Inorganic Chemistry

Article

Impact of Growth Kinetics on Morphology and Pore Structure of TiO$_2$—One-Pot Synthesis of Macroporous TiO$_2$ Microspheres

Ziyi Zhong,*,[†] Fengxi Chen,[†] Thiam-Peng Ang,[†] Yifan Han,[†] Weiqiang Lim,[†] and Aharon Gedanken*,[‡]

Institute of Chemical Engineering and Sciences, 1 Pesek Road, Jurong Island, Singapore 627833, and Department of Chemistry and Kanbar Laboratory for Nanomaterials, Bar-Ilan University Center for Advanced Materials and Nanotechnology, Bar-Ilan University, Ramat-Gan 52900, Israel

Titanium dioxide was synthesized by the hydrolysis of titanium tetraisopropoxide (TTIP) in the presence of acetic acid, 2-propanol, and organic amines (octylamine, aniline, and isobutylamine). H$_2$O was supplied by an esterification reaction between acetic acid and 2-propanol (denoted as H$_2$Oe), and/or by intentionally adding it (denoted as H$_2$Oa). It was found that the quantity of H$_2$Oa plays a crucial role in the morphology and porous structure of the final TiO$_2$ product. Without the addition of H$_2$Oa, 1D and porous TiO$_2$ was synthesized. With the addition of H$_2$Oa, and when the H$_2$Oa:TiO$_2$ molar ratio was in the range of 1:1 to 60:1, macroporous TiO$_2$ microspheres possessing a large surface area and high thermal stability were obtained. When the H$_2$Oa:TiO$_2$ molar ratio exceeded 60:1, porous TiO$_2$ with an irregular shape was formed. The variation in the morphology and porous structure is attributed to the manipulation of the growth kinetics by the addition of water.

Introduction

Titanium dioxide (TiO$_2$) has a variety of applications in photocatalysis,[1] heterogeneous catalyst support,[2] sensors,[3] and ductile ceramics.[4] The technological potential of TiO$_2$ is expected to be remarkably extended if the particle morphology, crystalline phase state, and dimensions can be tuned, as the properties and performances of TiO$_2$ often depend on these factors.[5] For example, low quantum yields in photocatalysis are observed for spherical nanocrystals of TiO$_2$ below 10 nm, because of the significant possibility for bulk recombination among electrons (e$^-$) and holes (h$^+$), whereas for 1D nanorods of TiO$_2$, a lower e$^-$/h$^+$ recombination probability is obtained because delocalization of the carriers

is higher in rods.[6] For catalysis application, the ideal material of TiO$_2$ should be porous and highly crystalline and should have a high surface-to-volume ratio. Mesoporous TiO$_2$ was first prepared in 1995 using alkyl phosphate as a surfactant.[7] Later, phosphorus-free processes for the synthesis of mesoporous TiO$_2$ were developed using organic amine surfactants,[8] block copolymers,[9] or cationic surfactants[10] as structure-directing agents, because it is difficult to remove the phosphorus from the TiO$_2$ product, which limits its application in catalysis. For biomedical and pharmaceutical applications, e.g., transferring and delivering some large drug molecules, biomolecules, and cells, macroporous materials[11] are desired. We first fabricated macroporous, ordered 3D TiO$_2$ hollow spheres by templating against the crystalline lattices of monodispersed polymer beads.[12] However, in this

---

(1) (a) Pelizzetti, E.; Serpone, N., Eds. *Photocatalysis: Fundamentals and Applications*; Wiley: New York, 1989. (b) Wang, X. C.; Yu, J. C.; Yip, H. Y.; Wu, L.; Wong, P. K.; Lai, S. Y. *Chem.—Eur J.* **2005**, *11*, 2997.

(2) (a) Haruta, M.; Yamada, N.; Kobayashi, T.; Iijima, S. *J. Catal.* **1989**, *115*, 301. (b) Valden, M.; Lai, X.; Goodman, D. W. *Science* **1998**, *281*, 1647.

(3) (a) Wang, R.; Hashimoto, K.; Fijishima, A. *Nature* **1997**, *388*, 431. (b) Travers, E.; Gusmano, G.; Gnappi, G.; Monternero, A. *Sens. Actuators, B* **1996**, *31* (1−2), 59.

(4) Karch, J.; Birringer, R.; Gleiter, H. *Nature* **1987**, *330*, 556.

(5) Cozzoli, P. D.; Kornowski, A.; Weller, H. *J. Am. Chem. Soc.* **2003**, *125*, 14539.

