JOURNAL OF
Materials
CHEMISTRY

Synthesis of mesoporous titanium dioxide materials by using a mixture of organic compounds as a non-surfactant template

Jin-Yu Zheng,[a,b] **Jie-Bin Pang,**[a] **Kun-Yuan Qiu***[a] **and Yen Wei***[b]

[a]*Department of Polymer Science and Engineering, College of Chemistry & Molecular Engineering, Peking University, Beijing 100871, China. E-mail: kyqiu@chem.pku.edu.cn*
[b]*Department of Chemistry, Drexel University, Philadelphia, PA 19104, USA. E-mail: weiyen@drexel.edu*

Received 4th July 2001, Accepted 25th September 2001
First published as an Advance Article on the web 23rd October 2001

Mesoporous titanium dioxide materials have been successfully prepared at ambient temperature *via* HCl-catalyzed hydrolysis and polycondensation reactions of titanium(IV) *n*-butoxide by employing a mixture of β-cyclodextrin (CD) and urea (U) as a non-surfactant template, followed by removal of the mixture with water extraction. FT-IR analysis demonstrates the complete removal of the template molecules after extraction with water. The characterization results of nitrogen adsorption–desorption measurements show that the obtained materials have type IV isotherms with H2 hysteresis loops. The BJH pore size distribution plots indicate that the pore sizes show no obvious changes with the decrease in weight ratio of CD/U (3.7–4.1 nm) or increase in template content (3.9–3.6 nm). The interactions induced by hydrogen bonding between these two molecules and inorganic species play important roles in the above results. Small- and large-angle powder X-ray diffraction patterns and transmission electron microscopy reveal that the afforded titanium dioxide materials have anatase structures as well as disordered pore structures.

Introduction

Much attention has been attracted to mesoporous materials in the last ten years since the first synthesis of mesoporous materials was achieved by Kresge *et al.*[1,2] in 1992. They exploited quaternary ammonium surfactant compounds as templates and used hydrothermal methods to prepare mesoporous silica and the aluminosilicate M41S, which possess hexagonal uniform channels. Since then further research work has been devoted to investigations on the selection of templates, synthesis methods, characterization technologies, as well as practical applications.[3–25] Hydrothermal and modified sol–gel processes are common methods used to prepare mesoporous materials. Nitrogen sorption measurement, X-ray diffraction pattern (XRD), transmission electron microscopy (TEM), nuclear magnetic resonance (NMR) and thermogravimetric analysis (TGA) are widely utilized to record the physicochemical sorption properties, crystal phases, channel structures and stability of the resulting materials. Atom force microscopy (AFM) was also employed by Pang *et al.*[26] to characterize the pore structures.

Based on the high surface areas, pore volumes and controllable pore sizes, mesoporous materials can act as separating agents, adsorption media and catalysts. Metal oxides, as an important family of catalysts, are widely utilized in both fundamental and practical catalytic research areas. Many research groups focus their work mainly on the synthesis of pure mesoporous metal oxides or metal-incorporated mesoporous silica materials and their catalytic applications.[14–23] Metals, such as Al, Ti, Zr, Sn and Mn, have been successfully incorporated into the silica frameworks. Titanium dioxide is well known for its high catalytic activity especially for its photocatalytic properties, which have been investigated for many years and widely used in the photocatalytic oxidation of organic chemicals, such as the oxidation of toluene, 1-butene, *etc.*[27–30] The preparation of pure mesoporous titania Ti-HMS1 was reported by Antonelli's group in 1995.[15] It was obtained by a modified sol–gel process in the presence of alkylphosphate surfactant acting as template. Ionic and nonionic surfactants or block polymers have been exploited as template to direct the formation of mesoporous titania materials based on electrostatic and hydrogen bonding interactions.[13,16–18] Most of the titania materials have honeycomb arrays of regular mesopores and anatase phase. Some organic reactions have been successfully carried out in the presence of mesoporous titania.[22–25]

In 1998, a convenient, low-cost, environmental friendly, non-surfactant templated route was reported by Wei *et al.*[31] Mesoporous silica materials with high surface areas, pore volumes and narrow pore size distributions could be prepared by HCl-catalyzed sol–gel reactions of tetraethyl orthosilicate compounds in the presence of non-surfactant organic molecules. Changing the template contents is an easy way to control the pore sizes. D-Glucose,[31] D-maltose,[31] hydroxyacetic acid derivatives,[32] hydroxy-multiacids,[26] and urea[33] have been utilized as templates or pore-forming agents in these syntheses. Due to the potential catalytic activities, mesoporous titania materials[34] were also prepared by employing glycerol and 2,2-bis(hydroxymethyl)propionic acid as templates *via* a sol–gel process. These titania materials have high surface areas and pore volumes. They show anatase crystal structures but the pores are disordered. In an effort to obtain ordered pore structures, we chose β-cyclodextrin (CD) as a template (or pore-forming agent) to synthesize mesoporous titanium dioxide materials due mainly to the special cylinder-shaped structure of CD, which consists of seven glucose units linked through α-1,4-glucosidic bond. The depth of its cavity and the internal dimension are both around 0.7 nm. Its outer surface is hydrophilic but the cavity shows hydrophobic character. However, the low solubility of CD is a disadvantage for using CD as template. Urea has been successfully employed as a non-surfactant template in the synthesis of mesoporous materials.[33,35] Urea is a general agent used to increase the solubility of β-cyclodextrin in aqueous solution through increasing the cavity polarity of CD *via* hydrogen bonding interactions with urea.[36] The increased solubility of CD in

