

Nanoporous Metal Oxides Synthesized by the Nanoscale Casting Process Using Supercritical Fluids

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Nanoporous metal oxides (TiO_2 , Al_2O_3) have been synthesized using activated carbon templates with supercritical fluid solvents by using the nanoscale casting (NC) process. The precursors were dissolved in supercritical CO_2 and attached to activated carbon fibers or powders as templates. After removal of the activated carbon templates by calcination in air at 873 K or by treatment in oxygen plasma, the nanoporous TiO_2 or Al_2O_3 replicating the macroscopic shapes of the activated carbon templates was obtained. The surface area of the titania sample was $387 \text{ m}^2/\text{g}$. The titania sample crystallized in the anatase form. The alumina samples have mesopores corresponding to the graphene crystallite size of the activated carbon. The alumina samples crystallized in the γ -alumina form.

Introduction

Porous materials have been focused on due to their practical applicability for adsorption, separation, catalysis, ion exchange, and chemical sensing as well as their fundamental properties in a variety of areas including chemistry, physics, electronics, optics, material science, and biomedical science. Industrial applications in many catalytic or separation reaction processes require the control of their porous structures, crystallization, and macroscopic shapes.

Template synthesis is widely used as a route to porous materials. By using this process, porous metals,^{1–2} oxides,^{3–5} polymers,⁶ and carbon⁷ have been prepared. A forming process is generally necessary to fabricate porous materials with controlled macroscopic shapes.

We recently proposed a novel process to prepare porous materials replicating not only macroscopic shapes (e.g., fibers, granules, or powders) but also porous structures on a nanometer scale.^{8–10} In this nanoscale casting (NC) process, precursors dissolved in supercritical fluids are coated on activated carbon templates, followed by removal of the activated carbon templates, as shown in Figure 1. Supercritical fluids¹¹ have unique properties of high diffusivity and controllable solubility.

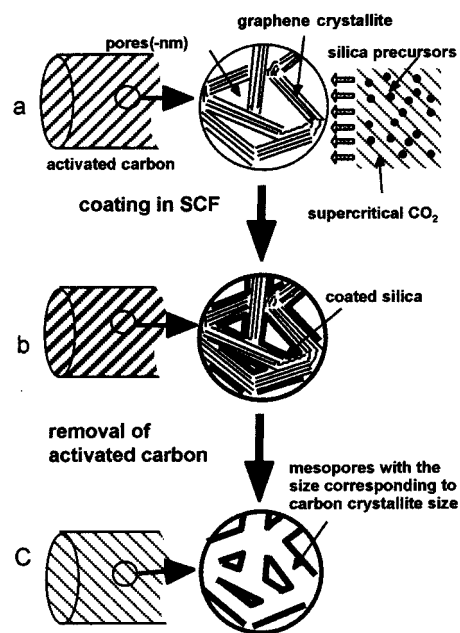


Figure 1. Schematic description of the nanoscale casting process. Randomly stacked graphene crystallites are shown in part a. Panel b shows the activated carbon template coated with SiO_2 . The surfaces of the micropores between the graphene layers are coated with SiO_2 using supercritical fluid. After removal of the activated carbon, mesopores with sizes corresponding to the size of the graphene crystallites appeared, as shown in part c.

On the basis of these properties, supercritical fluids are expected to overcome the limitation in mass transport and diffusivity of conventional solvents. The CVD process is one of the most useful methods for coating materials. However, in the CVD process, the precursors are limited to those of high volatility and thermal stability. By using the NC process, porous materials

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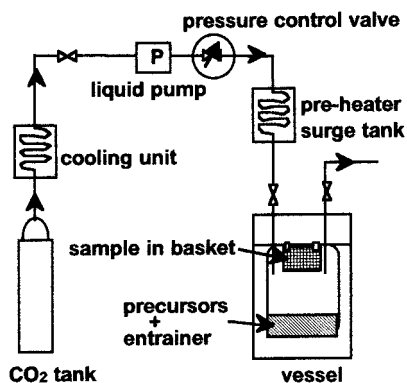


Figure 2. Diagram of the apparatus for the treatment in supercritical CO₂.

with a high surface area of Pt⁸ and SiO₂^{9–10} can be prepared. The pore size of the porous SiO₂ prepared by the NC process corresponds to the size of the graphene crystallite in the activated carbon templates. However, a faithful replication of the molecular dimensions in porous Pt prepared by the NC process appears difficult due to rearrangements by crystallization during removal of the activated carbon templates. Many industrial applications of porous metal oxides in a wide variety of reactions require crystallization.