(6) (a) Zhang, Z.; Wang, C. C.; Zakaria, R.; Ying, J. R. *J. Phys. Chem. B* **1998**, *102*, 10871. (b) Kominami, H.; Muratami, S.; Kato, J.; Kera, Y.; Ohtani, B. *J. Phys. Chem. B* **2002**, *106*, 10501.

(7) Antonelli, D. M.; Ying, J. Y. *Angew. Chem., Int. Ed.* **1995**, *34*, 2014.

(8) (a) Antonelli, D. M. *Microporous Mesoporous Mater.* **1999**, *121*, 7302. (b). Wang, Y.; Tang, X.; Yin, L.; Huang, W.; Hacohen, Y. R.; Gedanken, A. *Adv. Mater.* **2000**, *12*, 1183.

(9) Yang, P. D.; Zhao, D. Y.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Nature* **1998**, *396*, 152.

(10) On, D. T. *Langmuir* **1999**, *15*, 8561.

(11) Peppas, N. A.; Huang, Y.; Torres-Lugo, M.; Ward, J. H.; Zhang, J. *Annu. Rev. Biomed. Eng.* **2000**, *2*, 9.

(12) Zhong, Z. Y.; Yin, Y.; Gates, B.; Xia, Y. *Adv. Mater.* **2000**, *12* (3), 206.

---

method, expensive polymer beads are sacrificed, and the prepared TiO_2 hollow spheres cannot stand high-temperature calcination (>300°C). Thus, interest in the synthesis of macroporous TiO_2 without sacrificing core materials has been motivated.

In industry, TiO_2 is mainly produced by the so-called sulfate and chloride processes. These processes are quite complicated, and in the latter one, the requirements for equipment and materials are very demanding because of the high reaction temperature (>1400 °C) and the release of highly corrosive Cl_2.[13] Using Ti alkoxide as a starting material is amenable for the production of high purity TiO_2 both in composition and in phase, if the thermal treatment steps are carefully controlled.[14] However, the process requires several time-consuming steps that should be carefully selected. For the one-pot synthesis of TiO_2 with good control of size, shape, and porous structure, the difficulty arises from the very fast hydrolysis and condensation of Ti alkoxides. As a result, a massive precipitation of amorphous TiO_2 is generally accompanied by the uncontrolled branching of the resulting Ti−O−Ti network,[5,15] or the guided growth becomes difficult. By controlling the hydrolysis of titanium alkoxide via coupling with an esterification reaction between acetic acid and 2-propanol, we recently succeeded in synthesizing one-dimensional and mesoporous TiO_2 nanostructures.[16] During synthesis, the hydrolysis and condensation of TiO_2 were slowed and well-separated by controlling the water supply, thus surfactant-guided (organic amine) unidirectional growth was achieved. In this report, we try to further manipulate the growth kinetics of TiO_2 by providing additional water besides the supply from the esterification reaction. We improved the synthetic procedures by increasing the organic amine concentration 3−10-fold, after which a certain quantity of deionized (DI) H_2O was added to initiate the formation of some small titanate particles prior to hydrothermal treatment. We found that the amount of H_2Oa plays a crucial role in the final morphology and the porous structure of the formed TiO_2. Through this improvement, the impact of growth kinetics on TiO_2 morphology and the pore structure is revealed.

Experimental Section

All chemicals were used as received. Acetic acid (>99.9%), titanium tetraisopropoxide (TTIP), octylamine, aniline, and isobutylamine were purchased from Aldrich. In a typical synthesis, 20 mL of high-purity acetic acid was put in a screw-capped autoclave containing a Teflon liner. TTIP (300 μL, 1.0 mmol) was dissolved in 1.0 mL of 2-propanol under stirring until a transparent solution was observed. The TTIP solution was then transferred to the Teflon liner, and 0.5 mL of octylamine was added. Finally, 1.0 mL of DI H_2O was added and a milky solution was obtained. The autoclave was held at 100 °C for 3−4 h. After the reaction, the

(13) Cheng, H.; Ma, J.; Zhao, Z.; Qi, L. *Chem. Mater.* **1995**, *7*, 663.
(14) Smarsly, B.; Grosso, D.; Brezesinski, T.; Pinna, N.; Boissière, C.; Antoniette, M.; Sanchez, C. *Chem. Mater.* **2004**, *16*, 2948.
(15) Murakami, Y.; Matsumoto, T.; Takasu, Y. *J. Phys. Chem. B* **1999**, *103*, 1836.
(16) Zhong, Z. Y.; Ang, T. P.; Luo, J.; Gan, H.; Gedanken, A. *Chem. Mater.* **2005**, *17*, 6814−6818.

