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Microstructural Control of Mesoporous Bulk Composed of TiO_2-Derived Titanate Nanotubes

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ABSTRACT The mesoporous bulks composed of TiO_2-derived titanate nanotubes fabricated from a hydrothermal treatment of commercial TiO_2 particles in a concentrated NaOH aqueous solution were obtained by a hydrothermal hot-pressing (HHP) method and subsequent steam-curing process with HCl solutions. The mesopore size and sodium concentration for the bulky TiO_2-derived titanate nanotubes were dependent on the treatment conditions on the steam curing process with HCl solutions. The effect of the sodium concentration (Na/Ti) on microstructures were examined on the steam curing process for the application of the bulky TiO_2-derived titanate nanotubes to several new fields.

KEYWORDS: nanotube • titanate • nanomaterials • bulk • hydrothermal treatment • mesopore

1. INTRODUCTION

Nanosized materials have attracted growing interest as a result of their unique nanostructure and physical properties (1–4). TiO_2-derived titanate nanotubes, which are prepared by a hydrothermal treatment of TiO_2 particles in a concentrated NaOH aqueous solution, are notable nanoscale-materials because of their nanotubular structures and high surface areas (5–14). Therefore, many studies on electrochromism (15), bone regeneration (16), proton conduction (17), photoinduced hydrophilicity (18), photocatalysts (19–22), and dye-sensitizing solar batteries (23) have been conducted for nanotubes.

To make full use of the characteristics of these TiO_2-derived titanate nanotubes for several applications, it is important to prevent the nonuniformed aggregation and to control the arrangement of these nanotubes in terms of size and morphology. In fact, many studies on the molophologic control such as preparations of film and bulk for these nanotubes have been attempted vigorously (15, 18, 24–26). On another direction, no study on fabrication of bulky TiO_2-derived titanate nanotubes has been performed because a bulk with high density and nanotubular structure was difficult to fabricate by the conventional method. For example, in the case of the bulks solidified with silicate, nanotubular structures are filled with an amorphous phase as a binder. Furthermore, the sintered body of TiO_2-derived titanate nanotubes could not be fabricated because they could not keep nanotubular structures at high temperatures. The application area of TiO_2-derived titanate nanotubes can be expected to expand if the fabrication of these bulks becomes possible. For these reasons, the development of a bulk synthetic technique for TiO_2-derived titanate nanotubes is desired. Recently, we have successfully fabricated bulky TiO_2-derived titanate nanotubes with high density by a hydrothermal hot-pressing (HHP) technique (27). The bulk obtained by HHP possessed the mesopores derived from characteristic nanonetwork structures, which is expected to be a useful material for applications such as dye-sensitizing solar batteries. In our previous work, the functional bulk forms of hydroxyapatite (HAp), Y-zeolite, and mesoporous silica (FSM and MCM) materials have been successfully fabricated using this HHP method (28–35).

To apply the bulky TiO_2-derived titanate nanotubes to several fields including dye-sensitizing solar batteries, it is thought to be important to control the sodium concentration (Na/Ti) and microstructures for the bulky TiO_2-derived titanate nanotubes (36, 37). For example, in the case of dye-sensitizing solar batteries, bulky TiO_2-derived titanate nanotubes have some advantages, e.g., high-surface-area from both nanotubular space inside nanotubes, mesopores caused by bulk formation and surface hydrophilicity properties of nanotubes for dyes, and so on. Therefore, we focused on the steam-curing treatment for the preparation of bulks for TiO_2-derived titanate nanotubes in this study. It is expected that ion-exchange of Na^+ for H^+ in bulky TiO_2-derived titanate nanotubes could proceed without decreasing mechanical strength properties by this process (38).