In this study, we tried to extend the NC process for synthesis of crystallized metal oxide (TiO₂, Al₂O₃). Crystallization and structural replication in these samples are discussed. The results are compared to that of the porous Pt and SiO₂ made by the NC process. A modification of the experimental apparatus is also reported.

Experimental Section

Synthesis of Nanoporous Metal Oxides by the NC Process. *Nanoporous Titanium Oxide.* 2-Propanol (Wako Pure Chemical Industries, Ltd.) (5 mL) along with titanium isopropoxide (Wako Pure Chemical Industries, Ltd.) (5 mL) were placed in a stainless steel vessel (50 mL). A stainless steel cage with 1 g of activated carbon (BW103 Toyobo Co., Ltd.) was fixed in the upper part of the vessel so that the activated carbon template is not in contact with the 2-propanol and titanium isopropoxide in the liquid phase directly. The closed vessel was filled with solid carbon dioxide and kept at 423 K and 32 MPa for 2 h in an oil bath. After this treatment, the samples were calcined at 873 K for 6 h in air flow (8L/min.) or treated in an oxygen plasma using a Yamato Scientific oxygen plasma instrument (PC-103, RFG-500) at 500 W in flowing oxygen (160 mL/min.) for removal of the activated carbon templates.

Nanoporous Aluminum Oxide. A high-pressure vessel (1000 mL) was used for the treatment in supercritical CO₂. Figure 2 shows a diagram of the apparatus for the treatment in supercritical CO₂. CO₂ was liquefied through a cooling unit and compressed by a liquid pump. The CO₂ was preheated through a surge tank. Acetone (Wako Pure Chemical Industries, Ltd.) (30 mL) along with aluminum acetylacetonate (Al(acac)₃, Kanto Kagaku) was placed in the vessel, and 10 g of the activated carbon templates (BW103; Toyobo Co., Ltd., or M30; Osaka Gas Chemical Co.) in a stainless basket was fixed in the upper part of the vessel. Supercritical CO₂ was pumped into the vessel up to 30 MPa. The treatment temperature was regulated at 423 K by an external electric heater. After a contact time of 24 h, the pressure was released by venting. The removed samples were calcined in flowing air at 873 K for 6 h for removal of the activated carbon templates.

Analyses. The micromorphology was observed with a scanning electron microscope (SEM) using a JEOL JSM-890

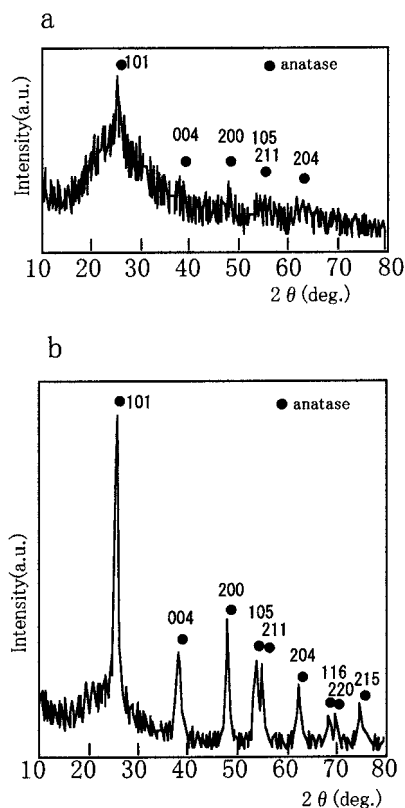


Figure 3. X-ray diffraction patterns for (a) titania sample treated in oxygen plasma, and (b) titania sample calcined in air at 873 K.

and the transmission electron microscope (TEM) images with a JEOL transmission electron microscope. The X-ray diffraction data were recorded on a Rigaku RINT-2000 using Cu K α radiation at a scanning speed of 2° (2 θ)/min within the 2 θ range of 10–80°. The nitrogen adsorption–desorption isotherms at 77 K were collected on a QUANTACROME AUTOSORP-1-MP. The samples were heated at 423 K in 10^{−6} Torr for 3 h before this measurement. The Barret–Joyner–Hallender (BJH) method was used to calculate the pore size distributions. The TGA patterns were collected on a thermogravimetric analyzer, a Rigaku Thermoplus TG8120. The samples were heated in air and the temperature rate was 2 K/min.

