

## Synthesis of Novel Structured TiO<sub>2</sub> with Mesopores by Anodic Oxidation

Atsushi Nakahira,<sup>\*,†</sup> Koichi Konishi,<sup>‡</sup> Koji Yokota,<sup>‡</sup> Takashi Kubo,<sup>†</sup> Yukichi Sasaki,<sup>§</sup> and Yuichiro Ikuhara<sup>⊥</sup>

<sup>†</sup>Osaka Prefecture University, 1-1 Gakuencho, Sakai, Japan 599-8531, <sup>‡</sup>Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto, Japan 606-8585, <sup>§</sup>JFCC, Mutsumo, Atsuta, Nagoya, Japan 456-8587, and <sup>⊥</sup>The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan 113-8654

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In this study, a simple anodic oxidation process resulted in the successful synthesis of novel N-ion-doped TiO<sub>2</sub> with one-dimensionally aligned and large-sized mesopores. TiO<sub>2</sub> obtained by this anodic oxidation process possessed the high values of specific surface area and a large amount of one-dimensional mesopores with 30–50 nm diameter. Furthermore, X-ray photoelectron spectroscopy and UV–vis results suggested the possibility that these TiO<sub>2</sub> products were composed of a N-ion-doped powder. Thus, novel structured TiO<sub>2</sub> with large-sized mesopores was simply synthesized by an anodic oxidation of Ti metal in a nitric acid solution. These uniquely nanostructured mesoporous TiO<sub>2</sub> products will expand possibilities for applying mesoporous TiO<sub>2</sub> in new fields.

### 1. Introduction

TiO<sub>2</sub> is one of the useful materials for a photocatalyst. Also, mesoporous TiO<sub>2</sub> is greatly expected to be applicable as a photocatalyst and solar cell.<sup>1,2</sup> These mesoporous TiO<sub>2</sub> compounds have been attractive for improving their photocatalytic properties because the successful syntheses of mesoporous silica of a few nanometers in diameter, such as Mobil's Composition of Matter (MCM, which was reported by Mobil in 1992<sup>3</sup>) and the folded sheets mechanism (FSM, which was reported by Inagaki et al.<sup>5</sup>), were reported.<sup>3–12</sup> However, there are no reports on the synthesis of mesoporous materials with large diameters of some tens of nanometers. Additionally, a lot of effort is paid to studies about ion doping and implantation into TiO<sub>2</sub> for improving the

photoactivities of TiO<sub>2</sub>.<sup>13–16</sup> Since Asahi et al. reported that N-ion-doped TiO<sub>2</sub> prepared by sputtering and post-heat-treatment methods had high photocatalytic properties under visible light,<sup>15</sup> a lot of studies about ion doping into TiO<sub>2</sub> for improving the properties of TiO<sub>2</sub> have been carried out by many researchers.<sup>13–18</sup> Furthermore, these mesoporous TiO<sub>2</sub> compounds doped with N ions will expand the possibilities for applying mesoporous TiO<sub>2</sub> in new fields.

Here, the synthesis of large-sized mesoporous TiO<sub>2</sub> compounds doped with N ions was attempted by a simple process, i.e., anodic oxidation. Anodic oxidation processes are well-known as an old technique for modifying the surface of Al and Ti metals. Although this anodic oxidation of Ti is a simple and useful technique that can synthesize TiO<sub>2</sub> for the significantly short treatment time, at the same time doping anions into TiO<sub>2</sub> can be achieved using this anodic oxidation process.<sup>19–23</sup>

\*To whom correspondence should be addressed. E-mail: nakahira@mtr.osakafu-u.ac.jp.