The main purpose is to control the sodium concentration (Na/Ti) and microstructures for the bulky TiO_2-derived tita-

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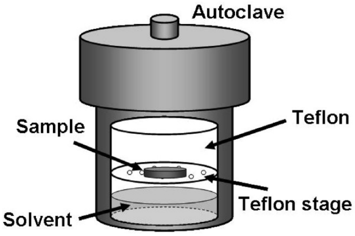

FIGURE 1. Autoclave for steam curing used in this study.

nate nanotubes by the steam curing process. The bulky TiO_2-derived titanate nanotubes were fabricated by a hydrothermal treatment of commercial TiO_2 particles in a concentrated NaOH aqueous solution and a subsequent hydrothermal hot-pressing (HHP) method. Subsequently, HHP-processed bulks were treated by the steam curing with HCl aqueous solutions. Furthermore, the effect of these steam treatments on microstructures for bulky TiO_2-derived titanate nanotubes was in detail investigated by various analyses.

2. EXPERIMENTAL SECTION

The synthesis of TiO_2-derived titanate nanotubes was attempted through the hydrothermal process. As a source material, 2 g of anatase-type TiO_2 powder (particle size = 50−100 nm, specific surface area = 3 m^2/g, Kojundo Chem., Saitama, Japan) were used. The powder was added in a 10 M NaOH aqueous solution (20 mL). Then, the mixture was hydrothermally treated at 383 K for 96 h in a stainless bomb. The product was separated by filtration and sufficiently washed with deionized water. After the sufficient washing treatments with deionized water, obtained powders were dried at 323 K for 12 h in an oven.

Subsequently, the fabrication of bulky TiO_2-derived titanate nanotubes was attempted by HHP technique (27, 39). Synthesized titanate nanotubes-powder (1.0 g) was placed in this autoclave for HHP, and deionized water (0.2 mL) was poured into the autoclave. The sample was heated at a rate of 10 K/min under pressure with 40 MPa, and held at 423 K for 2 h. After HHP treatments, the autoclave was cooled under the pressure and product was taken out.

HHP-processed bulks were treated by the steam curing. Steam curing was attempted in a stainless-steel autoclave as shown in Figure 1. A case made of teflon was set in the inside of the autoclave. The autoclave was sealed off tightly and kept at 423 K for 2 and 24 h in an oven. HCl aqueous solutions (0.1 and 1 M) as a solvent were used for the steam curing. After this steam curing treatment, the bulk samples were removed from the autoclave and dried at 323 K for more than 12 h in an oven. For comparison with samples prepared by the steam curing process with HCl solutions, the bulks obtained by HHP were treated by soaking in a 0.1 M HCl solution at room temperature for 2 h.

Crystalline phase of samples were determined by X-ray diffraction method (XRD, RINT 2100, Rigaku, Tokyo, Japan) using CuKα radiation at 40 kV and 20 mA. XRD profiles were collected between 5 to 60° of 2θ angles. Various microstructural analyses were carried out by using scanning electron microscopy (SEM, S-4500, Hitachi, Tokyo, Japan) with an accelerating voltage of 15 kV, transmission electron microscopy (TEM, JEM2000FX, JEOL, Tokyo, Japan) with an accelerating voltage of 200 kV and energy-dispersive X-ray (EDX) analysis. Nitrogen adsorption isotherms at 77 K were obtained by automatic gas adsorption measure apparatus (BELSORP 18PLUS-SPL, Japan-BEL, Osaka, Japan). Some pieces of product were pretreated at 403 K for 10 h. The bulk density of obtained products was measured with volume and weight.

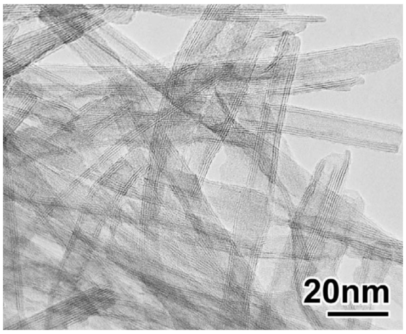

FIGURE 2. TEM image of TiO_2-derived nanotube prepared by the hydrothermal process.