DOI: 10.1039/b105907f

This journal is © The Royal Society of Chemistry 2001

Table 1 The physicochemical sorption properties and pore parameters of mesoporous titanium dioxide materials prepared at fixed 10 wt% template content with varying weight ratios of CD/U

Sample[a]	CD/U weight ratio[b]	BET surface area/m^2 g^{-1}	BJH surface area/m^2 g^{-1}	Total pore volume[c]/cm^3 g^{-1}	SP volume[d]/cm^3 g^{-1}	Average pore size[e]/nm
TCU-CD	Pure CD	227	263	0.217	0.195	3.8
TCU-1-1	2/1	265	315	0.257	0.234	3.7
TCU-1-2	1/1	245	300	0.248	0.228	3.8
TCU-1-3	1/2	283	344	0.279	0.271	3.8
TCU-1-4	1/3	295	377	0.314	0.296	3.8
TCU-1-5	1/4	290	366	0.300	0.280	3.8
TCU-1-6	1/5	282	346	0.301	0.277	3.8
TCU-1-7	1/6	290	375	0.315	0.297	3.9
TCU-1-8	1/9	258	344	0.279	0.264	3.9
TCU-1-9	1/19	287	371	0.321	0.303	4.0
TCU-1-10	1/27	268	350	0.307	0.293	4.1
TCU-1-11	1/49	265	346	0.303	0.289	4.1
TCU-U	Pure U	224	295	0.303	0.306	4.8

[a] All the samples were prepared with same template content of 10 wt% with the assumption that TBT is converted to TiO_2 completely. [b] CD = β-cyclodextrin and U = urea. [c] Total pore volume of pores with diameters between 1.7 and 300 nm was calculated using the BJH method. [d] Single point pore volume was measured at P/P_0 of ~1. [e] Average pore size was calculated from the BJH pore size distribution plot obtained from the desorption branches of the isotherms.

aqueous urea is also thought to result from a smaller free energy of cavity formation due to the replacement of water by larger urea molecules.[37]

Hence, we utilized mixtures of β-cyclodextrin and urea as the template (or pore-forming agent) to prepare titanium dioxide materials. Using a mixture of organic compounds as templates has not been reported before in the synthesis of mesoporous titanium dioxide materials *via* non-surfactant templated sol–gel route. The resultant materials have surface areas of 240–300 m^2 g^{-1} and pore volumes of 0.23–0.31 cm^3 g^{-1}. The pore sizes only change a little with different weight ratios of CD/U (3.7–4.1 nm) and varying template content (3.9–3.6 nm). Therefore, even though this mixed-template route increases the interactions of template molecules, it has no pronounced effect on controlling the pore sizes of mesoporous titanium dioxide materials synthesized by the non-surfactant templated process.

Experimental

Preparation of mesoporous titanium dioxide materials

Similar to the typical synthetic procedure of mesoporous titania materials described previously,[34] a given amount of titanium(IV) *n*-butoxide (TBT, 97%, Aldrich) ethanol solution with a weight ratio of 1/7 was prehydrolyzed for about 3 h in the presence of 0.28 M HCl aqueous solution (TBT : HCl = 100 : 1 molar ratio) at ambient temperature. A given amount of the template mixture solution, calculated by assuming complete conversion of TBT to TiO_2 after hydrolysis and polycondensation reactions, was added to serve as template under vigorous stirring and then stirred for another 2 h to obtain the template-containing solution (sol). Beakers containing the sol solutions were sealed by paraffin films and kept at ambient temperature to gel and age. The solution of the template mixture was prepared by dissolving β-cyclodextrin (Fluka) and urea (Fisher Scientific) in distilled water according to designed weight ratios such as 1/3. A series of weight ratios were used to prepare samples with 10 wt% fixed template content (TCU-1-X) shown in Table 1. To compare the effect of the mixture of template molecules with the single compounds, two control samples TCU-CD and TCU-U were synthesized by using β-cyclodextrin and urea as sole templates, respectively. The other set of samples with different template contents were obtained using the same weight ratio of CD/U at 1/3 (TCU-X) listed in Table 2. For example, 3.00 g TBT was mixed with 21.08 g absolute EtOH first, then 0.315 mL 0.28 M HCl solution was added dropwise into the solution to catalyze the hydrolysis reaction for 3 h. 0.36 g β-cyclodextrin–urea solution with 1/6 weight ratio was added to direct the formation of sample TCU-1-7 with a template content of 10 wt%. After aging for 15–20 days until without further weight loss, the obtained template-containing titania composite materials were ground into fine powder and extracted with distilled water for 3 days to wash out the template molecules. Upon drying at 100 °C for one day porous titanium dioxide materials were obtained.