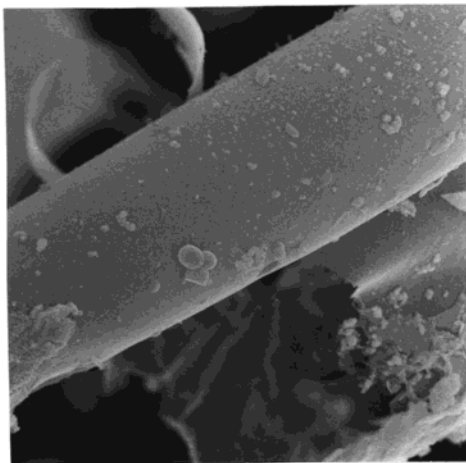
Results and Discussion

Nanoporous Titanium Oxide. As shown in Figure 3, the titania sample calcined at 873 K or treated in oxygen plasma has the characteristic XRD peaks of anatase crystals. The average crystallite sizes calculated from the XRD peaks using the Sherrer equation were 8 nm for the titania sample treated in the oxygen plasma and 15 nm for the titania sample calcined at 873 K. During the calcination at 873 K, the growth of the crystals in the anatase form proceeded, resulting in the larger crystallite size. In contrast, the treatment in oxygen plasma resulted in the smaller crystallite size.

TGA results of titania sample oxidized in plasma or calcined in air show that weight loss between 473 and 1273 K in air flow is less than 4 wt %. This confirms that no activated carbon template is left in the titania samples.

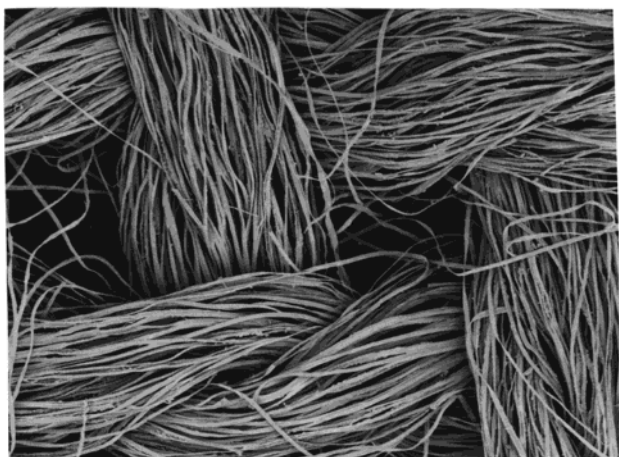
The fibrous shape of the activated carbon cloth was replicated in the titania after removal of the activated carbon template. Figure 4 shows the SEM images for

a



— 5 μm

b



— 100 μm

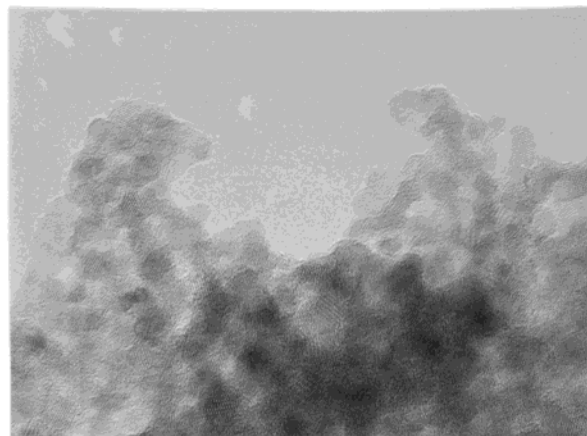
Figure 4. Scanning electron microscopy (SEM) images for (a) titania sample treated in oxygen plasma and (b) titania sample calcined in air at 873 K.

the titania samples treated in oxygen plasma or calcined at 873 K. As shown in Figure 4a, the diameter of the titania fiber treated in the oxygen plasma is 7 μm , which is almost the same as that of the activated carbon template (6–10 μm). Figure 4b illustrates that the fibrous shape of the activated carbon cloth was retained in the calcined titania sample.