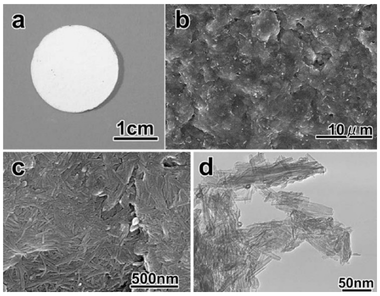

FIGURE 3. (a) Photograph, (b, c) SEM images, and (d) TEM image of the bulky titanate nanotube prepared by HHP with 0.2 mL of H_2O under 40 MPa at 423 K for 2 h.

3. RESULTS AND DISCUSSION

Nanotubular product with high BET surface area (over 150 m^2/g) was synthesized through a hydrothermal process from commercial anatase-type TiO_2 powder. Figure 2 shows typical TEM image of the product prepared by the hydrothermal treatment of anatase-type TiO_2 at 383 K for 96 h. As shown in Figure 2, the obtained products possessed nanotubular structures about 10 nm in outer diameter, 5 nm in inner diameter, and a few hundred nanometers in length, and were open-ended with several wall layers on both sides. XRD patterns of the synthesized nanotubular product in this study were consistent with ones of nanotubular products prepared in other previous reports (6–14, 21, 22, 26, 27, 36–38, 40–42). The results of X-ray absorption fine structure (XAFS) analysis indicated that these nanotubular products prepared by the hydrothermal process were mainly composed of titanate compound and that the anatase-like structure was locally present in the titanate-based nanotubes (12, 13).

The fabrication of bulky TiO_2-derived titanate nanotubes was attempted by HHP technique of titanate nanotubes containing remnant sodium (27). Figure 3 shows photographs of SEM and TEM images of bulky TiO_2-derived titanate nanotubes prepared by HHP treatment of TiO_2-derived titanate nanotubes with for 2 h under 40 MPa at 423 K. The bulks prepared by HHP under this condition was sufficiently solidified with considerably dense structures and no voids existed (Figure 3b). This bulk density value of the bulk was 2.08 g/cm^3. From results of N_2-adsorption measurements and microstructural observations by SEM and

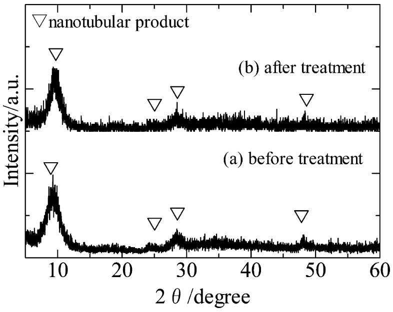

FIGURE 4. XRD patterns of the bulks prepared by soaking in a 0.1 M HCl solution at room temperature for 2 h: (a) before and (b) after treatments.

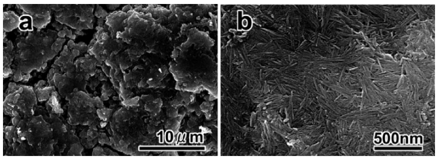

FIGURE 5. SEM images of the bulks prepared by soaking in a 0.1 M-HCl solution at room temperature for 2 h: (a, b) were images observed at low and high magnifications, respectively.

TEM, it was obvious that bulk samples by HHP were composed of nanotubular structures and that obtained bulks possessed mesopores derived from characteristic nanonetwork and high BET surface area (79.1 m^2/g). Na/Ti atomic ratio for this bulk was 0.24 according to EDX analysis. Thus, the mesoporous bulks composed of TiO_2-derived titanate nanotubes were successfully fabricated. Next, the effects of soaking treatment and steam curing with HCl solutions on the microstructures for the bulk composed of TiO_2-derived titanate nanotubes were investigated.