Characterization methods

A Perkin-Elmer 1600 FT-IR spectrophotometer was employed to determine the extent of the template removal after water extraction. The physicochemical sorption properties of the resulting materials were measured using a Micromeritics ASAP2010 analyzer, which collected data automatically at −196 °C. The samples were degassed at 110 °C under 1 Pa for at least 4 h before isotherm measurements. The crystal phase of

Table 2 The physicochemical sorption properties and pore parameters of mesoporous titanium dioxide materials prepared at 1/3 weight ratio with different template contents

Sample[a]	Template content (wt%)	BET surface area/m^2 g^{-1}	BJH surface area/m^2 g^{-1}	Total pore volume[b]/cm^3 g^{-1}	SP volume[c]/cm^3 g^{-1}	Average pore size[d]/nm
TCU-0	0	21	8	0.006	0.017	<1.7
TCU-5	5	252	337	0.289	0.277	3.9
TCU-10	10	295	377	0.314	0.296	3.8
TCU-30	30	279	336	0.270	0.251	3.7
TCU-40	40	284	308	0.243	0.214	3.8
TCU-60	60	260	257	0.192	0.202	3.6

[a] The numbers in the sample codes are the template content in the final inorganic composite. [b] Total pore volume of pores with diameters between 1.7 and 300 nm was calculated using the BJH method. [c] Single point pore volume was measured at P/P_0 of ~1. [d] Average pore size was calculated from the BJH pore size distribution plot obtained from the desorption branches of the isotherms.

the obtained materials before and after water extraction was examined by small- and large-angle powder X-ray diffraction (XRD) measurements recorded on a Rigaku DMAX2400 X-Ray Diffractometer at 40 kV and 100 mA using Cu-Kα radiation with $\lambda = 0.15418$ nm. The sample scans were collected at 2θ values in the ranges of 0.6–8 and of 8–60° at scan rates of 1 and 8° min^{-1}, respectively. A JEOL JEM-200CX transmission electron microscope (TEM) with an acceleration voltage of 200 kV was used to characterize the morphology of the samples. The TEM samples were prepared by dipping an ethanol suspension of the fine powder onto a Cu grid coated with a holey C film and drying at ambient temperature.

Results and discussion

Mesoporous titanium dioxide materials with 3.6–4.1 nm pore sizes and anatase structures were successfully synthesized under ambient temperature by HCl-catalyzed sol–gel reactions of TBT in the presence of mixtures of β-cyclodextrin and urea as non-surfactant templates, followed by water extraction.

In contrast to the silica system we reported earlier,[38] at fixed 1/3 weight ratio of CD/U, transparent titania composite samples were obtained directly at low template contents. When the template content was increased to 30 wt% or higher, the samples were opaque at first but then became transparent after some time. The higher the template content used, the less time was needed for gelation and disappearance of phase separation. For instance, the opaque sample TCU-40 gelled after 10 min after addition of the template solution and became transparent after 24 h whereas sample TCU-60 only required 5 and 40 min for the same processes. In addition, high weight ratios of β-cyclodextrin to urea also shortened the gelation time, which might result from the higher water content used to dissolve the β-cyclodextrin. These phenomena perhaps relate to the interactions induced by hydrogen bonding of these two molecules with inorganic species.

The FT-IR spectra measured before and after water extraction confirmed that the template molecules have been removed completely. The two typical NH stretching vibrations (asymmetrical and symmetrical) of NH_2 groups of urea at 3435 and 3342 cm^{-1} as well as the 1664 cm^{-1} absorption peak of the C=O group disappeared after extraction. The absorption peaks at 1458 and 1155 cm^{-1} that are found in both β-cyclodextrin and urea, could not be seen after extraction, which suggests the complete removal of the template molecules.