precipitate was washed with acetone or anhydrous ethanol by centrifuge and dried in vacuo at 100 °C. The shape and size of the TiO_2 samples were observed on a transmission electron microscope (TEM, Tecnai TF20 Super Twin, 200kV) and scanning electron microscope (SEM, JEOL-6700F). The powder XRD analysis was conducted on a Bruker D8 Advance X-ray diffractometer with Cu Kα1 radiation, and the identification of crystal phases was carried out using a JCP data basis. The surface area was measured at 77 K (liquid nitrogen) on a Quantachrome Autosorb-6B surface area and pore size analyzer. The average pore size and surface area were determined on the basis of the Brunauer−Emmett−Teller (BET) model of adsorption. The thermal analysis (thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)) was performed on an SDT 2960 instrument under air flow. For TG analysis, as-prepared TiO_2 was used, whereas for DSC analysis, the sample was pretreated at 300 °C for 1 h.

Results and Discussion

Figure 1 shows TEM images of TiO_2 nanostructures. Similar to our previous observation,[16] when water was supplied solely from the esterification reaction between acetic acid and 2-propanol, 1D and porous TiO_2 was obtained. When octylamine (OLA) was used as a surfactant, fibers with a diameter of 40−60 nm and a length of 0.3−3 μm were obtained (Figure 1A,B). When aniline (AL) was used as a surfactant, fibers with cross sections in the range of 40−250 nm and lengths from 0.5 to 5 μm were obtained. A similar structure, but with a shorter length, was obtained for TiO_2 when isobutylamine (IBL) was used as a structure-directing agent (the TEM images are not shown here). Many of these fibers are clustered together. However, when subjected to strong ultrasonic irradiation, these florets can be dispersed.

Figure 2 shows the SEM and TEM images of the TiO_2 microspheres. (In fact, the TiO_2 is a precursor form and contains copious levels of H_2O and organic ligands, which will be addressed later). When octylamine is used as a surfactant, and with the addition of H_2Oa, an almost 100% yield of TiO_2 microspheres is obtained. Under SEM observation, it was found that these TiO_2 microspheres comprise many plates that stretch out from the core of the spheres (Figure 2B). As a result, these TiO_2 microspheres look like bundled "cauliflowers" with diameters ranging from 1.5 to 3 μm. In each of such TiO_2 microspheres, many macropores are observed on the outer surface, walled by several pieces of TiO_2 nanoplates. The pore sizes range from 50 to 200 nm (Figure 2B). Detailed structures are shown in their TEM images (Figure 2C,D). The measured surface area for the TiO_2 microspheres is 221m^2/g after calcination at 300 °C and degassing at 200 °C for 24 h, and the average pore diameter is 3.1 nm. The measured adsorption/desorption isotherm represents typical materials with macropores or without pores (Figure 3),[17] as the macropores can be measured only by the mercury penetration method.

Similar results are observed when aniline and isobutylamine are used as structure-directing agents (Figure 4). As