First, the influence of soaking treatments with HCl solutions for these bulks composed of TiO_2-derived titanate nanotubes was examined. The bulks of TiO_2-derived titanate nanotubes was treated by soaking in HCl solutions. Figures 4 and 5 show XRD pattern and SEM images of the bulk prepared by soaking in a 0.1 M HCl solution at room temperature for 2 h, respectively. XRD pattern of the bulks treated in a 0.1 M HCl solution for 2 h represented almost the same diffraction pattern as that of TiO_2-derived titanate nanotubes. From SEM observation at high magnification, as shown in Figure 5b, it was found that this bulk sample had nanowhisker like morphologies. These XRD and SEM results implied that the sample maintained nanotubular structures after soaking in a 0.1 M HCl solution. However, this bulk after the HCl soaking treatment had many voids between gains (Figure 5a). Additionally, this bulk had the bulk density of 1.61 g/cm^3, whereas the density of the bulk before the HCl treatment was 2.08 g/cm^3. Thus, the dense structures had not been maintained after soaking treatments with the HCl solution.

Furthermore, the bulks composed of TiO_2-derived titanate nanotubes were treated by steam curing with HCl solutions. Figures 6 and 7 show XRD patterns and SEM images of the bulks treated by steam curings with 0.1 and 1 M HCl solutions at 423 K for 2 and 24 h, respectively. From XRD results, the diffraction peaks derived from anatase-type TiO_2 was observed in the bulk treated by steam curing with 1 M HCl solution at 423 K for 24 h, although the bulks treated with 0.1 M HCl solution at 423 K for 2 h represented the same diffraction patterns as that of TiO_2-derived titanate nanotubes. Furthermore, the bulks prepared by the steam curing with a 1 M HCl solution at 423 K for 24 h were composed of small particles with a spherical-shaped morphology from SEM observation at a high magnification (Figure 7f). According to XRD, it was considered that these particles could be identified as anatase-type TiO_2. As a result, the excess steam curing with HCl solutions brought about the destruction of nanotubular structure and the transition to anatase-type TiO_2. On the other hand, from SEM images at a low magnification of the bulks prepared by the steam curing with 0.1 and 1 M HCl solutions at 423 K for 2 h, it was found that these kept having nanowhisker like morphologies (Figure 7d,e), indicating that that these bulks maintained nanotubular structures. In fact, it was confirmed that these bulks possessed nanotubular structures by TEM observations (Figure 8). Thus, these bulks after steam curings were still composed of titanate nanotubes.

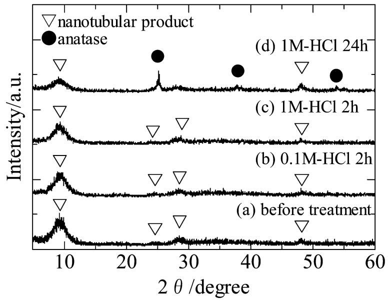

FIGURE 6. XRD patterns of the bulks prepared by steam curings with HCl solution at 423 K: (a) before treatment, (b) 0.1 M HCl for 2 h, (c) 1 M HCl for 2 h, and (d) 1 M HCl for 24 h.

These bulks treated with 0.1 and 1 M HCl solutions for 2 h also had high bulk density values of 2.08 and 1.91 g/cm^3, respectively. Images a and b in Figure 7 show SEM images at low magnification of the bulks treated by steam curings with 0.1 and 1 M HCl solutions at 423 K for 2 h. From SEM observations at a low magnification, as shown in images a and b in Figure 7, there were no voids in these bulks. Therefore, it was found that these bulks sufficiently possessed the dense microstructures.