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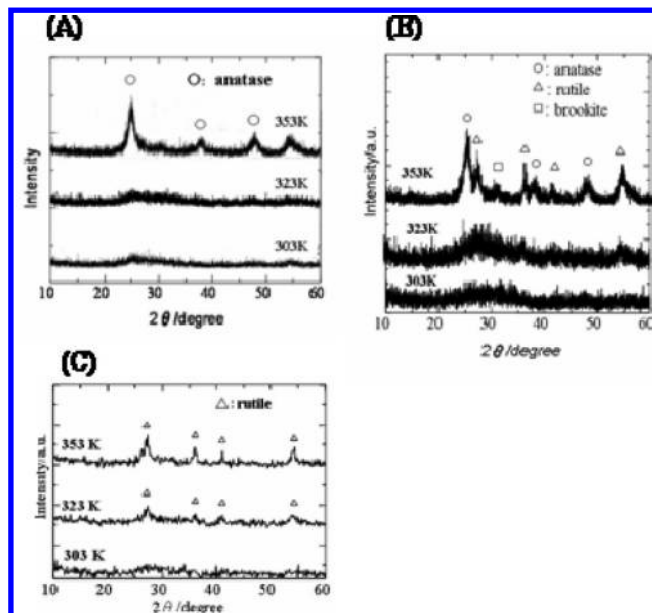
According to previous papers, it was reported that the anion, such as a S or P ion, could be doped in the anodic oxide during anodic oxidation of Ti in a  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$  solution,<sup>20,21</sup> leading to a low environmental technique for developing high-performance  $\text{TiO}_2$ . In this study, by the anodic oxidation technique of Ti metal in a nitric acid solution, N-ion-doped  $\text{TiO}_2$  powders having one-dimensionally aligned mesoporous structure with large diameters of 30–50 nm were successfully synthesized. This simple technique is in one operation for the synthesis of a photocatalyst activated with visible light, leading to the development of a green synthesis technique.

## 2. Experimental Procedures

In this experiment, a commercial Ti metal sheet (5 mm × 10 mm × 0.12 mm, Nilaco Co., Ltd.) was polished using various abrasive papers. After polishing, polished Ti was soaked in a  $\text{HNO}_3/\text{HF}$  solution ( $\text{HNO}_3:\text{HF} = 3:1$ ) in order to remove the oxide film resulting from natural oxidation. Finally, it was washed with deionized water and dried before it was used as an electrode. This Ti metal sheet was set as an anode and C (diameter 5 mm × 10 mm, Toyo Carbon Co., Ltd.) as a cathode. The distance between Ti and C electrodes was about 40 mm in the beaker. Upon anodic oxidation, a nitric acid solution (0.05, 0.25, and 1.0 M) was used as the electrolyte in this study. Then, a nitric acid solution was stirred during the anodic oxidation process. Anodic oxidation was performed at 303, 323, and 353 K for 30 min under 100  $\text{mA}/\text{cm}^2$  of current density supplied direct current power (TP0650-01, Takasago Seisakusyo). The precipitation during anodic oxidation was confirmed in the nitric acid solution and subsequently neutralized with aqueous  $\text{NH}_4\text{OH}$  after anodic oxidation. This precipitation was collected with a Buchner filter and sufficiently washed with ethanol. Dried products obtained by anodic oxidation were identified by powder X-ray diffraction (XRD) analysis. The microstructure was observed with scanning electron microscopy (SEM; Hitachi S-4000) and transmission electron microscopy (TEM; JEOL FX2000). Samples for TEM observation were prepared by cutting of the epoxy-embedded section of the samples. Products prepared by anodic oxidation of Ti under various synthetic conditions were embedded in epoxy resin. They were cut by a microtome equipped with a diamond knife (JEOL, ultramicrotome, ULTRACUT-J) to cut very thin sections (below 100 nm). These thin sections were observed by TEM. Brunauer–Emmett–Teller (BET) measurements of these products were carried out with nitrogen gas absorption equipment. UV–vis spectra were measured with the equipment (Perkin-Elmer, LAMBDA-19). Electronic states of N 1s for products synthesized by this anodization were investigated by X-ray photoelectron spectroscopy (XPS; JEOL JPS9010MC). The amount of nitrogen in the products was measured by the inert gas fusion and thermal conductivity method (LECO TCH600).<sup>24</sup>

## 3. Results and Discussion

Products obtained by anodic oxidation of Ti in a nitric acid solution and subsequently neutralized with  $\text{NH}_4\text{OH}$  were powders. These powders were generated by the dielectric breakdown of the oxide layer caused by anodic oxidation of Ti. Figure 1 shows the XRD results of these products prepared by this anodic oxidation in various nitric acid solutions at 303, 323, and 353 K. Products prepared in a 0.05 M nitric acid solution at 353 K were composed of