(17) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*; Academic Press: London, 1982; p 4.
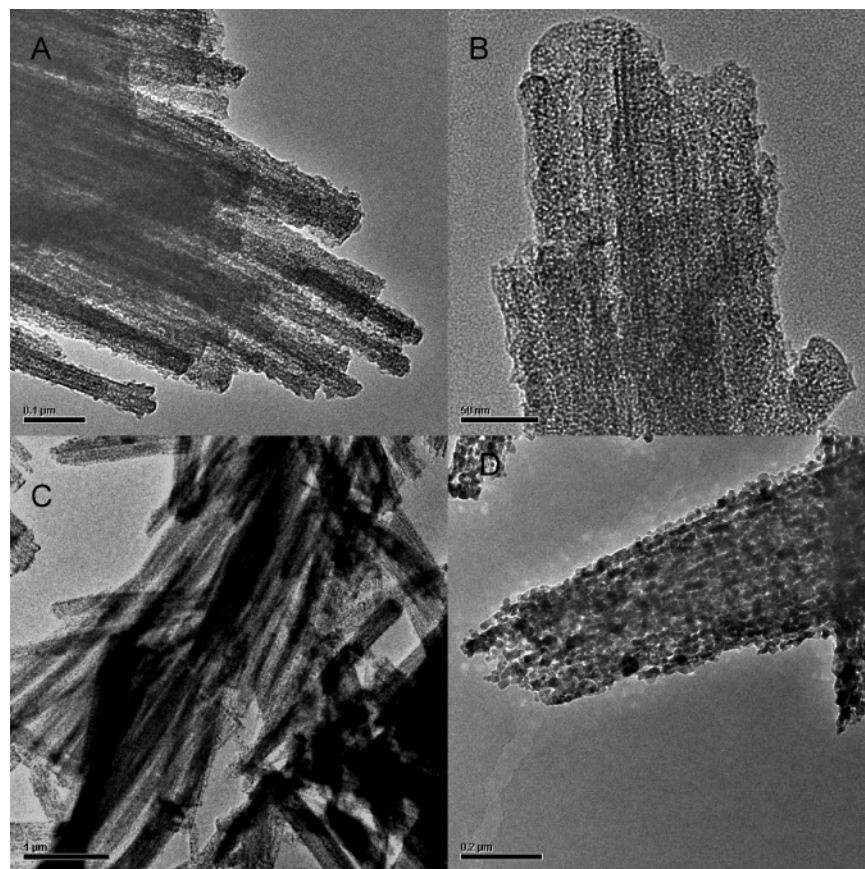
Figure 1. TEM images of the 1D and porous TiO₂ nanostructures calcined at 300 °C for 2 h at low and high magnification. Octylamine (OLA) and aniline (AN) were used as structuring-directing agents in (A, B) and (C, D), respectively. In both cases, the molar ratio of acetic acid:2-propanol:amine:H₂O:TTIP is 350:13:3:0:1.
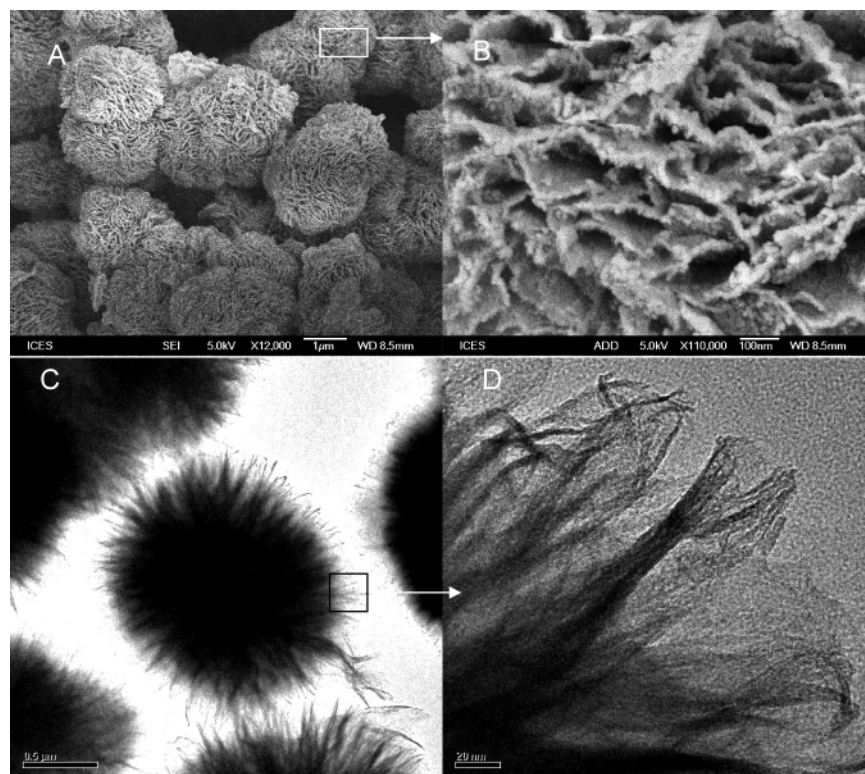