The TEM micrographs of the titania sample treated in oxygen plasma or calcined at 873 K are shown in Figure 5. The crystal lattice of the titania sample treated in oxygen plasma shows the crystallized domains with a size of 5–15 nm. This value is consistent with the crystallite size calculated from the XRD peaks. The particle sizes in the titania sample calcined at 873 K are 20–80 nm. This value is larger than that calculated from the XRD peaks. This would be due to the anisotropy or polycrystal particles observed in the TEM image.

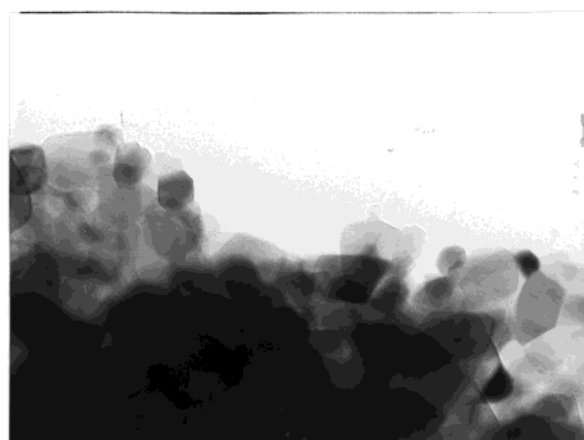
The BET surface areas calculated from the nitrogen adsorption isotherms were 387 m^2/g for the titania sample treated in oxygen plasma and 61 m^2/g for the

a



— 20nm

b



— 50nm

Figure 5. Transmission electron microscopy (TEM) images for (a) titania sample treated in oxygen plasma and (b) titania sample calcined in air at 873 K.

titania sample calcined at 873 K. The calcination at 873 K collapsed the porous structures in the titania sample, yielding the smaller surface area. The value of the BET surface area for the titania treated in oxygen plasma is almost the same as that expected from the silica sample synthesized by the NC process, taking into account the difference in the density between the silica and titania. The temperature of the sample during the treatment in oxygen plasma was below 453 K. The porous structures of the activated carbon template are well-replicated in the titania sample treated in oxygen plasma.

Nanoporous Aluminum Oxide. Figure 6 shows the XRD patterns of the alumina samples calcined in air at 873 K after the treatment in supercritical CO_2 . The diffraction peaks from γ -alumina can be confirmed in both cases using BW103 activated carbon fibers template and M30 activated carbon powders template. The broad peaks from the alumina samples imply a low crystallinity, signifying a significant degree of structural disorder.

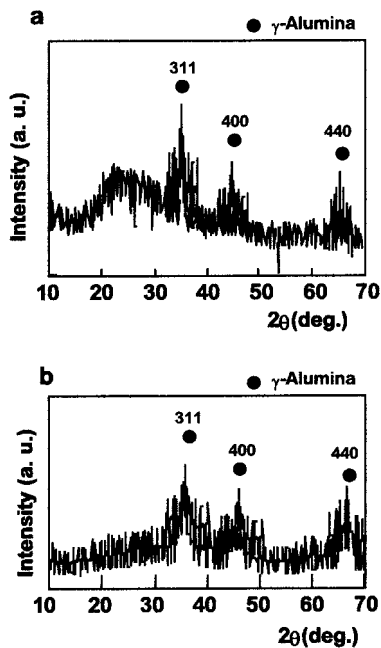


Figure 6. X-ray diffraction patterns for (a) alumina sample prepared with BW103 activated carbon fibers and (b) alumina sample prepared with M30 activated carbon powders.

The SEM images of the alumina samples calcined in air at 873 K after the treatment in supercritical CO_2 are shown in Figure 7. The fibrous shape of the cloth of BW103 activated carbon templates was replicated in the alumina sample, as shown in Figure 7a. The texture of the cloth of the alumina sample is slightly finer than that of the activated carbon templates. The diameter of the alumina fibers is $5 \mu\text{m}$. This value is slightly smaller than that of the activated carbon templates ($6\text{--}12 \mu\text{m}$). As seen in Figure 7c, the spherical shape of M30 activated carbon template can also be replicated in the alumina sample. The alumina sphere sample with a $13 \mu\text{m}$ diameter was slightly smaller when compared with the original activated carbon spherical template of $15\text{--}25 \mu\text{m}$ diameter. As seen in Figure 7a–c, a slight shrinkage in the alumina samples can be observed. During the treatment in supercritical CO_2 , the alumina precursors dissolved in supercritical CO_2 were carried into the pores of the activated carbon and were polymerized through the reaction with water molecules and functional units on the surface of the activated carbon templates. During the calcination process at 873 K, the polycondensed alumina structures crystallized into γ -alumina with a slight shrinkage.

