Efficient Preparation Process for TiO$_2$ Through-Hole Membranes with Ordered Hole Arrangements

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Ordered TiO$_2$ 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. To obtain an ordered TiO$_2$ 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 TiO$_2$ 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 CrO$_3$ was found to be effective for selective dissolution of the oxide. This is the first report on the repeated preparation of a TiO$_2$ through-hole membrane with an ordered hole arrangement from a single Ti substrate. TiO$_2$ 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 TiO$_2$ 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 TiO$_2$ during the anodization is affected by the water concentration of an electrolyte. 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% NH$_4$F 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 anodic porous TiO$_2$. 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 precoated 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 TiO$_2$. For the preparation of two-layered porous TiO$_2$ with different solubilities, the sample was anodized again under the same conditions for 10 min. Ordered TiO$_2$
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 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
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.

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 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 4](https://example.com/f4.png)

**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.
Figure 6. SEM images of ordered TiO\textsubscript{2} through-hole membrane; (a) top surface, (b) back surface, and (c) cross-sectional views.

Figure 7. Surface SEM images of residual Ti substrates after etching in (a) HF and (b) mixture of HF and CrO\textsubscript{3}.

The hole period of the anodic porous TiO\textsubscript{2} can be controlled by adjusting the anodizing voltage. Figure 9 shows SEM images of ordered TiO\textsubscript{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\textsubscript{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\textsubscript{2} through-hole membranes with controlled hole periods can be repeatedly obtained from a single Ti substrate by repeated preparation of an ordered TiO\textsubscript{2} though-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\textsubscript{2} can decrease even by a short-time heat-treatment. The processing time for the preparation of ordered TiO\textsubscript{2} through-hole membranes can be saved by optimizing heat-treatment conditions.

The hole period of anodic porous TiO\textsubscript{2} can be controlled by adjusting the anodizing voltage. Figure 9 reveals that ordered TiO\textsubscript{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\textsubscript{2} through-hole membranes with controlled hole periods can be repeatedly obtained from a single Ti substrate by the present process. These obtained through-hole membranes can be applied to various functional devices.

Conclusions

Ordered TiO\textsubscript{2} through-hole membranes were repeatedly obtained from a single Ti substrate. For the preparation of the TiO\textsubscript{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\textsubscript{2} was carried out using a mixed solution of HF and CrO\textsubscript{3}. Ordered TiO\textsubscript{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\textsubscript{2} through-hole membranes with controlled hole periods. These membranes can be used in various applications requiring an ordered hole arrangement.
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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