Adsorption/desorption isotherms of these bulk samples were also measured by N_2-adsorption. The BJH methjod was employed to analyze the pore size distribution. The typical isotherms and pore size distributions for bulks prepared by HHP processe and the bulks by the steam curing with HCl solutions (0.1 and 1 M) at 423 K for 2 h are showed in Figure 9, respectively. The pore volume, the average diameter of pore-size, and BET surface area obtained from N_2-adsorption measurements for these bulks are also summarized in Table 1. As shown in Figure 9, the adsorption hysteresis results for all bulk samples were observed in the region of a relative pressure P/P_0 above 0.4, and the isotherm also represented type IV, suggesting that these bulks possessed unique microstructure with sharp size of mesopores. Furthermore, these bulks prepared by the

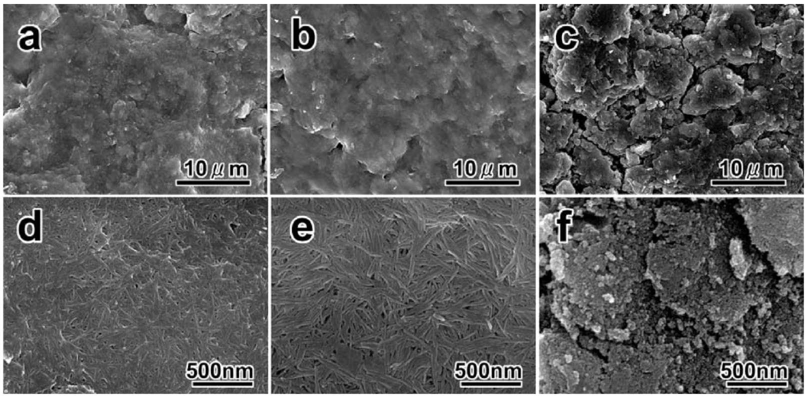

FIGURE 7. SEM images at low and high magnification of the bulks prepared by steam curings with HCl solution at 423 K: (a, d) 0.1 M HCl for 2 h, (b, e) 1 M HCl for 2 h, and (c, f) 1 M HCl for 24 h.

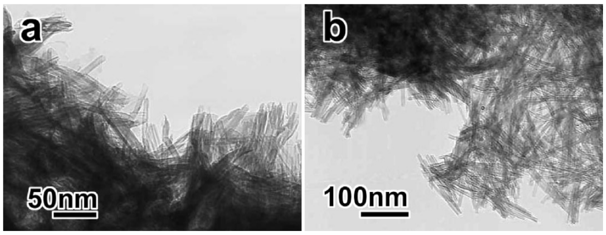

FIGURE 8. TEM images of the bulks prepared by steam curings with HCl solution at 423 K: (a) 0.1 M HCl for 2 h, (b) 1 M HCl for 2 h.