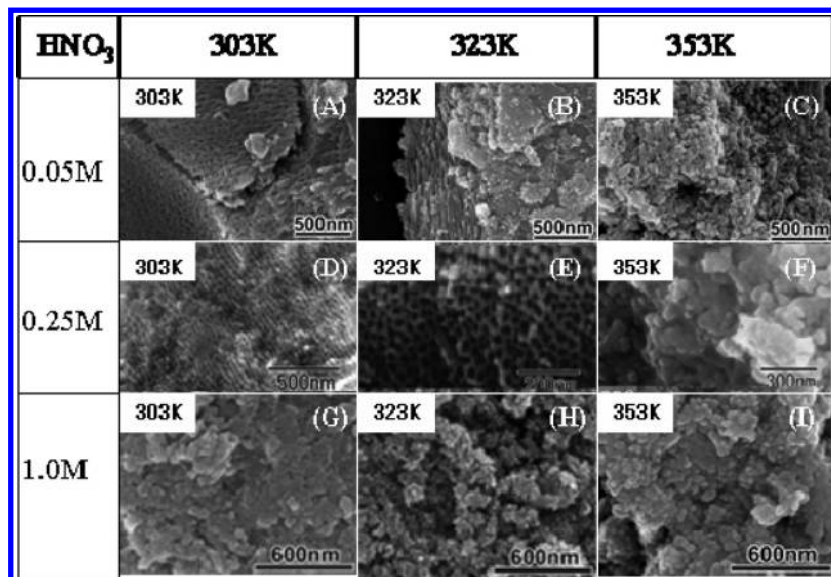
**Figure 1.** XRD of products synthesized by anodic oxidation of Ti in a nitric acid solution [(A) 0.05 M, (B) 0.25 M, and (C) 1.0 M] at 303–353 K. Anodic oxidation was performed at 303, 323, and 353 K for 30 min under 100  $\text{mA}/\text{cm}^2$  of current density supplied direct current power.

anatase. In the case of a 0.25 M nitric acid solution on anodic oxidation, products synthesized at 353 K were composed of anatase and rutile. However, the products prepared in 0.05 and 0.25 M nitric acid solutions at 303 and 323 K showed a broad peak between  $2\theta = 20$  and  $30^\circ$ , that is, amorphous structures. On the other hand, the products prepared in a 1.0 M nitric acid solution at 323 and 353 K were composed of rutile, whereas the product prepared at 303 K, as well as in 0.05 and 0.25 M nitric acid solutions at 303 K, was amorphous.

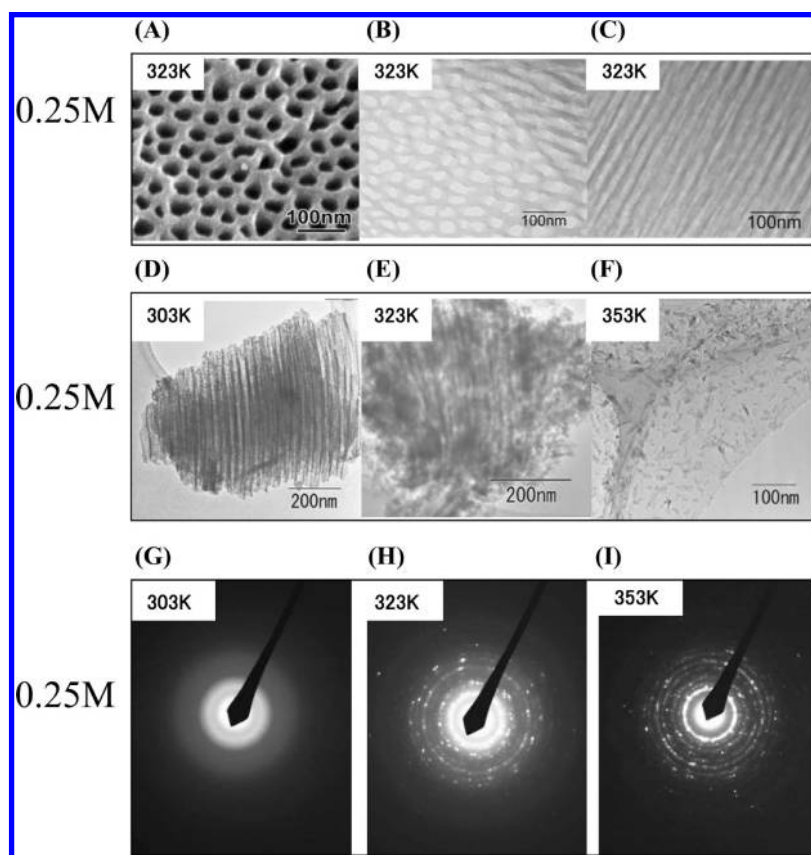
Figure 2 shows SEM images of products prepared by anodic oxidation of Ti at various temperatures in 0.05–1.0 M nitric acid solutions. Parts A–F of Figure 2 show SEM images of products prepared by anodic oxidation in 0.05 and 0.25 M nitric acid solutions at various temperatures. Samples prepared in 0.05 and 0.25 M nitric acid solutions at 323 and 353 K had one-dimensional and mesoporous structures with some tens of nanometers diameters, although ones at 353 K were granular and fine (nanosized). On the contrary, all samples prepared in 1.0 M at 303–353 K (Figure 2G–I), as well as ones in a 0.05 M nitric acid solution at 353 K (Figure 2F), were granular and nanosized. These samples possessed no mesoporous structures.