The physicochemical sorption properties and pore parameters of the samples prepared with 10 wt% template content and different weight ratios of CD/U are collected in Table 1. The surface areas and pore volumes reach up to 290 m^2 g^{-1} and 0.3 cm^3 g^{-1} as calculated from Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods after water extraction. From *t*-plot analysis, all the samples prepared either from a single compound or from mixtures as template mainly consist of mesopores. The pore sizes change a little from 3.7 to 4.1 nm with decreased weight ratios of CD/U. It is of note that sample TCU-CD using β-cyclodextrin alone as template has the lowest surface area and pore volume. The largest pore size of 4.8 nm is shown by sample TCU-U, in which urea is the sole template. In the investigated scale of CD/U weight ratios from 2/1 to 1/49, the pore sizes do not show a strong correlation with the weight ratio. By contrast, for silica materials synthesized with the same process, the pore sizes decrease dramatically from mesopore (3.7–3.4 nm) to micropore (<1.7 nm) with a similar decrease of weight ratio.[38]

The nitrogen adsorption–desorption isotherms are shown in Fig. 1(a). All the samples display type IV isotherms with H2 hysteresis loops, no matter which type of template, single or mixture, was utilized in the synthesis. This phenomenon is in agreement with the mesoporous titania materials synthesized by other non-surfactant templates, which always show type IV isotherms, independent of the nature and content of the templates.[34,35] The shifts of the relative pressures corresponding to the hysteresis loops in desorption isotherms are not significant for different samples, which indicate the only slight changes of the pore sizes. Fig. 1(b) shows the pore size distribution plots obtained from the BJH method for the various samples. The widths at the half peak heights, which identify the distributions of pore sizes, are very narrow and most of the pore sizes are mainly in the range 3.7–4.1 nm. In the synthesis of mesoporous titanium dioxide materials, β-cyclodextrin can act as template alone and results in the formation of mesopores. This is clearly different from silica materials prepared by the same method, in which β-cyclodextrin alone cannot be used as the template due to its low solubility and high content needed (*e.g.*, 50 wt%). However, for titania synthesis, the solubility is no longer a problem since low template contents are sufficient (*e.g.*, 10 wt%). The gelation process of titania materials is very sensitive to the content of water in the system. Therefore, the low solubility of β-cyclodextrin, which thus requires a high water content, shortens the gelation time and the β-cyclodextrin molecules might be wrapped up by inorganic species and do not separate

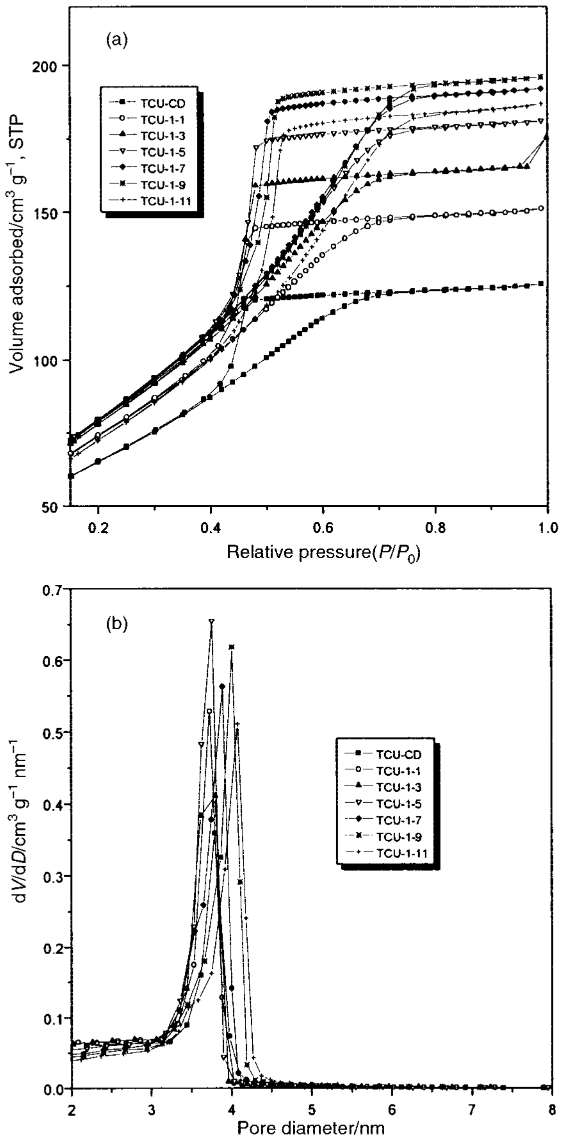

Fig. 1 N_2 adsorption–desorption isotherms (a) and BJH pore size distribution plots calculated from the desorption branches of the isotherms (b) for the extracted samples of system TCU-1-X prepared at fixed 10 wt% template content with different weight ratios.

out in such a short time. Taking all these factors into consideration, when adding urea to increase the solubility of β-cyclodextrin, some urea molecules enter into the cavities and eject some water molecules, while other urea molecules are adsorbed at the outside of the β-cyclodextrin molecules. The urea-held or urea-wrapped β-cyclodextrin molecules aggregate together and act as a template to direct the formation of the mesophase. By reducing the CD/U weight ratio, only a limited number of urea molecules can enter the cavities of CD so resulting in an increase in the proportion of urea molecules adsorbed outside the CD. The dimensions of the urea-wrapped β-cyclodextrin molecules and their aggregates may thus be enlarged a little, leading to some increase in the pore sizes.

