b) disordered hole arrangements. The ordered

Figure 2. SEM images of anodic porous TiO_2 with (a) ordered and (b) disordered hole arrangements. The ordered anodic porous alumina was prepared by a two-step anodization process. The disordered anodic porous TiO_2 was prepared by the anodization of flat Ti substrate under the same anodizing conditions.

porous TiO_2 was prepared by the two-step anodization method reported previously.^{19,20} In this process, the oxide layer formed by the initial anodization was removed to obtain the Ti substrate with an ordered concave array on its surface. Subsequent anodization under the same conditions as the initial anodization generated an ordered array of holes because each concave acts as an initiation site for hole development during the second anodization. In the SEM image shown in Fig. 2a, an ordered array of uniform-size holes can be observed. The hole period of the sample shown in Fig. 2a is 150 nm. In contrast, as shown in Fig. 2b, a disordered hole array was formed at the surface of the sample formed by anodization of the untextured Ti substrate. Although the mechanism is not clear at the present stage, the ordered anodic porous TiO_2 could not be obtained by anodization of a Ti substrate using a fresh electrolyte without ageing treatment.

Figure 3 shows the XRD patterns of anodic porous TiO_2 before and after heat-treatment at 100, 200, 350, and 400°C for 1 h. From Fig. 3, it can be confirmed that the as-anodized sample was amorphous, as well as the samples heat-treated at 100 and 200°C . However, for the samples heat-treated at 350 and 400°C for 1 h, diffraction peaks corresponding to anatase can be clearly observed.

To investigate the relationship between the solubility of the oxide layer and the heat-treatment temperature, anodic porous TiO_2 heat-treated at different temperatures was etched in 0.07 M HF and

Figure 3. XRD patterns of anodic porous TiO_2 (a) before and after heat-treatment at (b) 100, (c) 200, (d) 350, and (e) 400°C .

Figure 4. (a) Surface SEM images of anodic porous TiO₂ before and after etching using a mixed solution of HF and CrO₃. (b) Relationship between hole size and etching time.

0.17 M CrO₃. Figure 4a shows surface SEM images of anodic porous TiO₂ before and after etching for 20 and 30 min. From Fig. 4a, it can be observed that the solubility of the oxide layer decreased with increasing the heat-treatment temperature. The as-anodized sample was almost completely dissolved after 30 min of etching. However, the porous structure of the sample heat-treated at 350°C was maintained even after etching for 30 min. Figure 4b shows the relationship between the hole size and etching time for different heat-treatment temperatures. From this graph, the hole size in TiO₂ increased with increasing etching time, except for the sample heat-treated at 400°C. In this case, the hole size hardly changed during the etching treatment. Figure 4b reveals that the solubility of TiO₂ decreased with increasing heat-treatment temperature.

For the preparation of two-layered porous TiO₂ with different solubilities, the heat-treated samples were anodized under the same conditions for 10 min. After the anodization, the formation of two-layered structures was confirmed, except for the sample heat-treated at 400°C. Although the reason for this is not yet clear, we believe that the formation of a porous oxide layer under the present anodizing conditions cannot proceed because of the low solubility of the bottom part of the porous TiO₂ heat-treated at 400°C. Figure 5 shows a cross-sectional SEM image of two-layered porous TiO₂ after anodization.

Figure 5. Cross-sectional SEM image of two-layered porous TiO₂ formed by combination of anodization and heat-treatment.

The formation of a porous layer underneath the porous TiO₂ heat-treated at 350°C by the subsequent anodization can be observed. There was no difference in the anodizing behavior between the first and second anodization. The average current density of a Ti substrate during both anodizations was 25 mA/cm².

Figure 6 shows an SEM image of an ordered TiO₂ through-hole membrane obtained by selective etching of the lower layer of porous TiO₂. For this sample, the upper porous layer was heat-treated at 350°C for 1 h. From the top and back surface images respectively shown in Figs. 6a and 6b, it can be observed that the uniform-size through-holes were arranged hexagonally over the sample. The period and diameter of the holes were 150 and 90 nm, respectively. The thickness of the obtained membrane was 13 μm, as shown in Fig. 6c. This value is in good agreement with the thickness of the upper layer of the two-layered porous TiO₂. This result means that the through-hole membranes were detached from the Ti substrate by selective dissolution of the lower layer of the two-layered structure. From the SEM observations, a difference in film thickness of anodic porous TiO₂ shown in Figs. 5 and 6 was observed. This is because there was an error of film thickness between samples obtained by the present anodizing conditions. For the preparation of through-hole membranes, the heat-treatment temperature of the upper oxide layer is important. In the case of a heat-treatment temperature lower than 300°C, it was difficult to obtain a through-hole membrane because the upper oxide layer was also dissolved after removing the lower layer by etching.