Figure 3A shows highly magnified SEM images of products prepared by anodic oxidation in a 0.25 M nitric acid solution at 323 K. Samples prepared by anodic oxidation of Ti in a 0.25 M nitric acid solution at 323 K possess a lot of mesopores with diameters of 30–50 nm. Thus, uniform pores with some tens of nanometers diameters were observed on the surface of the samples. Parts B and C of Figure 3 show TEM images for cross-sectional and longitudinal/vertical sections for these porous samples. From TEM observations, it was obvious that the samples had a lot of one-dimensional (i.e., unidirectional) pores with 30–50 nm diameter, that is, large-sized mesopores. Parts D–F of Figure 3 show TEM images for samples in a 0.25 M nitric acid solution at various temperatures. From the observation results of Figure 3D–F, samples prepared by anodic oxidation of Ti in a 0.25 M nitric acid solution at

(24) ASTM E 1019-94 Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel and Iron, Nickel, and Cobalt Alloys.



**Figure 2.** SEM (A–I) images of products prepared by anodic oxidation of Ti in 0.05, 0.25, and 1.0 M nitric acid solutions at 303, 323, and 353 K. Anodic oxidation was performed at 303, 323, and 353 K for 30 min under 100 mA/cm<sup>2</sup> of current density supplied direct current power: (A) 0.05 M at 303 K, (B) 0.05 M at 323 K, (C) 0.05 M at 353 K, (D) 0.25 M at 303 K, (E) 0.25 M at 323 K, (F) 0.25 M at 353 K, (G) 1.0 M at 303 K, (H) 1.0 M at 323 K, and (I) 1.0 M at 353 K.



**Figure 3.** SEM and TEM images of products prepared by anodic oxidation of Ti in a 0.25 M nitric acid solution at 303, 323, and 353 K. Anodic oxidation was performed at 303, 323, and 353 K for 30 min under 100 mA/cm<sup>2</sup> of current density supplied direct current power. (A) SEM image for samples prepared in 0.25 M nitric acid at 323 K. (B and C) TEM image of sample A. (D–F) TEM images for samples in a 0.25 M nitric acid solution at 303, 323, and 353 K. (G–I) Diffractions for samples in a 0.25 M nitric acid solution at 303, 323, and 353 K.

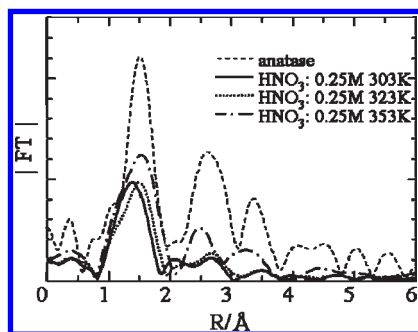
303 and 323 K possessed one-dimensional mesopores, although samples prepared by anodic oxidation of Ti in a 0.25 M nitric acid solution at 353 K were finely granular without one-dimensional mesopores (Figure 3F). The results

show that the diameter of one-dimensional mesopores decreased with temperature upon anodic oxidation. Parts G–I of Figure 3 show the results of electron diffraction for products prepared by anodic oxidation of Ti in a 0.25 M nitric acid