To investigate the effect of template content on the pore parameters, we synthesized mesoporous titanium dioxide materials at five template contents with fixed weight ratio of CD/U at 1/3. A control sample without any template (TCU-0) was also prepared under the same condition. The results of nitrogen adsorption–desorption measurements are compiled in Table 2. Titania sample prepared in the absence of template is essentially non-porous. However, mesoporous materials are readily attainable by adding template at the template content as low as 5 wt%. Similar to the results in Table 1, the pore sizes (3.9–3.6 nm) show little changes with the increase in the template content. The slight decrease in the pore size might be caused by the formation of accumulated pores of titania nanoparticles at high template contents. The decrease in the surface area and pore volume at high template contents could be attributed to phase separation of the templates from the sol–gel reaction system, so that only part of the template molecules were functioning. This hypothesis is confirmed by the X-ray diffraction pattern measured on composite samples prior to extraction. Fig. 2 shows as-synthesized samples with different template contents which present a broad peak at 25° before extraction. When template contents reach 60 wt%, a sharp peak appears at 22° corresponding to the crystal phase of β-cyclodextrin and urea. This result reveals that the template molecules crystallize from the composite materials during aging process and only some of them serve as template. Thus, in the synthesis of mesoporous titania materials by the non-surfactant templated sol–gel route, high template content is not necessary and a relatively low template content is adequate to lead to mesopores.

Fig. 3 shows isotherm plots and BJH pore size distributions of samples prepared at various template contents. A reversible isotherm plot for non-porous or microporous materials was found for the control sample (TCU-0). All other samples displayed type IV isotherms, similar to those in Fig. 1(a). However, the hysteresis loops and the relative pressures corresponding to the loops as well as the adsorbed volumes at $P/P_0 \sim 1$ became smaller with an increase in the template content. As shown in Fig. 3(b), the peaks identifying the pore sizes shifted to lower values when the template content was increased. There was no identifiable peak in the control sample.

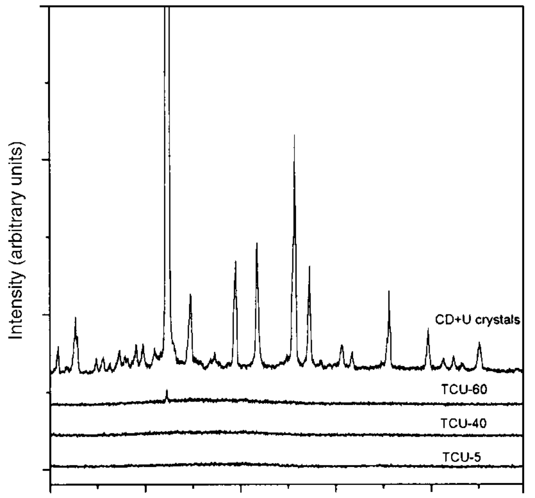

Fig. 2 Powder X-ray diffraction patterns for unextracted samples TCU-5, TCU-40, TCU-60 and pure template mixture.