Figure 2. Electronic microscopy images of the TiO₂ microspheres calcined at 300 °C for 2 h. (A and B) SEM images of the TiO₂ product using octylamine (OLA) as a structure-directing agent; (C and D) the corresponding TEM images. The molar ratio of acetic acid:2-propanol:OLA:H₂O:TTIP is 350:13:3:28:1.
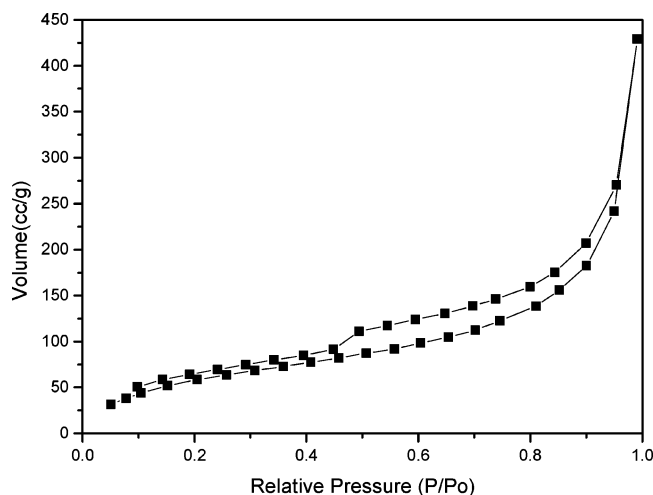
Figure 3. Nitrogen adsorption and desorption isotherms for the TiO_2 microsphere sample (shown in Figure 2A,B) calcined at 300 °C for 2 h and degassed at 200 °C for 24 h.

opposed to the cases of octylamine and isobutylamine, when aniline is used, the yield for TiO_2 microspheres as estimated by the TEM and SEM observations is only about 60−70%, because some one-dimensional and mesoporous TiO_2 nanostructures were formed (Figure 4A, marked with an arrow).[16]

To investigate the influence of the experimental parameters on the TiO_2 morphology and structure, we changed the molar ratio of some of the components separately. For example, the molar ratio of octylamine:TTIP was adjusted from 3:1 to 5:1 and 10:1, and that of H_2Oa:TTIP was tested at 20:1, 50:1, 60:1, 120:1, and 180:1 (in the preparation of the samples shown in Figure 2, the acetic acid:2-propanol: octylamine:H_2O:TTIP molar ratio is 350:13:3:28:1). We found that the morphology and size of the TiO_2 microspheres did not change with these adjustments. However, when H_2O: TTIP was increased to above 60:1, almost no TiO_2 microspheres were observed (Figure 5). The TiO_2 product becomes irregular in morphology, but still porous.

Figure 6A shows the TG analysis result for the TiO_2 microspheres shown in Figure 2. There are two stages for the weight loss (Figure 6A). One is from room temp to ca. 300 °C, with a weight loss of ca. 10.7%, whereas the second stage is in the range of 300−350 °C, with a weight loss of ca. 27.4%. The weight loss in the first stage can be attributed to the loss of adsorbed and structured water, and that in the second to the loss of organic ligands. Above 360 °C, almost no weight loss is observed. Both the X-ray diffraction (Figure 6C, bottom trace) and the selected area electron diffraction (SAD, result not shown here) showed that the as-prepared TiO_2 microspheres are amorphous. After heating at 400 °C for 3 h, the anatase phase is identified (JCP-78-2486, see Figure 6C, upper line.). The sharp exothermic peak at 364 °C in the DSC curve (Figure 6B) should be attributed to the
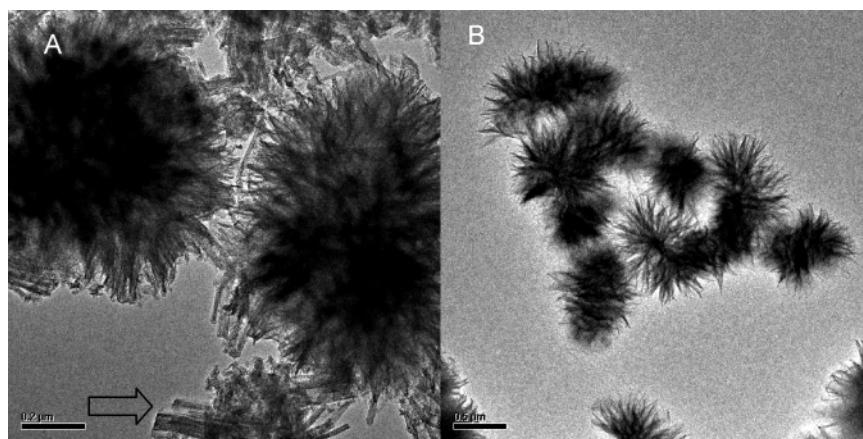

