864 *Chem. Mater.* **2006,** *18,* 864−866

Phase-Separation-Induced Titania Monoliths with Well-Defined Macropores and Mesostructured Framework from Colloid-Derived Sol−Gel Systems

Junko Konishi,[†] Koji Fujita,*[,†] Kazuki Nakanishi,[‡] and Kazuyuki Hirao[†]

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan, and Division of Chemistry, Graduate School of Science, Kyoto University, Oiwake-cho, Kitashirakawa, Sakyo-ku, Kyoto 606-8502, Japan

Received September 26, 2005
Revised Manuscript Received November 18, 2005

Titania has attracted considerable attention because of its potential uses in diverse areas such as photocatalysis[1], sensor devices[2], electrode materials[3], chromatographies[4], and optical devices[5]. The performance of these devices can be dramatically improved by structural control over the nanometer to micrometer ranges. A key step in the synthesis of transition metal oxide with well-defined porous structure continues to be the use of organic templates that spatially pattern the deposition of the corresponding alkoxide or colloidal suspensions. For instance, mesoporous titania can be prepared by using self-organized arrays of long-chain surfactants or amphiphilic block copolymers as the templates.[6] Stabilized-emulsion or latex-sphere templating has been shown to extend the pore size up to several micrometers.[7] In applications that utilize liquid-phase reactions such as catalyst supports, macroporous structures with mesotexture are highly desirable, because the interconnected macroporous channel facilitates the material transport to mesoporous internal regions where the reactions can take place. Dual templating techniques using surfactants and latex spheres can produce titania with bimodal pore size distribution.[8] Recent reports demonstrated that macro-mesoporous structures can be realized in the presence of a single surfactant[9] and even under a template-free condition.[10]

Despise the drastic progress in the synthesis of porous inorganic materials, however, the integration of porous structure into large monoliths still remains a challenging task; templating approaches ensure the formation of well-defined porous structures, but three-dimensional structural buildup of inorganic network, including the morphological control, is difficult to achieve in parallel. Only a few techniques have been reported to obtain the bimodal pore structure in a titania monolith with dimensions of several centimeters.[11]

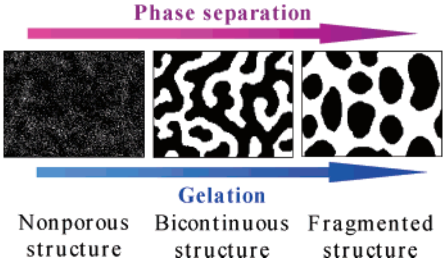

Figure 1. Schematic illustration of the coarsening of phase-separated domains. The bicontinuous structure is obtained by inducing the phase separation in parallel to the gelation.

In this paper, we demonstrate a simple and reproducible method based on the sol−gel route accompanied by the phase separation, which enables the fabrication of titania monoliths with well-defined macropores and accessible mesostructure. Special attention is paid to the systematic control of macroporous structures as well as the spontaneous formation of completely interconnected macroporous morphology. A lot of benefits are expected to arise not only from the pore structures integrated in monoliths but also from the novel functions of titania.

The sol−gel process on the basis of polymerization-induced phase separation has been proven successful for designing well-defined macroporous monoliths in various silica-based systems.[12] The bicontinuous structure, in which each separated phase is interconnected in three-dimensional space, is spontaneously formed when the transient structure of the phase separation is frozen by the sol−gel transition. Time evolution of the transient structure of the phase separation is schematically illustrated in Figure 1. The characteristic size of the bicontinuous structure, or domain size, is defined by the sum of the thickness of the gel-phase domain and the width of the solvent-phase domain, the latter of which becomes macropores after drying. The formation of phase domains in the course of the phase separation includes the coarsening process in which the domain size grows from shorter to larger length scale as time elapses. Consequently, the gel morphology is determined by the proceeding of the phase separation relative to the sol−gel transition. It has been well-accepted that the silica gels with bicontinuous structure exhibit much better performance than conventional particle-packed structure in high performance liquid chromatography (HPLC) separations.[13] The monolithic

---

[*] Corresponding author. E-mail: fujita@dipole7.kuic.kyoto-u.ac.jp. Tel.: +81-75-383-2432. Fax: +81-75-383-2420.
[†] Graduate School of Engineering.
[‡] Graduate School of Science.