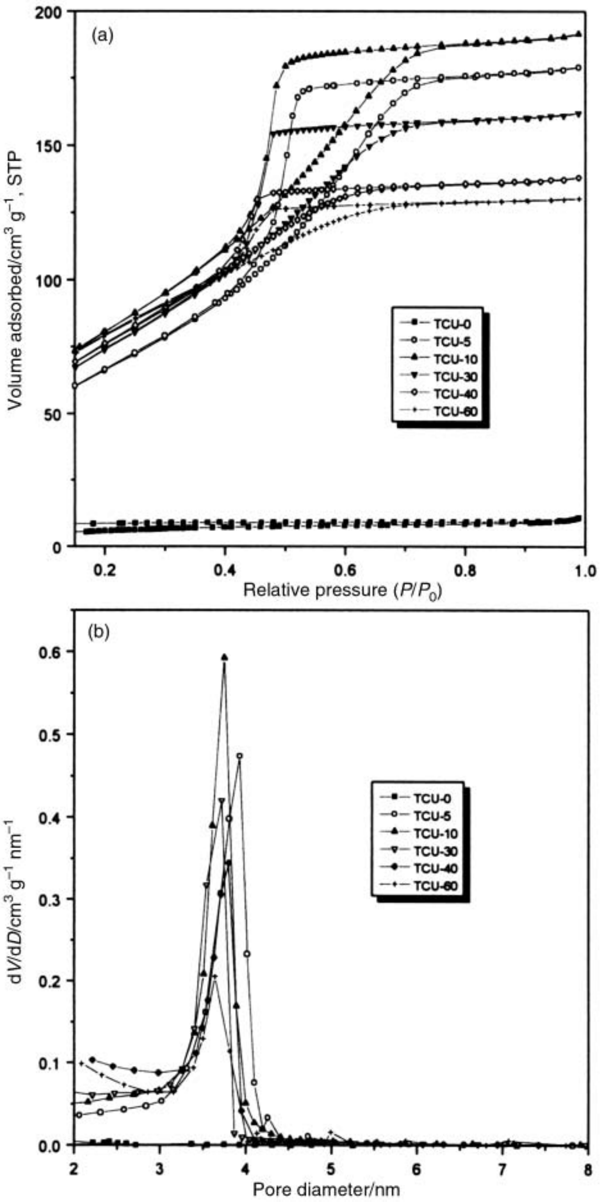

Fig. 3 N_2 adsorption–desorption isotherms (a) and BJH pore size distribution plots calculated from the desorption branches of the isotherms (b) for the extracted samples of systems TCU-X synthesized at 1/3 weight ratio with varying template content.

Fig. 4 shows the small- and large-angle powder X-ray diffraction patterns of the extracted sample TCU-10. In the measurement range 0.6–8°, as shown in Fig. 4(a), only a half peak is observable around a 2θ value of 0.6°, suggesting that the materials lack long-range ordered arrangements. In Fig. 4(b), there are four crystal peaks at high 2θ values of 25, 38, 48 and 54.5°, which is consistent with the anatase phase of titania materials.

From the transmission electron microscopy images of samples TCU-1-8, TCU-5 and TCU-40 (Fig. 5), we can see that the porous materials have disordered pore structures. At high CD/U weight ratios, the pore structures do not show any better ordered arrangements, which indicates that the special

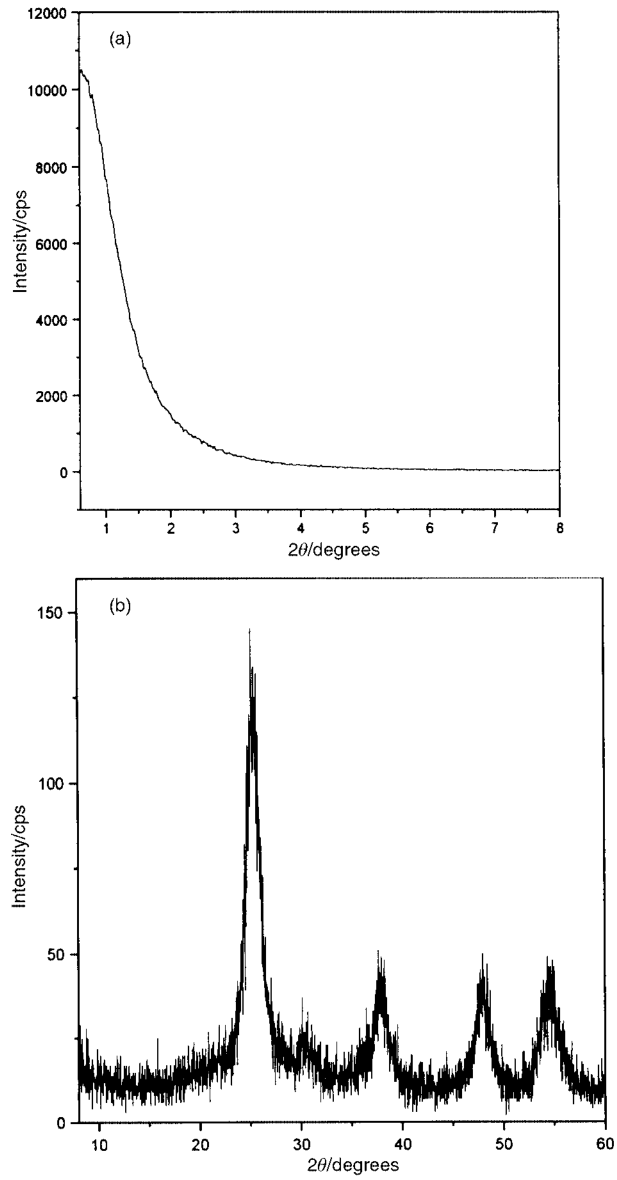

Fig. 4 Small- (a) and large-angle (b) powder X-ray diffraction patterns for the extracted sample TCU-10.

cylinder-shaped structure of β-cyclodextrin molecules did not play the anticipated role in the formation of ordered pore structures. When the template content was increased, the tendency to form connected pore structures lessened. In addition, some titania nanoparticles were found to accumulate tightly together and form interparticular pores. Such accumulated pores perhaps lead to the observed decrease in the pore size and pore volumes as well as the surface areas.