Figure 4. TEM images of the as-prepared TiO_2 microspheres using aniline (A) and isobutylamine (B) as structure-directing agents.
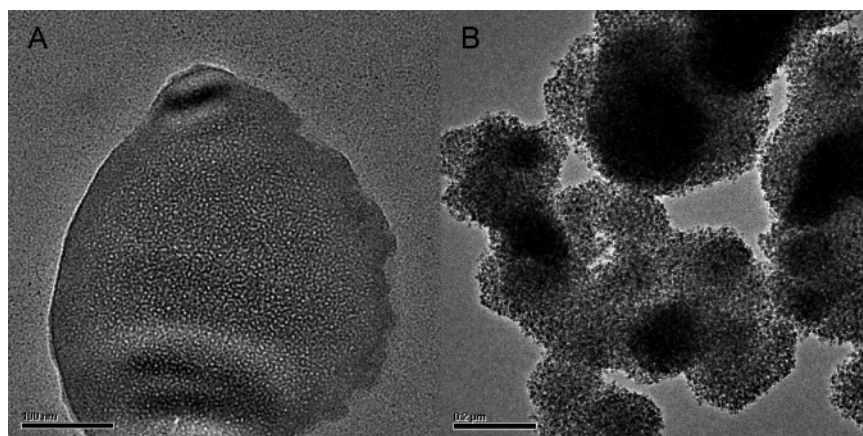

Figure 5. Porous TiO_2 prepared in the presence of a large amount of H_2Oa and OLA and AN. (A) 350:250:3:120:1 acetic acid:2-propanol:OLA:H_2Oa: TTIP. (B) 350:250:3:120:1 acetic acid:2-propanol:AN:H_2Oa:TTIP. The sample was calcined at 300 °C for 2 h.
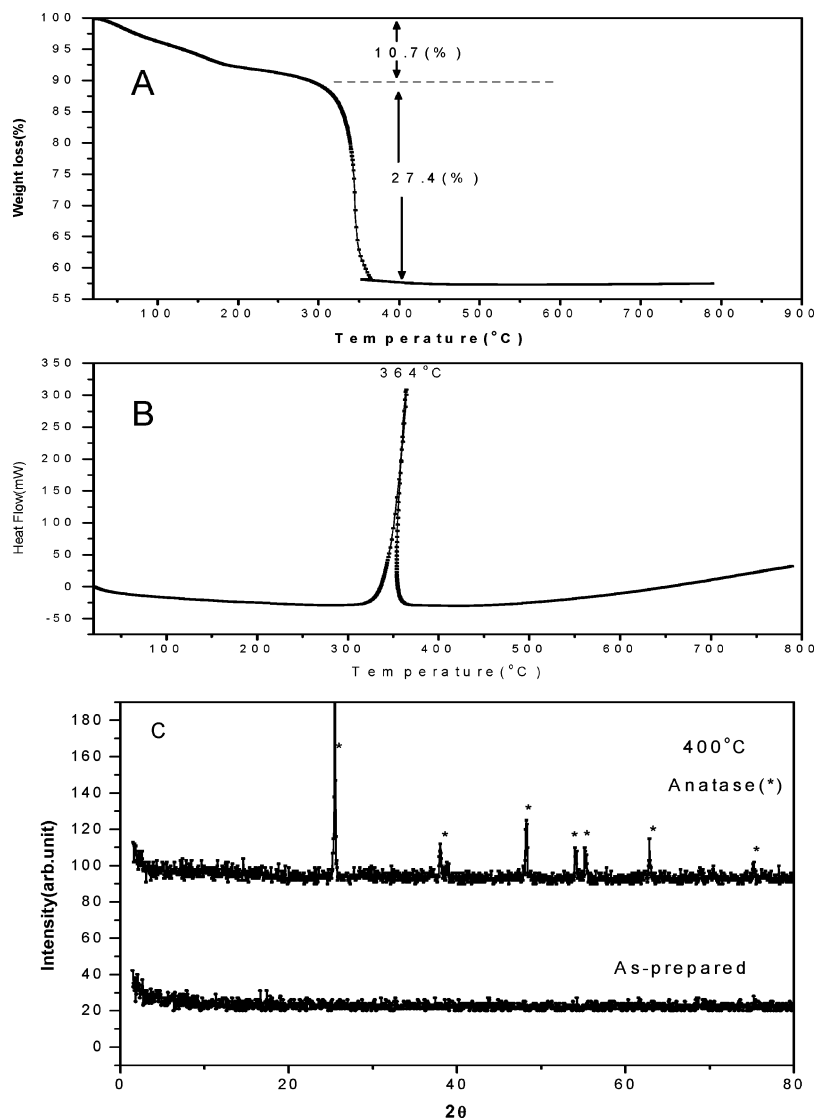
Figure 6. (A) TGA, (B) DSC, and (C) XRD patterns of the TiO₂ microspheres as shown in Figure 2. (A) depicts the results of the as-prepared sample, (B) the results of the calcined TiO₂ sample at 300 °C for 1 h.

decomposition of the organic compound and the loss of water. Though we detected anatase for the sample calcined at 400 °C, in the DSC curve, none of the exothermic peaks show the exact transformation temperature from the amorphous phase to anatase, and from anatase to rutile.