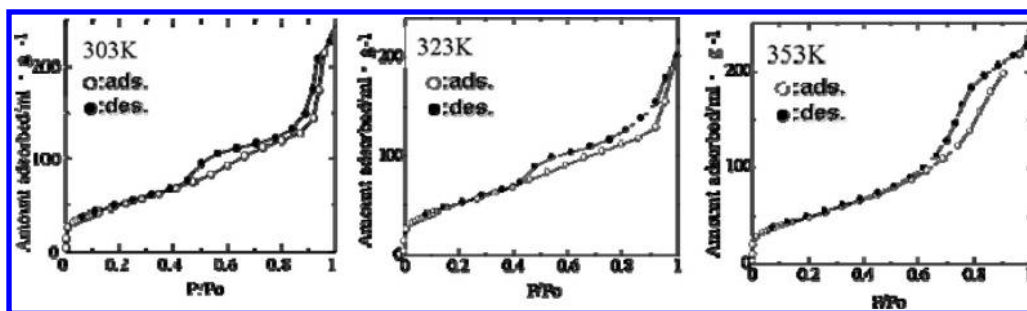
solution at 303 K (D), 323 K (E), and 353 K (F). These samples prepared by anodic oxidation of Ti in a 0.25 M nitric acid solution at 303 K showed the halo pattern (Figure 3G), suggesting amorphous products. This electron diffraction result was consistent with the results of XRD (Figure 1B). However, samples prepared by anodic oxidation of Ti in a 0.25 M nitric acid solution at 323 and 353 K (Figure 3H,I) indicated crystalline titanium oxide, which agreed with the XRD results (Figure 1B).

These TiO<sub>2</sub> products with unique structures with large-sized and one-dimensionally aligned mesopores were amorphous, so their local structures of Ti K-edge were evaluated with X-ray absorption fine structure (XAFS). Figure 4 shows the results of XAFS measurements for products prepared by anodic oxidation in a 0.25 M nitric acid solution at 303, 323, and 353 K. Samples prepared by anodic oxidation in a 0.25 M nitric acid solution at 303 and 323 K had a coordination number ( $N$ ) of 2.2–2.3 surrounding the Ti atom and a Ti–O distance ( $R$ ) of 0.191–0.1943 nm, although the second neighborhood was not confirmed. On the contrary, ones by anodic oxidation in a 0.25 M nitric acid solution at 353 K had a higher coordination number and a longer Ti–O distance ( $N = 3.5$  and  $R = 0.1970$  nm) compared to amorphous TiO<sub>2</sub> prepared by anodic oxidation in 0.25 M at 303 and 323 K. The results of XAFS were consistent with the ones of XRD.

Figure 5 shows the results of nitrogen gas adsorption/desorption isotherms of products prepared by anodic oxidation in a 0.25 M nitric acid solution at 303, 323, and 353 K. Samples prepared by anodic oxidation in a 0.25 M nitric acid solution at 303 and 323 K show the typical isotherms from mesoporous structure, although samples at 353 K showed macroporous structure, including, in part, mesoporous struc-

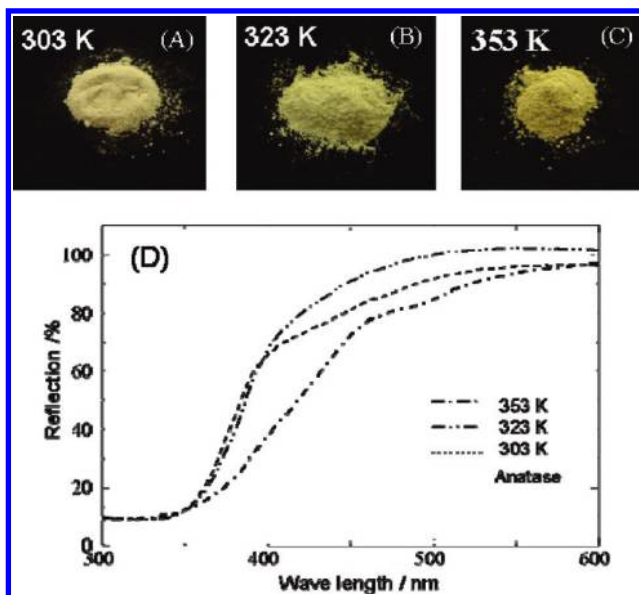


**Figure 4.** XAFS of products synthesized by anodic oxidation of Ti in a nitric acid solution [(a) 0.05 M, (b) 0.25 M, and (c) 1.0 M] at 303–353 K. Anatase was measured as a reference material. Anodic oxidation was performed at 303, 323, and 353 K for 30 min under 100 mA/cm<sup>2</sup> of current density supplied direct current power.