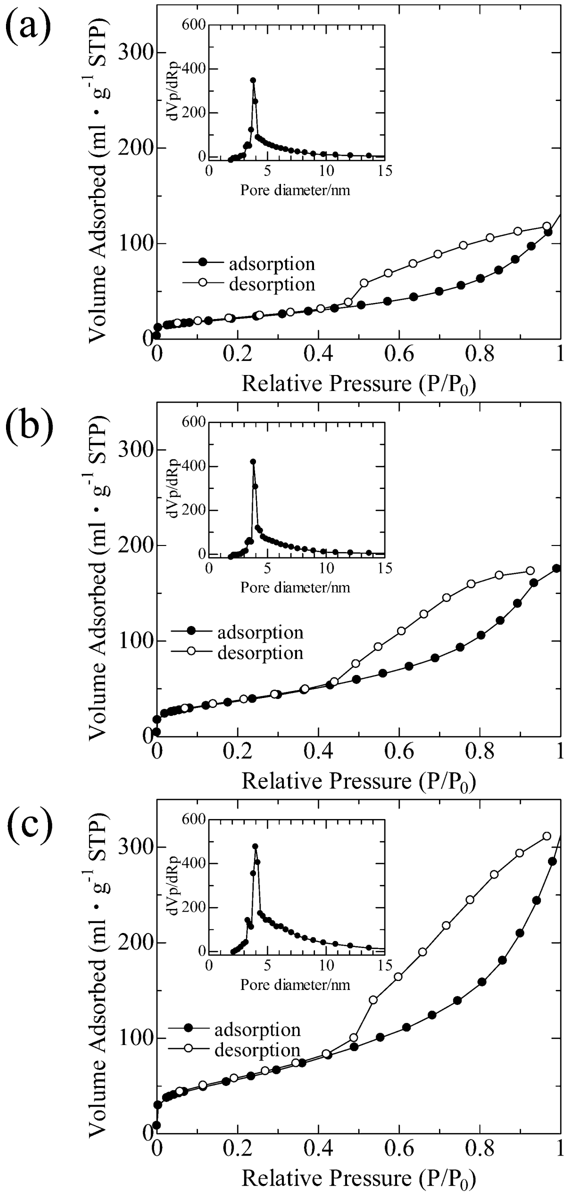

FIGURE 9. Typical isotherms and pore size distributions of the bulks prepared by steam curings with HCl solution at 423 K: (a) before treatment, (b) 0.1 M HCl for 2 h, and (c) 1 M HCl for 2 h.

steam curing with HCl solutions had significantly sharp distributions of mesopores as shown in Figure 9, indicating that the bulks are also composed of microstructures of mesopores and nanochannels before/after the steam curing with HCl solutions. The average diameter of the mesopore size increased after the steam curing. Furthermore, the mesopore size increased as the concentration of the HCl solution was high. The bulks prepared by the steam curing with 0.1 and 1 M HCl solutions had an larger average pore size diameter of 3.9 and 4.1 nm, respectively, compared to the bulk without the steam curing having an average pore size diameter of 3.8 nm. These results suggest that the size of mesopores in the bulky TiO_2-derived titanate nanotubes can be controlled by the steam curing with HCl solutions. Moreover, as shown in Table 1, the steam curing resulted in the increase in pore volume and BET surface area values. According to the previous reports, the value of BET surface area of TiO_2-derived titanate nanotubes depends on Na/Ti (40–42). Therefore, the increase in surface area is thought to be caused by the ion-exchange Na^+ for H^+ or H_3O^+ in bulky titanate nanotubes. In particular, the bulk prepared by the steam curing with a 1 M HCl solution for 2 h had a very high BET value over 200 m^2/g in spite of bulks having dense structures. For the bulks prepared by the steam curing with 0.1 and 1 M HCl solutions, Na/Ti atomic ratios according to EDX analysis were 0.21 and 0.14, respectively. The detailed pore size control mechanism for the bulky TiO_2-derived titanate nanotubes is now under investigation. Consequently, the mesopore size and sodium concentration (Na/Ti) for the bulky TiO_2-derived titanate nanotubes were successfully controlled by the steam curing. This mechanical strength of bulks obtained in this experiment is thought to be derived mainly from the entanglement of naotubes enhanced by the densification of powder and the increase

Table 1. The Average Size of Pore Diameter and BET Surface Areas of the Bulks Prepared by Steam Curings with HCl Solutions at 423 K for 2 h

	before steam curing	after steam curing	
		0.1 M HCl 2 h	1 M HCl 2 h
pore diameter (nm)	3.8	3.9	4.1
pore volume (mm^3 g^{-1})	220.7	239.67	543.97
BET value (m^2/g)	79.1	133.9	205.7

in contact area between nanotubes. It is expected that the steam curing under various conditions can control the microstructures for bulky TiO_2-derived titanate nanotubes.