Figure 8 shows the nitrogen adsorption–desorption isotherms for the alumina samples after the removal of BW103 activated carbon template and M30 activated carbon powders template. The uptake at low relative pressures is due to the micropore filling and the monolayer coverage of the mesopores. The increase in the adsorbed volume at relative pressures above 0.4 is accounted for by the filling of the mesopores. Hysteresis loops are present in both isotherms for the alumina samples. The BET surface areas were calculated from the nitrogen adsorption isotherms. The BET surface area values of the alumina samples were 332 and $249 \text{ m}^2/\text{g}$ for the sample synthesized using M30 and BW103 activated carbon template, respectively. Figure 9 shows

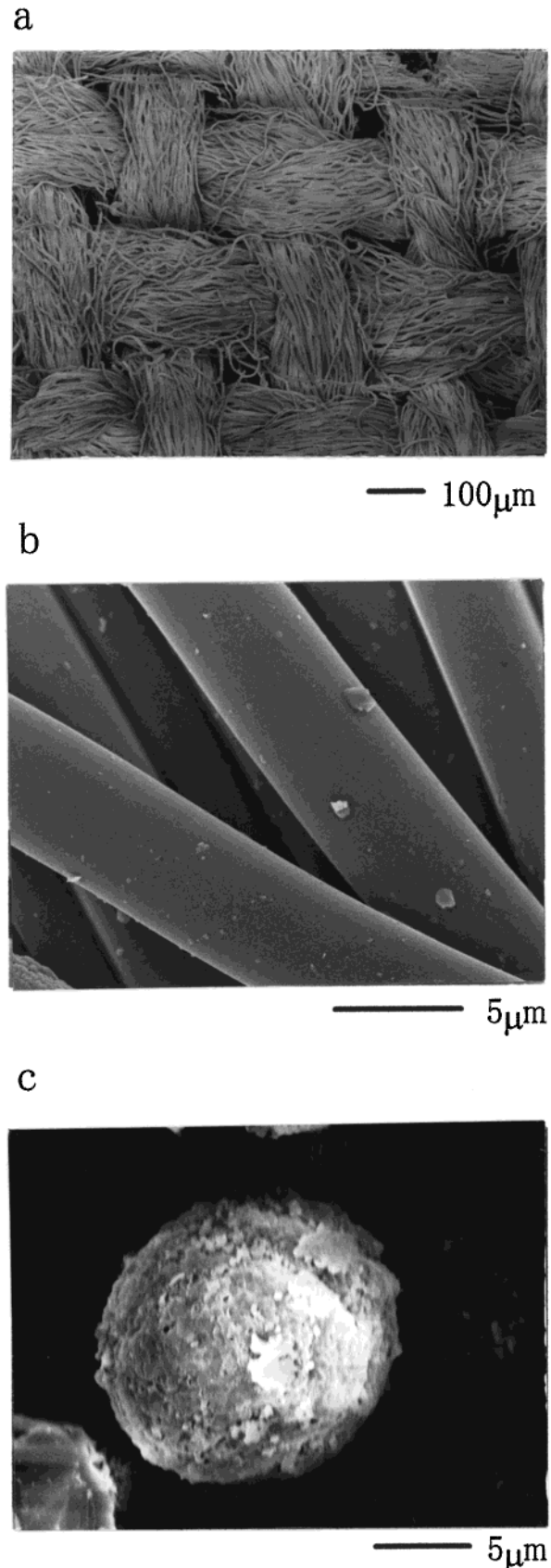


Figure 7. Scanning electron microscopy (SEM) images for (a, b) alumina sample prepared with BW103 activated carbon fibers as templates and (c) alumina sample prepared with M30 activated carbon powders.

the pore size distributions of the alumina samples calculated by the BJH method from the nitrogen sorp-