For the repeated preparation of ordered through-hole membranes, it is necessary to maintain the concave array on the surface of the residual Ti substrate after etching. Figure 7 shows surface SEM images of the residual Ti substrate after etching treatment using (a) 0.07 M HF and (b) a mixed solution of 0.07 M HF and 0.17 M CrO₃. In both cases, through-hole membranes were obtained by selective etching of the lower TiO₂ layer. However, there was a significant difference in the surface structure of the residual Ti. The surface of the residual Ti was dissolved and roughened after etching in HF solution, as shown in Fig. 7a. However, in the case of etching in the mixed solution of HF and CrO₃, an ordered concave array was observed on the surface of the residual Ti. This is because a passivation thin film was formed immediately on the surface of Ti by Cr⁶⁺ after the Ti surface was exposed during the etching treatment.

Figure 8 shows a surface SEM image of a TiO₂ through-hole membrane obtained by two repetitions of this process. Etching treatment using a mixed solution of HF and CrO₃ did not affect the subsequent anodization even though the thin Cr₂O₃ passivating layer was created on the surface of Ti substrate. From the SEM image, it was confirmed that the ordered hole arrangement was maintained even after repetitions of this process. This means that the present process allows the

Figure 6. SEM images of ordered TiO_2 through-hole membrane; (a) top surface, (b) back surface, and (c) cross-sectional views.

repeated preparation of an ordered TiO_2 through-hole membrane from a single Ti substrate. In the present study, samples were heat-treated for 1 h. However, the heat-treatment time may be shortened because the solubility of TiO_2 can decrease even by a short-time heat-treatment. The processing time for the preparation of ordered TiO_2 through-hole membranes can be saved by optimizing heat-treatment conditions.

The hole period of the anodic porous TiO_2 can be controlled by adjusting the anodizing voltage. Figure 9 shows SEM images of ordered TiO_2 through-hole membranes with hole periods of 100, 130, and 150 nm. For these samples, the anodization of Ti was carried out under constant voltages of 40, 60, and 80 V, respectively. In each sample, the anodizations for the first and second membranes were performed under same constant voltage. Figure 9 reveals that ordered TiO_2 through-hole membranes with various hole periods can be obtained by the present process. In all cases, the ordered hole arrangement was maintained even after two repetitions of this process. As a result, ordered TiO_2 through-hole membranes with controlled hole periods can be repeatedly obtained from a single Ti substrate by

Figure 7. Surface SEM images of residual Ti substrates after etching in (a) HF and (b) mixture of HF and CrO_3 .

the present process. These obtained through-hole membranes can be applied to various functional devices.

Conclusions

Ordered TiO_2 through-hole membranes were repeatedly obtained from a single Ti substrate. For the preparation of the TiO_2 through-hole membranes, a two-layer structure with different solubilities was formed. The selective dissolution of the lower part of the two-layered porous TiO_2 was carried out using a mixed solution of HF and CrO_3 . Ordered TiO_2 through-hole membranes were repeatedly obtained from a single Ti substrate because the ordered concave array on the surface of Ti was maintained even after etching treatment. The hole period of these ordered through-hole membranes could be controlled by adjusting the anodizing voltage. The present process provides a high-throughput preparation method for ordered TiO_2 through-hole membranes with controlled hole periods. These membranes can be used in various applications requiring an ordered hole arrangement.

Figure 8. Surface SEM image of ordered TiO_2 through-hole membrane obtained by two repetitions of this process.

Figure 9. SEM images of ordered TiO_2 through-hole membranes with 100, 130, and 150 nm hole periods obtained by one iteration and two repetitions of the process. The anodization of these samples was performed at 40, 60, and 80 V, respectively.

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