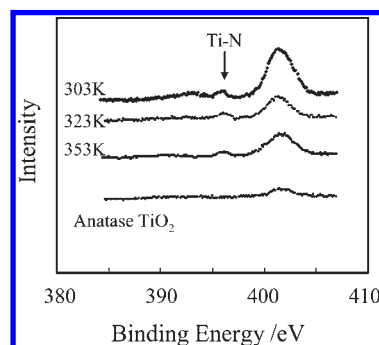


**Figure 5.** Nitrogen adsorption/desorption isotherms of products prepared by anodic oxidation of Ti in a 0.25 M nitric acid solution at 303 K (A), 323 K (B), and 353 K (C).

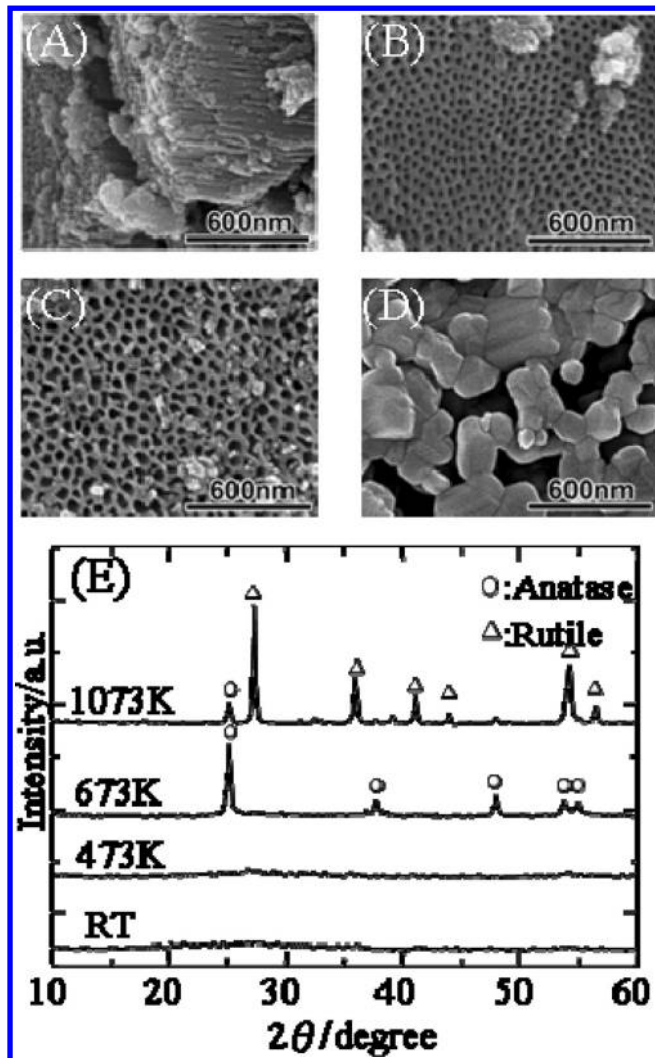
ture. Nitrogen gas adsorption measurements showed that the products synthesized by an anodic oxidation process possessed significantly high BET values. Products synthesized by anodic oxidation in 0.25 M at 303 and 323 K had BET values of 176 and 183 m<sup>2</sup>/g, respectively. On the contrary, samples synthesized by anodic oxidation at 353 K showed a small decrease of the BET value, 175 m<sup>2</sup>/g. The reason why samples synthesized by anodic oxidation at 323 K also have such a high surface area is now under investigation. Thus, the results



**Figure 6.** Photographs of products synthesized by anodic oxidation of Ti in a 0.25 M nitric acid solution at 303 K (A), 303 K (B), and 353 K (C). (D) Results of UV-vis spectra for products synthesized by anodic oxidation of Ti in a 0.25 M nitric acid solution at 303–353 K.



**Figure 7.** XPS results of products synthesized by anodic oxidation of Ti in a 0.25 M nitric acid solution at 303–353 K.



