



ELSEVIER

Colloids and Surfaces A: Physicochem. Eng. Aspects 227 (2003) 45–48

COLLOIDS  
AND  
SURFACES

A

www.elsevier.com/locate/colsurfa

## Recovery of TiO<sub>2</sub> nanoparticles synthesized in reverse micelles by antisolvent CO<sub>2</sub>

Dongxia Liu, Jianling Zhang, Buxing Han\*, Jing Chen,  
Zhonghao Li, Dong Shen, Guanying Yang

*Centre for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China*

Received 21 February 2003; accepted 1 July 2003

### Abstract

The possibility to recover the titanium dioxide (TiO<sub>2</sub>) nanoparticles synthesized in sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse micelles by compressed CO<sub>2</sub> was investigated. UV-Vis study showed that TiO<sub>2</sub> nanoparticles could be deposited from the reverse micelles by the dissolved CO<sub>2</sub>. The nanoparticles were prepared and characterized by the transmission electron microscopy (TEM). The results showed that the TiO<sub>2</sub> nanoparticles of very small size could be obtained. The effect of the operation conditions on the particle size is discussed.

© 2003 Elsevier B.V. All rights reserved.

*Keywords:* Nanoparticles; Titanium dioxide; Antisolvent; CO<sub>2</sub>; Reverse micelles

Titanium dioxide (TiO<sub>2</sub>), a traditional material, is widely utilized in ceramic materials as a white pigment, enamel, and membrane [1,2]. Nano-sized TiO<sub>2</sub> particles have recently been researched because they have excellent physical, chemical and opto-electrical properties [3–5]. To date, many efforts have been made to prepare TiO<sub>2</sub> nanoparticles, including the plasma process [6], sol–gel processing technique [7,8], synthesis in supercritical fluids [9–11], and reverse micellar method [12–14]. The reverse micellar method is one of the most preferred candidates. In this method, recovery of the nanoparticles from the reverse micelles is one of the key steps. The conventional recovery

methods include flocculation [15], evaporation [16], or adding certain chemical reagent to cause phase separation [17], which precipitate the surfactant simultaneously. The post-process is troublesome because the products contain a large amount of surfactant.

It is well known that compressed CO<sub>2</sub> can dissolve in many organic solvents, which results in considerable change in the solvent power of the solvents. Thus, the property of the liquid solvent can be tuned by pressure because the solubility of CO<sub>2</sub> in the solvent is a function of pressure, and the separation of the gas and the liquid solvent can be achieved easily by depression. In recent years, utilization of this principle has been widely explored in various areas, such as extraction and fractionation [18,19], recrystallization of chemicals [20–22], and micronization [23,24]. Recently, we proposed a new method to recover ZnS

\* Corresponding author. Tel.: +86-10-62562821;  
fax: +86-10-62559373.

E-mail address: hanbx@iccas.ac.cn (B. Han).

nanoparticles synthesized in AOT reverse micelles by dissolving compressed CO<sub>2</sub> into the reverse micellar solution [25].

In this work, we investigated the possibility to recover the TiO<sub>2</sub> nanoparticles from the reverse micelles using CO<sub>2</sub> as antisolvent. The present work consisted of three related parts: (1) studying the related phase behaviour, which was the basis of this work; (2) probing the possibility of recovering TiO<sub>2</sub> nanoparticles from the water/AOT/isooctane reverse micelles by compressed CO<sub>2</sub>; (3) investigating the effects of the experimental conditions on the size of the recovered TiO<sub>2</sub> nanoparticles. The results demonstrated that this method has some potential advantages for preparing TiO<sub>2</sub> nanoparticles, such as simple, timesaving and the solution can be recycled.

The apparatus used to determine the phase behaviour was the same as that used previously [26]. The volume expansion coefficient  $\Delta V = (V - V_0) / V_0$  ( $V$  and  $V_0$  are respectively the volumes of the CO<sub>2</sub>-expanded and the CO<sub>2</sub>-free solutions) of the micellar solution ([AOT] = 100 mmol/l) were determined at 303.2 K, and the results are demonstrated in Fig. 1. As can be seen, the volume expansion coefficient increases with increasing pressure because more CO<sub>2</sub> is dissolved in the solution at higher pressure. The volume expansion coefficient is nearly independent of  $w_0$ . The volume expansion curves allows us to determine how much CO<sub>2</sub>-free reverse micellar solution should be loaded into the sample cell in the UV investigation and nanoparticle recovery processes. As