(1) Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37.
(2) Göpel, W.; Kirner, U.; Wiemhöfer, H. D.; Rocker, G. *Solid State Ionics* **1998**, *28−30*, 1423.
(3) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.
(4) Pinkse, M. W. H.; Uitto, P. M.; Hilhorst, M. J.; Ooms, B.; Heck, A. J. R. *Anal. Chem.* **2004**, *76*, 3935.
(5) Imfof, A.; Pine, D. J. *Nature* **1997**, *389*, 948.
(6) (a) Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D.; *Nature* **1998**, *396*, 152. (b) Wang, H.; Oey, C. C.; Djurišić, A. B.; Xie, M. H.; Leung, Y. H.; Man, K. K. Y.; Chan, W. K.; Pandey, A.; Nunzi, J. M.; Chui, P. C. *Appl. Phys. Lett.* **2005**, *87*, 023507.
(7) (a) Davis, S. A.; Burkett, S. L.; Mendelson, N. H.; Mann, S. *Nature* **1997**, *385*, 420. (b) Holland, B. T.; Blanford, C. F.; Stein, A. *Science* **1998**, *281*, 538. (c) Wijnhoven, J. E. G. J.; Vos, W. L. *Science* **1998**, *281*, 802. (d) Wang, D.; Caruso, R. A.; Caruso, F. *Chem. Mater.* **2001**, *13*, 364.
(8) Holland, B. T.; Blanford, C. F.; Do, T.; Stein, A. *Chem. Mater.* **1999**, *11*, 795.
(9) (a) Antonelli, D. M. *Microporous Mesoporous Mater.* **1999**, *33*, 209. (b) Yuan, Z.-Y.; Vantomme, A.; Léonard, A.; Su, B.-Li. *Chem. Commun.* **2003**, *13*, 1558. (c) Yuan, Z.-Y.; Ren, T. Z.; Su, B.-L. *Adv. Mater.* **2003**, *15*, 1462. (d) Deng, W.; Toepke, M. W.; Shanks, B. H. *Adv. Funct. Mater.* **2003**, *13*, 61. (e) Blin, J. L.; Léonard, A.; Yuan, Z.-Y.; Gigot, L.; Vantomme, A.; Cheetham, A. K.; Su, B.-L. *Angew. Chem., Int. Ed.* **2003**, *42*, 2872. (f) Carn, F.; Colin, A.; Achard, M.-F.; Deleuze, H.; Sanchez, C.; Backov, R. *Adv. Mater.* **2004**, *16*, 140. (g) Morris, M. A.; Reidy, H. M. *Ceram. Int.* **2005**, *31*, 929.
(10) Collins, A.; Carriazo, D.; Davis, S. A.; Mann, S. *Chem. Commun.* **2004**, *5*, 568.
(11) (a) Carn, F.; Colin, A.; Achard, M.-F.; Deleuze, H.; Sanchez, C.; Backov, R. *Adv. Mater.* **2005**, *17*, 62. (b) Toberer, E. S.; Seshadri, R. *Adv. Mater.* **2005**, *17*, 2244.
(12) Nakanishi, K. *J. Porous Mater.* **1997**, *4*, 67.

10.1021/cm052155h CCC: $33.50

Table 1. Calculated Starting Compositions of the TiO_2−PEO−Formamide−Nitric Acid−Water System

sample	content [g]					fraction of TiO_2 [wt %]
	TiO_2	PEO	formamide	HNO_3	H_2O	
P1-215	1.98[a]	w_{PEO} (M_v = 100 000)	1.16	0.177[b]	5.84[c]	21.5
P3-215	1.98[a]	w_{PEO} (M_v = 300 000)	1.16	0.177[b]	5.84[c]	21.5
P10-215	1.98[a]	w_{PEO} (M_v = 1 000 000)	1.16	0.177[b]	5.84[c]	21.5
P3-215	1.98[a]	w_{PEO} (M_v = 300 000)	1.16	0.322[b]	9.26[c]	15.5

[a] The amount of titania in the aqueous colloidal titania. [b] The sum of the amount of nitric acid in the aqueous colloidal titania and that was separately added in the process of gel preparation. [c] The sum of the amount of water in the aqueous colloidal titania and that was separately added in the process of gel preparation.