4. CONCLUSIONS

In this paper, the sodium concentration (Na/Ti) and microstructures for the bulky TiO_2-derived titanate nanotubes were attempted by the steam curing with HCl solutions. The bulks of TiO_2-derived titanate nanotubes were fabricated using hydrothermal hot-pressing (HHP) method of TiO_2-derived titanate nanotubes prepared by hydrothermal treatment of commercial TiO_2 particles in a concentrated NaOH aqueous solution. Bulks prepared by HHP were composed of nanotubular structures and that obtained bulks possessed sharp distribution of mesopores and high BET surface area. After the steam curing with 0.1 and 1 M HCl solutions for 2 h at 423 K, these bulks were also composed of nanotubular structures and possessed significantly sharp distribution of mesopores and high BET surface area. The average diameter of the mesopore size and BET value increased in width by the steam curing, and the mesopore size increased as the concentration of the HCl solution was high. Thus, the mesopore size for the bulky TiO_2-derived titanate nanotubes were varied with the steam-curing process in HCl solutions. The analysis of these bulky TiO_2-derived titanate nanotubes prepared in this study will lead to the investigation of mechanical, physical, and chemical properties of TiO_2-derived titanate nanotubes itself. Additionally, this fabrication of advanced bulky TiO_2-derived titanate nanotubes will lead to applications for not only dye-sensitizing solar batteries but also gas separation filters, etc.