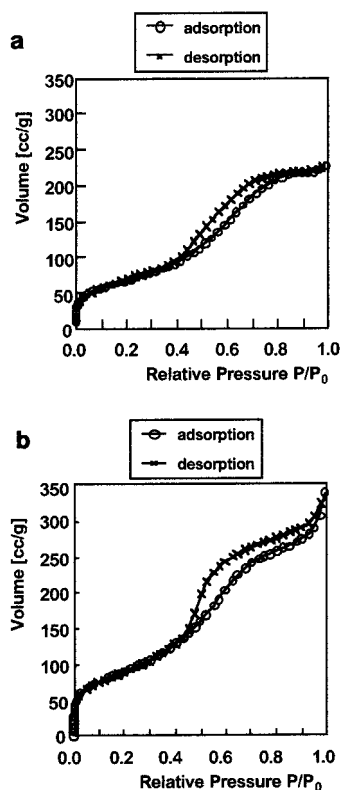


Figure 8. Nitrogen adsorption–desorption isotherms for (a) alumina sample prepared with BW103 activated carbon fibers and (b) alumina sample prepared with M30 activated carbon powders.

tion isotherms. The results of the porosity, BET surface areas, pore diameter, and total pore volume are summarized in Table 1. The mesopore sizes of the alumina samples are almost the same as those of the silica samples prepared by the NC process. The pore size in the alumina samples corresponds to the graphene crystallite size in the activated carbon templates, as is the case for the SiO_2 samples prepared by the NC process.^{9,10} The surface area of the alumina sample prepared with M30 was half of that expected on the basis of the silica samples prepared by the NC process taking into account the difference in the density of the alumina and silica. The pore volumes of the alumina samples were smaller than that of the silica samples prepared by the NC process (1.7 mL/g). The XRD results show that the alumina samples crystallize into γ -alumina. The crystallization procedure in the alumina samples results in the collapse such that the alumina samples have smaller pore volumes and smaller surface areas. The broad XRD peaks from γ -alumina imply smaller crystallite sizes. Alumina is transformed into α -alumina above 1273 K. During the calcination process at 873 K, the crystallites of γ -alumina in the samples did not significantly grow and mesopores corresponding to the size of the graphene crystallites in the activated carbon templates still remained. The crystal sizes are finer than that for the porous Pt^8 and titania prepared

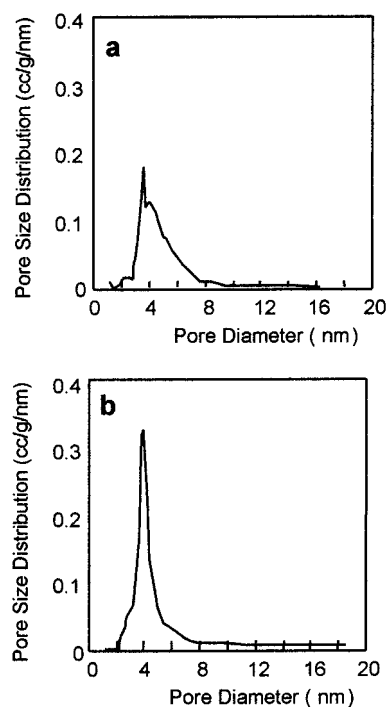


Figure 9. Pore size distributions calculated by the BJH method from nitrogen adsorption–desorption isotherms for (a) alumina sample prepared with BW103 activated carbon fibers and (b) alumina sample prepared with M30 activated carbon powders.

Table 1. Results of the Nanoporous Alumina Porosity Prepared by the NC Process: BET Surface Areas, Pore Diameter, and Total Pore Volume

	activated carbon template	BET surface area, m^2/g	pore diameter, nm	total pore volume, mL/g
a	BW103	249	3.6	0.35
b	M30	332	3.9	0.53

by the NC process. By using the NC process, crystallized porous materials replicating fine structures on a nanometer scale could be synthesized.

Conclusions

Nanoporous titania and alumina were prepared by the nanoscale casting process. The surface area of the titania sample was $387 \text{ m}^2/\text{g}$. The titania sample crystallized in the anatase form. Nanoporous alumina with mesopores corresponding to the size of the graphene crystallite in the activated carbon templates crystallized into γ -alumina. By the NC process, crystallized porous materials replicating fine structures in molecular dimensions can be prepared. The NC process is a promising route to the synthesis of a wide variety of porous materials.

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