column with large through-pores leads to lower back pressure and shorter separation time. At the same time, the mesopores on the surface of the monolithic skeleton gain the surface area required for the chromatographic adsorption−desorption process. If the stationary phase of HPLC columns could be made of titania, they would be extremely effective in the field of biochemistry, because titania selectively adsorbs phosophorylated peptides.[4] Despite such potential applications, however, the sol−gel process accompanied by the phase separation has not been extended to metal oxide systems other than silica-based systems. This is because the corresponding alkoxides are highly reactive toward hydrolysis and polycondensation compared with silicon alkoxides, which makes it hard to control the gelation accompanied by the phase separation. To avoid this problem, aqueous colloidal titania (Ishihara Sangyo Kaisha, Ltd., particle diameter ∼7 nm, anatase type) was used as a titania source.

Table 1 shows the starting compositions of gels prepared in this study. Poly(ethylene oxide) (PEO) having viscosity-average molecular weights (M_v) of 100 000 (P1), 300 000 (P3), and 1 000 000 (P10) was used to induce the phase separation. Hereafter, the content of PEO (unit: g) will be denoted as w_{PEO}. Starting from a homogeneous mixture of the listed components, the phase separation and gelation take place spontaneously in a closed and static condition at a constant temperature (40 °C). In the strongly acidic aqueous solutions used here, titania particles are positively charged and stably dispersed by the electrostatic repulsion, because the isoelectric point of titania is pH = 5.5−6.0.[14] Formamide, which is hydrolyzed to yield ammonia in the presence of strong acid, raises the pH in the mixture gradually, facilitating the gelation as a result of the particles aggregation due to the reduction of electrostatic repulsion. For all the compositions, the solution pH is below 0.5 immediately after mixing all the reagents, monotonically increases with time, and approaches 2 after about 30 min. The gelation occurs in the range of pH = 1.5−2.0, depending on the starting composition. On the other hand, the phase separation is driven by the reduction of miscibility between the solvent mixture and PEO chains adsorbed on titania particles, and the initially homogeneous mixture separates into solvent-rich and titania-rich phases.[15] Depending on the timing of the gelation relative to the onset of phase separation, various morphologies can be obtained. Figure 2a−d shows four specific morphologies of titania gels prepared from the P3-215 system with varied PEO contents. When the amount of PEO is too small, the resultant gels are nonporous in the micrometer range (Figure 2a) because the phase separation does not effectively take place until structural freezing due to the sol−gel transition. The bicontinuous structures (Figure 2b) can be obtained in a limited compositional range near w_{PEO} = 0.040. One can readily obtain monolithic titania gels in large dimensions (up to 5 × 5 × 15 mm) as shown in the inset of Figure 2b. The domain size of bicontinuous structure becomes larger as the PEO concentration is increased, as shown in Figure 2b,c. This result reflects the enhanced phase-separation tendency, that is, the earlier onset of the phase separation relative to the sol−gel transition. A close look at Figure 2c also reveals the existence of small particles in the macropore. This kind of morphology is often observed as a result of the secondary phase separation of the solvent-rich phase.[16] Further addition of PEO significantly enhances the phase-separation tendency, and, hence, the gel networks are fragmented in the process of the phase separation (Figure 2d).

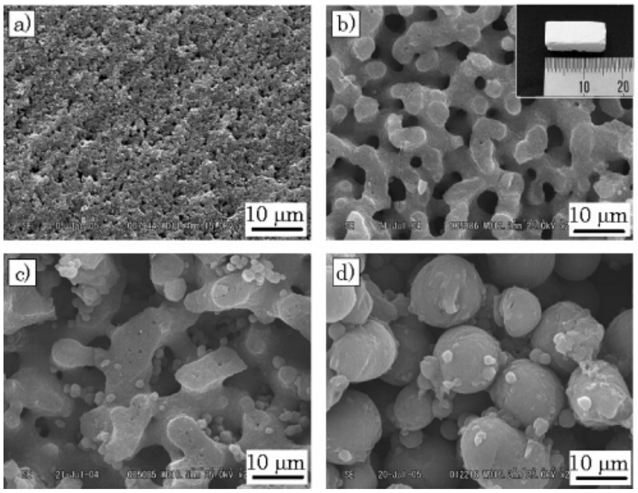

Figure 2. SEM images of dried P3-215 gels prepared with varied PEO amounts: (a) w_{PEO} = 0.025, (b) w_{PEO} = 0.040, (c) w_{PEO} = 0.045, and (d) w_{PEO} = 0.080. Inset of part b: digital picture of a large-dimension monolithic titania gel with bicontinuous structure.