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REFERENCES AND NOTES

(1) Iijima, S. *Nature* **1991**, *354*, 56.
(2) Patzke, G. R.; Krumeich, F.; Nepsper, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2446.
(3) Kovtyukhova, N. I.; Mallouk, T. E.; Mayer, T. S. *Adv. Mater.* **2003**, *15*, 780.
(4) Hoyer, P. *Langmuir* **1996**, *12*, 1411.
(5) Kasuga, T.; Hiramatsu, M.; Hoson, A.; Sekino, T.; Niihara, K. *Langmuir* **1998**, *14*, 3160.
(6) Chen, Q.; Du, G. H.; Zhang, S.; Peng, L. M. *Acta Crystallogr., Sect. B* **2002**, *58*, 587.
(7) Chen, Q.; Zhou, W.; Du, G. H.; Peng, L. M. *Adv. Mater.* **2002**, *14*, 1208.
(8) Sun, X.; Li, Y. *Chem.—Eur. J.* **2003**, *9*, 2229.
(9) Nakahira, A.; Kato, W.; Tamai, M.; Isshiki, T.; Nishio, K.; Aritani, H. *J. Mater. Sci.* **2004**, *39*, 4239.
(10) Weng, L. Q.; Song, S. H.; Hodgson, S.; Baker, A.; Yu, J. *J. Eur. Ceram. Soc.* **2006**, *26*, 1405.
(11) Kubo, T.; Kato, W.; Yamasaki, Y.; Nakahira, A. *Key Eng. Mater.* **2006**, *317&318*, 247.
(12) Kubo, T.; Yamasaki, Y.; Nakahira, A. *J. Ion Exchange* **2007**, *18*, 310.
(13) Kubo, T.; Nakahira, A. *J. Phys. Chem. C* **2008**, *112*, 1658.
(14) Wang, W.; Varghese, O. K.; Paulose, M.; Grimes, G. A. *J. Mater. Res.* **2004**, *19*, 417.
(15) Tokudome, H.; Miyauchi, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 1974.
(16) Kubota, S.; Johkura, K.; Asanuma, K.; Okouchi, Y.; Ogiwara, N.; Sasaki, K.; Kasuga, T. *J. Mater. Sci.: Mater. Med.* **2004**, *15*, 1031.
(17) Thorne, A.; Kruth, A.; Tunstall, D.; Irvine, J. T. S.; Zhou, W. *J. Phys. Chem. B* **2005**, *109*, 5439.
(18) Tokudome, H.; Miyauchi, M. *Chem. Commun.* **2004**, *40*, 958.
(19) Adachi, M.; Murata, Y.; Harada, M.; Yoshikawa, S. *Chem. Lett.* **2000**, *29*, 942.
(20) Akita, T.; Okumura, M.; Tanaka, K.; Ohkuma, K.; Kohyama, M.; Koyanagi, T.; Date, M.; Tsubota, S.; Haruta, M. *Surf. Interface Anal.* **2005**, *37*, 265.
(21) Nakahira, A.; Kubo, T.; Yamasaki, Y.; Suzuki, T.; Ikuhara, Y. *Jpn. J. Appl. Phys.* **2005**, *44*, 690.
(22) Kubo, T.; Nagata, H.; Takeuchi, M.; Matsuoka, M.; Anpo, M.; Nakahira, A. *Res. Chem. Intermed.* **2008**, *34*, 339.
(23) Uchida, S.; Chiba, R.; Tomiha, M.; Masaki, N.; Shirai, M. *Electrochemistry* **2002**, *70*, 418–420.
(24) Tian, Z. R.; Voigt, J. A.; Lin, J.; Mckenzie, B.; Xu, H. *J. Am. Chem. Soc.* **2003**, *125*, 12384.
(25) Liu, A.; Wei, M.; Honma, I.; Zhou, H. *Anal. Chem.* **2005**, *77*, 8068.
(26) Yada, M.; Inoue, Y.; Uota, M.; Torikai, T.; Watari, T.; Noda, I.; Hotokebuchi, T. *Lamgmuir* **2007**, *23*, 2815.
(27) Kubo, T.; Yamasaki, Y.; Nakahira, A. *J. Mater. Res.* **2007**, *22*, 1286.
(28) Nakahira, A.; Murakami, T.; Onoki, T.; Hashida, T.; Hosoi, K. *J. Am. Ceram. Soc.* **2005**, *88*, 1334.
(29) Takimura, M.; Nagata, H.; Yamasaki, Y.; Suzuki, T.; Ikuhara, Y.; Nakahira, A. *J. Ceram. Soc. Jpn.* **2006**, *114*, 554.
(30) Nagata, H.; Takimura, M.; Yamasaki, Y.; Nakahira, A. *Mater. Trans.* **2006**, *47*, 2103.
(31) Nagata, H.; Hirao, N.; Onoki, T.; Baba, Y.; Yamasaki, Y.; Nakahira, A. *J. Ceram. Soc. Jpn.* **2008**, *116*, 216.
(32) Nakahira, A.; Takimura, M.; Yamasaki, Y. *J. Non-Cryst. Solids* **2007**, *353*, 4203.
(33) Nakahira, A.; Takezoe, S.; Yamasaki, Y. *Chem. Lett.* **2004**, *33*, 1400.
(34) Nakahira, A.; Takezoe, S.; Yamasaki, Y.; Sasaki, Y.; Ikuhara, Y. *J. Am. Ceram. Soc.* **2007**, *90*, 2322.
(35) Nagata, H.; Kubo, T.; Nakahira, A. *J. Ion Exchange* **2007**, *18*, 594.
(36) Yoshida, R.; Suzuki, Y.; Susumu, Y. *Mater. Chem. Phys.* **2005**, *91*, 409.
(37) Poudel, B.; Wang, W. Z.; Dames, C.; Huang, J. Y.; Kunwar, S.; Wang, D. Z.; Banerjee, D.; Chen, G.; Ren, Z. F. *Nanotechnology* **2005**, *16*, 1935.
(38) Nakamura, S.; Nakahira, A. *J. Ceram. Soc. Jpn.* **2008**, *116*, 42.
(39) Yamasaki, N.; Yanagisawa, K.; Nishioka, M.; Kanahara, M. *J Mater. Sci. Letters* **1982**, *5*, 355.
(40) Yang, J.; Jin, Z.; Wang, X.; Li, W.; Zhang, J.; Zhang, S.; Guo, X.; Zhang, Z. *Dalton Trans.* **2003**, 3898.
(41) Tsai, C. C.; Teng, H. *Chem. Mater.* **2004**, *16*, 4352.
(42) Tsai, C. C.; Teng, H. *Chem. Mater.* **2006**, *18*, 367.

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