The mechanism of mesophase formation in the non-surfactant templated sol–gel route is, as yet, not fully understood. From the results discussed above, we postulate that hydrogen bonding interactions might be the driving force to direct the mesophase formation. The aggregation of the template molecules as well as the interactions between the hydrolyzed inorganic titanate species based on hydrogen bonding could be a crucial factor in the synthesis of mesoporous materials *via* the non-surfactant templated route.

Conclusions

A mixture of organic compounds, *i.e.*, β-cyclodextrin and urea in this study, has been employed for the first time as a non-surfactant template to synthesize mesoporous titanium dioxide materials by HCl-catalyzed sol–gel reactions of TBT at ambient temperature followed by extraction with distilled water. The materials possess relatively high surface areas and pore volumes as well as narrow pore size distributions. At fixed

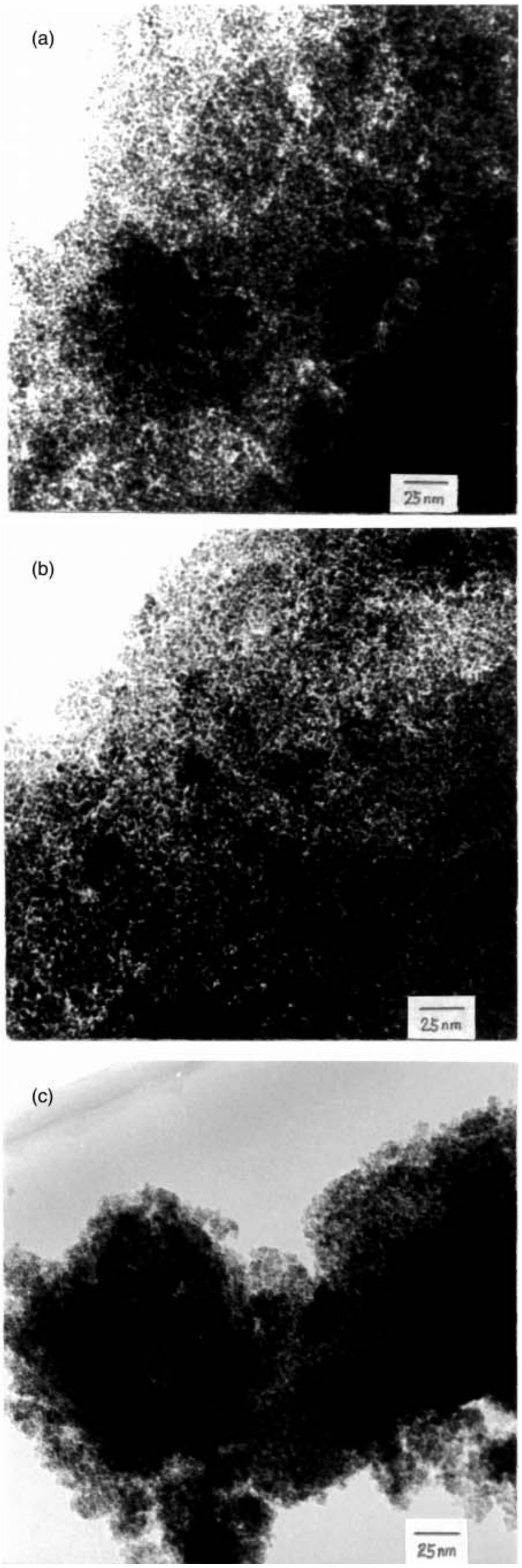

Fig. 5 TEM images of samples TCU-1-8 (a), TCU-5 (b) and TCU-40 (c) after water extraction.

template content (*e.g.*, 10 wt%), the weight ratios of β-cyclodextrin and urea in the mixtures have no significant effect on the pore size. The pore size changes slightly from 3.7 to 4.1 nm with a decrease in the CD/U weight ratio. Therefore, employing mixtures as a template is still not an effective method to adjust the pore size of mesoporous titania materials *via* the non-surfactant templated sol–gel route. At a fixed CD/U ratio, an increase in the template content results in a decrease in the surface areas and pore volumes, which would be induced by the formation of accumulated pores or by phase separation (*i.e.*, partial crystallization of template molecules) during the aging process. Low template content is suitable to prepare mesoporous titania materials by this method. The hydrogen bonding interactions between β-cyclodextrin and urea and between the template aggregates and inorganic titanate species might play significant roles in the mesophase formation.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 29874002 to K. Y. Q. and an Outstanding Young Scientist Award No. 29825504 to Y. W.). We are most grateful to Prof. X. H. Chen (Institute of Materials Science, Tsinghua University) for her kind assistance in the TEM characterization.