Figure 3a shows the dependence of the resultant morphologies on the viscosity average molecular weight (M_v) and content of PEO (w_{PEO}). As M_v becomes larger, the bicontinuous structure tends to be formed at lower w_{PEO}, as a result of the enhanced phase-separation tendency.[12] Here, it is worth emphasizing that the degree of the connectivity of the continuous gel skeleton is higher in the P3 systems with M_v = 30 000 as shown in Figure 2b, compared to that in the P1 systems with M_v = 10 000 as we previously reported;[15] the gel skeleton of the P1 systems showed loose connectivity or partial fragmentation (see Figure S1 of the Supporting Information). The use of P3 with larger M_v can provide the viscosity for the gel phase enough to withstand the fragmentation during the coarsening process of the phase separation, which increases the connectivity and thus makes the pore size distribution sharper.

Control over a wide range of the size and volume of continuous macropores is achieved by adjusting the w_{PEO} and the concentration of colloidal titania in staring solutions (Figure 3b). When the concentration of colloidal titania is kept constant, both the pore size and the volume increase

---

(13) Tanaka, N.; Kobayashi, H.; Nakanishi, K.; Minakuchi, H.; Ishizuka, N. *Anal. Chem.* **2001**, *73*, 420A.

(14) (a) Kallay, N.; Zalac, S.; Stefanic, G. *Langmuir* **1993**, *9*, 3457. (b) Kosmulski, M.; Gustafsson, J.; Rosenholm, B. J. *J. Colloid Interface Sci.* **1999**, *209*, 200.

(15) (a) Konishi, J.; Fujita, K.; Nakanishi, K.; Hirao, K. *Mater. Res. Soc. Symp. Proc.* **2004**, *788*, 391. (b) Fujita, K.; Konishi, J.; Nakanishi, K.; Hirao, K. *Appl. Phys. Lett.* **2004**, *85*, 5595.

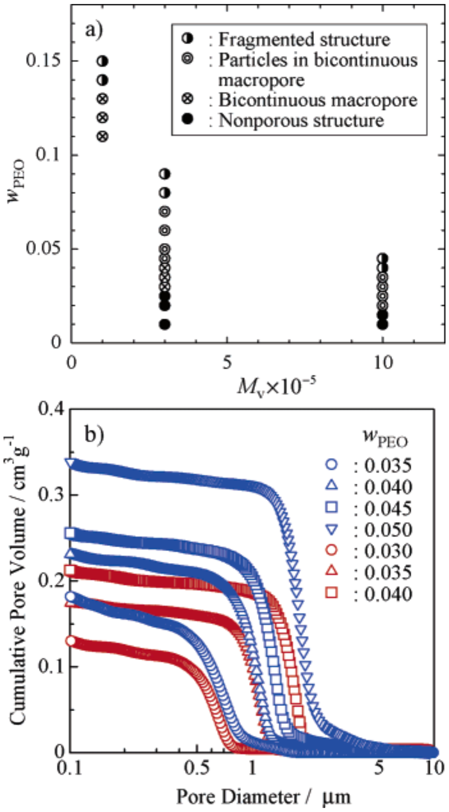

Figure 3. (a) Dependence of resultant morphologies on the viscosity average molecular weight (M_v) and content of PEO (w_{PEO}). (b) Pore size distribution of heat-treated gels measured by the mercury intrusion method; red symbols denote P3-215 gels prepared with varied w_{PEO}, and blue symbols denote P3-155 gels prepared with varied w_{PEO}.