High thermal stability was observed for the prepared TiO₂ microspheres. The microsphere structures are stable even after calcination at 600 °C (Figure 7). However, after calcination at 800 °C, some of the structures collapsed (TEM results are not shown here). Similar results were observed for TiO₂ microspheres prepared by using aniline and iso-butylamine as structure-directing agents.

The formation mechanism is still not very clear. We notice that the as-prepared TiO₂ microspheres comprise small particles on the surface (Figure 2B). This is further evidenced by the observation of a "pearl necklace-like" structure in the sample calcined at 600 °C (Figure 7B−D). Probably, the TiO₂ microspheres were formed via the self-assembly of small TiO₂ intermediate nanoparticles, as proposed in our previous report.[16] Indeed, in a TEM observation (image not

shown here) for the milky solution that was formed initially by the addition of water (see Experimental Section), we did not observe any TiO₂ microspheres; however, we did observe some small TiO₂ particles, indicating that the TiO₂ microspheres were not formed in the early stage of the synthesis process. In mesoporous silica synthesis, Pannavaia[18] proposed that between neutral primary amine (S⁰) and a neutral inorganic precursor, hydrogen bonds could be formed, and thus mesoporous silica could be formed through an electrically neutral (S⁰I⁰) assembly pathway. The formation of H-bonding was also reported between organic amine and titanium precursors,[8a] and can initiate the formation of rodlike micelles.[8b]

The morphology of the TiO₂ product is most probably determined by the growth kinetics of TiO₂ particles, and an explanation is given below. When water was supplied slowly through esterification between acetic acid and 2-propanol,

(18) (a) Tanev, P. T.; Pinnavaia, T. J. *Chem. Mater.* **1996**, *8*, 2068−2079. (b). Zhang, W.; Pauly, T. R.; Pinnavaia, T. J. *Chem. Mater.* **1997**, *9*, 2491.
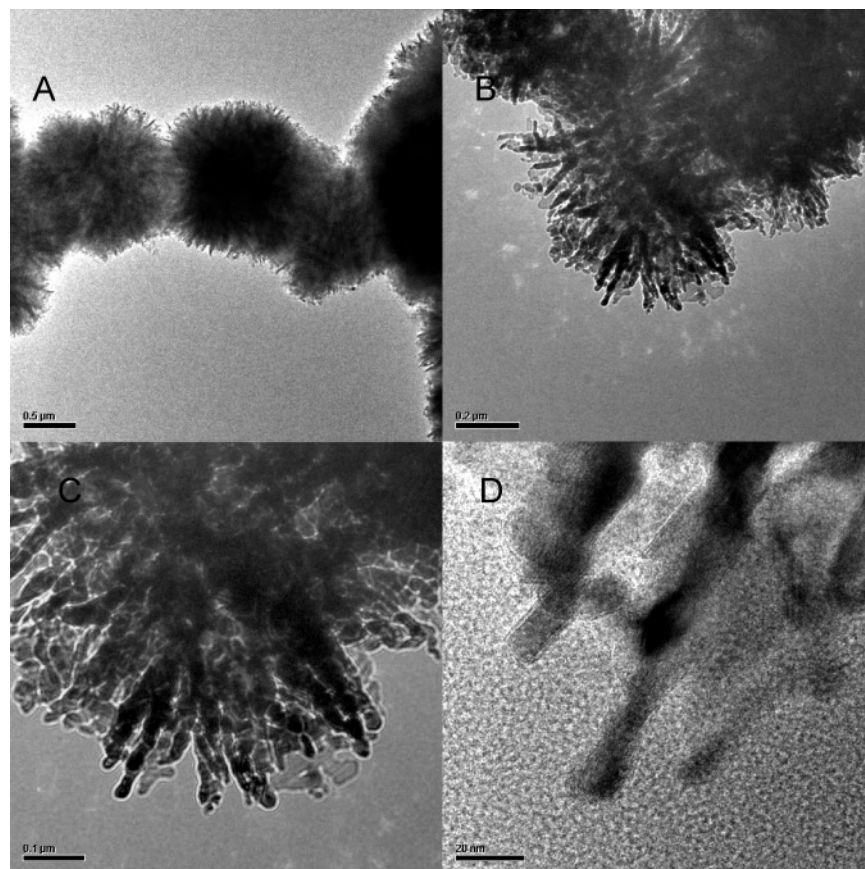
Figure 7. TiO$_2$ microspheres shown in Figure 2 were calcined with a heating rate of 2 °C/min from room temperature to 600 °C. From A to B, C, and D, the magnification increases sequentially.