**Figure 8.** SEM images and XRD results of products prepared by anodic oxidation in a 0.25 M nitric acid solution at 323 K. (A) SEM image for samples as-synthesized without a heat treatment. Subsequently, samples were heat-treated in a dihydrogen atmosphere at various temperatures and observed by SEM: 473 K (B), 673 K (C), and 1073 K (D). Anodic oxidation samples were performed at 303, 323, and 353 K for 30 min under 100 mA/cm<sup>2</sup> of current density supplied direct current power.

of nitrogen adsorption behavior suggest that samples possess a large number of large-sized mesopores.

Products obtained by anodic oxidation at 303, 323, and 353 K in a 0.25 M nitric acid solution were metallic yellow powders, as shown in Figure 6A–C. Figure 6D shows UV–vis spectra for products anodic-oxidized in a 0.25 M nitric acid solution at 303–353 K. Here, for comparison, the UV–vis results were also included for anatase TiO<sub>2</sub> as a reference. As is clearly shown in the figure, the products obtained in this study showed absorption at 400–500 nm, especially the one prepared by anodic oxidation at 353 K, although anatase TiO<sub>2</sub> possessed no absorption in the range of visible light. According to inert gas fusion and the thermal conductivity method, the amount of nitrogen in the products was in the range of 0.71–0.45 wt %. Samples prepared by anodic oxidation in a 0.25 m nitric acid solution at 303, 323, and 353 K had nitrogen contents of 0.71, 0.67, and 0.45%, respectively. The electric states for N ions in products

anodized in a 0.25 M nitric acid solution at 303, 323, and 353 K were evaluated by XPS analysis. Figure 7 shows the XPS results of TiO<sub>2</sub> obtained by anodic oxidation at 303, 323, and 353 K. Asahi et al. reported the results of XPS of N 1s for their samples obtained by the gas process reaction method. Their results of N 1s XPS showed small peaks at 395–396 eV caused by Ti–N in TiO<sub>2</sub>, whereas the peak at 400 eV was due to the interstitial solid solution of N ions in the TiO<sub>2</sub> structure.<sup>14</sup> According to their analysis, the formation of Ti–N bonding confirmed at 395–396 eV led to nitrogen doped to titanium dioxide with active photocatalytic properties under visible light.<sup>2</sup> As shown in Figure 7, the XPS results of products synthesized by anodic oxidation at 323 and 353 K in this study show small peaks at 395–396 eV, although samples anodic-oxidized at 303 K showed no peak at 395–396 eV. These XPS results suggest that N ions are incorporated into TiO<sub>2</sub> synthesized by anodic oxidation. From both UV–vis and XPS results, it is thought that N ions were substituted by O ions in TiO<sub>2</sub> by this anodic oxidation process.

Next, large-sized mesoporous TiO<sub>2</sub> prepared by anodic oxidation in a 0.25 M nitric acid solution at 323 K was heat-treated in a dihydrogen atmosphere at various temperatures and observed by SEM. Figure 8 shows SEM images and XRD results of products prepared by anodic oxidation in a 0.25 M nitric acid solution at 323 K and subsequently heat-treated in a dihydrogen atmosphere at various temperatures [473 K (B), 673 K (C), and 1073 K (D)]. Below 673 K, mesoporous structures were maintained, although mesopores for the samples diminished at 1073 K. From the XRD results (Figure 8E), samples heat-treated at 673 K were mainly composed of anatase, in part rutile. On the contrary, samples heat-treated at 1073 K had the main component of rutile. Thus, novel anatase-type TiO<sub>2</sub> powders with high specific surface area and one-dimensionally aligned and large-sized mesopores were successfully synthesized by simple anodic oxidation in a nitric acid solution and subsequently heat-treated in dihydrogen.

#### 4. Conclusion

In this study, novel mesoporous TiO<sub>2</sub> was successfully synthesized by simple anodic oxidation of Ti in a nitric acid solution at various temperatures for an extremely short synthetic time (30 min). Their component morphologies of products were dependent on the synthetic condition, the temperature, and the concentration of the nitric acid solution during the anodic oxidation process. Samples synthesized by simple anodic oxidation in a nitric acid solution at 303 and 323 K possessed the unique microstructure, one-dimensional with the large-sized mesopores of 30–50 nm diameter. Other results show that novel mesoporous TiO<sub>2</sub> by the anodic oxidation process in a nitric acid solution was doped with N ions, leading to a useful photocatalyst under visible light. Consequently, anodic oxidation of Ti in a nitric acid solution resulted in the easy synthesis of novel TiO<sub>2</sub> powders with one-dimensional and large-sized mesopores.

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