with an increase in w_{PEO}. The variation of pore size with w_{PEO} is due to the enhanced phase-separation tendency as mentioned above, while the change in pore volume may be caused by the compositional variation between the titania-rich and solvent-rich phases in the course of the development of the phase separation, which is characteristic of the intermediate stage of phase separation.[17] The shrinkage of the PEO-adsorbed gel skeleton, which is induced by the solvent exchange and subsequent evaporation drying after the gelation, also contributes to the change in the pore volume. Thus, by selecting adequately the concentration of colloidal titania, which mainly controls the pore volume, one can produce titania monoliths with almost the same pore size but different pore volumes, as shown in Figure 3b; for instance, P3-155 prepared with $w_{PEO} = 0.050$ and P3-215 with $w_{PEO} = 0.040$ have almost the same pore diameter, but their pore volumes are different from each other. Similar relations are observed between P3-155 prepared with $w_{PEO} = 0.040$ and P3-215 with $w_{PEO} = 0.035$ and between P3-155 with $w_{PEO} = 0.035$ and P3-215 with $w_{PEO} = 0.030$. We also confirmed that other parameters such as acid concentration and reaction temperature alter the timing of gelation relative to the onset of the phase separation, which allows one to control the domain size of the gels, that is, pore size.

The resultant titania gels possess the mesoporous structures in addition to the macroporous structures. Figure 4a depicts a field-emission scanning electron microscope (FE-SEM) image of dried P3-215 gel. The gel skeleton is composed of randomly aggregated nanoparticles. The X-ray diffraction (XRD) pattern revealed the single phase of anatase-type titania, reflecting the crystalline structure of colloidal titania used as the starting materials (see Figure S2 of the Supporting Information). The crystalline size estimated by Scherrer's equation was about 10 nm, which is consistent with the primary particles size of colloidal titania. A representative N_2 adsorption−desorption isotherm and its corresponding Barret−Joyer−Harenda (BJH) pore size distribution (obtained from an analysis of the adsorption branch of the isotherm) is shown in Figure 4b for the dried P3-215 gel. The isotherm is type IV, and its shape is typical for mesopores composed of the interstices of aggregated nanoparticles. The pore size distribution exhibits a broad distribution of mesopore with diameters of 10−50 nm, and the Brunauer−Emmet−Teller (BET) surface area is as high as 350 m^2 g^{-1}. These mesopores are readily accessible from open macroporous channels.

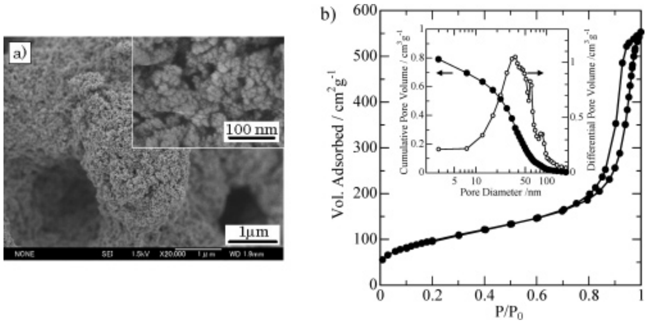

Figure 4. (a) FE-SEM image of P3-215 prepared with $w_{PEO} = 0.035$. Inset of part a: higher magnification image of the gel skeleton. (b) Nitrogen adsorption−desorption isotherm for P3-215 prepared with $w_{PEO} = 0.035$. Inset of part b: BJH pore size distribution.

In conclusion, we have described a simple and facile synthetic method to fabricate titania monoliths with well-defined macropores and a mesostructured skeleton. A remarkable feature of our method is the ability to produce macroporous monoliths via a spontaneous chemical process, without the aid of templates. This synthetic approach allows one to tailor the size and volume of macropores by adjusting the starting composition. Another feature is the ability to directly use nanocrystalline colloidal oxides particles. This makes it possible to produce well-defined macroporous monoliths with a crystalline framework without resorting to high-temperature treatment. The ease, reproducibility, and versatility of the present technique will facilitate the development of hierarchical macro-mesoporous monoliths based on transition metal oxides and open up the possibility of applications in diverse areas such as catalysis, biomolecular separations, and chromatographic supports.

Acknowledgment. This study was financially supported by the Industrial Technology Research Grant Program ('04A25023) from New Energy and Industrial Technology Development Organization (NEDO), Japan, and the Grant-in-Aid for Scientific Research (15206072) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. J.K. thanks the Grant-in-Aid for Fellow of Japan Society of the Promotion Science.

Supporting Information Available: Details about the experimental procedure, the comparison of macroporous morphologies between P1-T215 gels and P3-T215 gels by SEM, and the XRD pattern (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM052155H

---

(16) Nakanishi, K.; Soga, N. *J. Am. Ceram. Soc.* **1991**, *74*, 2518.
(17) Tanaka, H. *J. Phys.: Condens. Matter* **2000**, *12*, R207.