the formed TO$_2$ particles were covered fully on their surface[19] by organic amine molecules, or rodlike micelle structures are formed. The "packing" or assembling of the rodlike micelle structures or the TiO$_2$ intermediate particles can proceed under the guidance of the amine molecules (probably via hydrophobic interaction among these nanostructures because the alkyl groups will project from the surface of these TiO$_2$ nanostructures), leading to growth in certain directions or the formation of a 1D porous structure. This is illustrated in Scheme 1 (path I). When using isobutylamine as a structure-directing agent, the hydrophobic interaction should be weak because of its shorter carbon length, resulting in the formation of short 1D structures, as compared to the case where octylamine was used. When a certain quantity of water was added (Scheme 1, path II), some TiO$_2$ intermediate particles were formed immediately. At the beginning, their surfaces were probably only partially covered with the organic amine molecules. Thus, unidirectional growth became difficult. In this case, the packing or assembling process should proceed in a much more random way compared to the case when water was supplied slowly,[16] as the uncontrolled branching of Ti−O−Ti may occur at many sites or locations. After hydrothermal treatment, the structure exhibits the thermodynamically preferred form of the spherical morphology. However, on the surface, macropores were formed by walling several pieces of TiO$_2$ plates,

Scheme 1. Influence of Kinetic Control on TiO$_2$ Morphology and Pore Structure
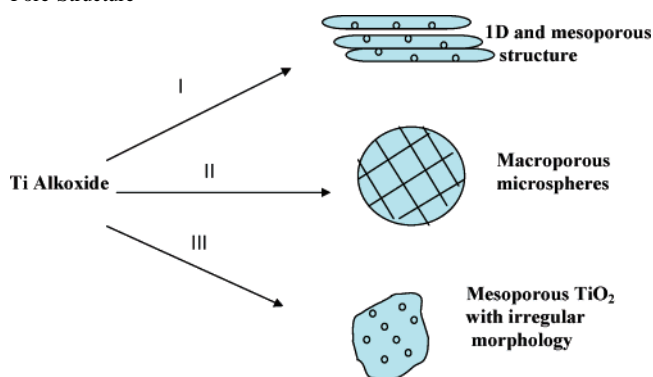
(I) The supply of H$_2$O is controlled by esterification reaction between acetic acid and 2-propanol. (II) The supply of H$_2$O is partially controlled. (III) No control on the supply of H$_2$O.

a result due to a locally guided growth by the amine molecules. In the case of a large excess of added water, a very fast precipitation of TiO$_2$ and the uncontrolled branching of the resulting Ti−O−Ti network[15] leads to the formation of TiO$_2$ with an irregular morphology (Scheme 1, path III). Of course, the adsorption of the organic amine molecules still occurred, forming some pores within the TiO$_2$ particles (Figure 5). Another factor is the existence of carboxylic acid that can coordinate to titania gel.[20] This may also influence the hydrolysis rate of the titanium alkoxide.

(19) Tentorio, A.; Canova, L. *Colloids Surf.* **1989**, *39*, 311.

(20) Roger, C.; Hampden-Smith, M. J. *J. Mater. Chem.* **2001**, *13*, 740.

In summary, we report herein on a novel one-step method for the preparation of TiO$_2$ microspheres by using octylamine, isobutylamine, and aniline as growth-directing agents and by the addition of a certain quantity of water prior to the hydrothermal treatment. The TiO$_2$ microspheres are stable up to 600 °C. The morphology and porous structures of the TiO$_2$ products are determined by the growth kinetics in the initial stage of forming TiO$_2$ particles or by the hydrolysis rate of Ti alkoxide. Unidirectional growth, partially controlled growth, and uncontrolled branching are observed when the water supply is completely controlled, partially controlled, or noncontrolled, respectively. As a result, 1D and meso-porous structure TiO$_2$, macroporous microsphere TiO$_2$, and porous TiO$_2$ with an irregular shape are synthesized in the three cases.

IC052080J