References

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
3 Q. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schuth and G. D. Stucky, *Nature*, 1994, **368**, 317.
4 C. A. Fyfe and G. Fu, *J. Am. Chem. Soc.*, 1995, **117**, 9709.
5 D. Zhao, P. Yang, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Chem. Commun.*, 1998, 2499.
6 A. Wang and T. Kabe, *Chem. Commun.*, 1999, 2067.
7 P. T. Tanev and T. J. Pinnavaia, *Science*, 1995, **267**, 865.
8 S. A. Bagshaw, E. Prouzet and T. J. Pinnavaia, *Science*, 1995, **269**, 1242.
9 A. Firouzi, F. Atef, A. G. Oertli, G. D. Stucky and B. Chmelka, *J. Am. Chem. Soc.*, 1997, **119**, 3596.
10 D. Zhao, Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, *J. Am. Chem. Soc.*, 1998, **120**, 6024.
11 W. Zhang, B. Glomski, T. R. Pauly and T. J. Pinnavaia, *Chem. Commun.*, 1999, 1803.
12 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.
13 Y. H. Yue, Z. Ma, W. M. Hua and Z. Gao, *Huaxue Xuebao*, 2000, **58**, 777.
14 U. Ciesla, D. Demuth, R. Leon, P. M. Petroff, G. Stucky, K. Unger and F. Schuth, *J. Chem. Soc., Chem. Commun.*, 1994, 1387.
15 D. M. Antonelli and J. Y. Ying, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2014.
16 R. L. Putnam, N. Nakagawa, K. M. McGrath, N. Yao, I. A. Aksay, S. M. Gruner and A. Navrotsky, *Chem. Mater.*, 1997, **9**, 2690.
17 V. F. Stone Jr. and R. J. Davis, *Chem. Mater.*, 1998, **10**, 1468.
18 M. Thieme and F. Schuth, *Microporous Mesoporous Mater.*, 1999, **27**, 193.
19 M. Schneider and A. Baiker, *J. Mater. Chem.*, 1992, **2**, 587.
20 B. D. Yao and L. D. Zhang, *J. Mater. Sci.*, 1999, **34**, 5983.
21 J. Retuert, R. Quijada and V. Arias, *Chem. Mater.*, 1998, **10**, 3923.
22 P. D. Yang, D. Y. Zhao, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Nature*, 1998, **396**, 152.
23 D. M. Antonelli, *Microporous Mesoporous Mater.*, 1999, **30**, 315.
24 J. L. Zhang, M. Minagawa, M. Matsuoka, H. Yamashita and M. Anpo, *Catal. Lett.*, 2000, **66**, 241.
25 L. Saadoun, J. A. Ayllon, J. Jimenez-Becerril, J. Peral, X. Domenech and R. Rodriguez-Clemente, *Mater. Res. Bull.*, 2000, **35**, 193.
26 J. B. Pang, K. Y. Qiu, Y. Wei, X. J. Lei and Z. F. Liu, *Chem. Commun.*, 2000, 477.
27 Y. Luo and D. F. Ollis, *J. Catal.*, 1996, **163**, 1.
28 S. C. Luo and J. L. Falconer, *J. Catal.*, 1999, **185**, 393.
29 L. X. Cao, A. M. Huang, F.-J. Spiess and S. L. Suib, *J. Catal.*, 1999, **188**, 48.
30 L. X. Cao, Z. Gao, S. L. Suib, T. N. Obee, S. O. Hay and J. D. Freihaut, *J. Catal.*, 2000, **196**, 253.
31 Y. Wei, D. Jin, T. Ding, W. H. Shih, X. H. Liu, S. Z. D. Cheng and Q. Fu, *Adv. Mater.*, 1998, **3**, 313.
32 J. Y. Zheng, J. B. Pang, K. Y. Qiu and Y. Wei, *J. Inorg. Organomet. Polym.*, 2000, **10**, 103.
33 J. B. Pang, K. Y. Qiu, J. G. Xu, Y. Wei and J. Chen, *J. Inorg. Organomet. Polym.*, 2000, **10**, 39.
34 J. Y. Zheng, K. Y. Qiu and Y. Wei, *Mol. Cryst. Liq. Cryst.*, 2000, **354**, 183.
35 J. Y. Zheng, J. B. Pang, K. Y. Qiu and Y. Wei, *Microporous Mesoporous Mater.*, in press.
36 Y. B. Jiang, X. Z. Huang and G. Z. Chen, *J. Chem. Phys.*, 1990, **3**, 201.
37 H. X. Liang and D. G. Durham, *J. China Pharm. Univ.*, 1999, **30**, 275.
38 J. Y. Zheng, J. B. Pang, K. Y. Qiu and Y. Wei, *J. Sol–Gel Sci. Technol.*, in press.