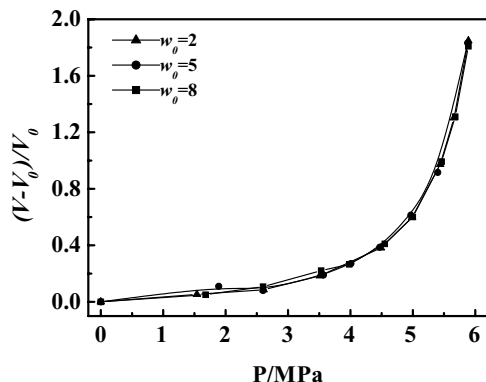


Fig. 1. Effect of pressure on volume expansion coefficients of the reverse micellar solution ([AOT] = 100 mmol/l) with different  $w_0$  at 303.2 K.

the pressure of CO<sub>2</sub> was high enough, the micellar solution became cloudy, indicating the precipitation of the surfactants from the micellar solution. The pressure at which AOT begins to precipitate from the solution is referred to as cloud pressure ( $P_c$ ). The  $P_c$  of the reverse micellar solution ([AOT] = 100 mmol/l) determined at 303.2 K was 5.91 MPa. In this work, all the experiments were conducted at pressures lower than the  $P_c$  for TiO<sub>2</sub> nanoparticle recovery, so that the precipitation of the surfactant was not occurred.

The method to synthesize TiO<sub>2</sub> nanoparticles in the reverse micelles was similar to that reported by other authors [22]. Typically, the desired amount of pre-diluted (13 wt.%) titanium(IV) isopropoxide/ isopropanol solution was added to the water/AOT/isooctane reverse micelles under mild stirring. UV-Vis spectrum is commonly used method to characterize the TiO<sub>2</sub> nanoparticles in reverse micelles. In this work, the UV spectrophotometer (Model TU-1201) was used to examine the precipitation of TiO<sub>2</sub> particles from the reverse micelles at different CO<sub>2</sub> pressures. The high-pressure UV sample cell and the experimental procedures were similar to those used previously [25]. In the experiment, the UV cell was full of solution after expansion with CO<sub>2</sub>. The concentration of TiO<sub>2</sub> in the solution was 0.022 mg/ml if precipitation did not occur. As examples, Fig. 2 shows the UV spectra of the reverse micellar solution containing TiO<sub>2</sub> particles at some pressures, and the water-to-AOT molar ratio in the solution ( $w_0$ ) is 8. The characteristic absorbance around 272 nm is attributed to TiO<sub>2</sub> nanoparticles [12]. The nanoparticles in the reverse micellar solution do not precipitate

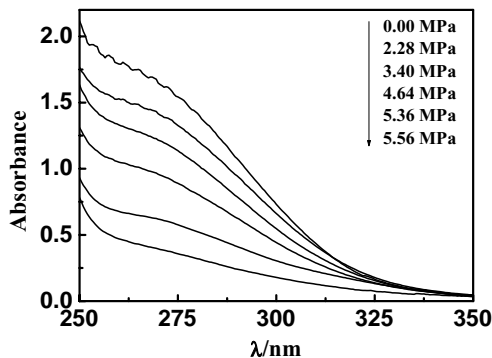


Fig. 2. UV spectra of TiO<sub>2</sub> in reverse micelles ([AOT] = 100 mmol/l,  $w_0$  = 8) at 303.2 K and different pressures.

in the absence of CO<sub>2</sub>. However, the absorbance of the TiO<sub>2</sub> decreases progressively with the increasing CO<sub>2</sub> pressure, which can be seen clearly from Fig. 2. This indicates that the precipitation of TiO<sub>2</sub> from the reverse micelles can be realized by adding CO<sub>2</sub>, and more TiO<sub>2</sub> nanoparticles are precipitated at higher pressures.

On the basis of the investigations above, we selected some suitable experimental conditions to prepare TiO<sub>2</sub> nanoparticles using CO<sub>2</sub> as antisolvent. The

known amount of reverse micellar solution with synthesized TiO<sub>2</sub> nanoparticles was added into the autoclave of 303.2 K. CO<sub>2</sub> was charged into the autoclave by a high-pressure pump until the desired pressure was reached. After 30 min, the stirrer was stopped to allow the precipitation of the TiO<sub>2</sub> particles. CO<sub>2</sub> was then released slowly. After the removal of the liquid solution, the deposits at the bottom of the autoclave were collected and washed several times using water and ethanol. The size and shape of the obtained TiO<sub>2</sub> par-

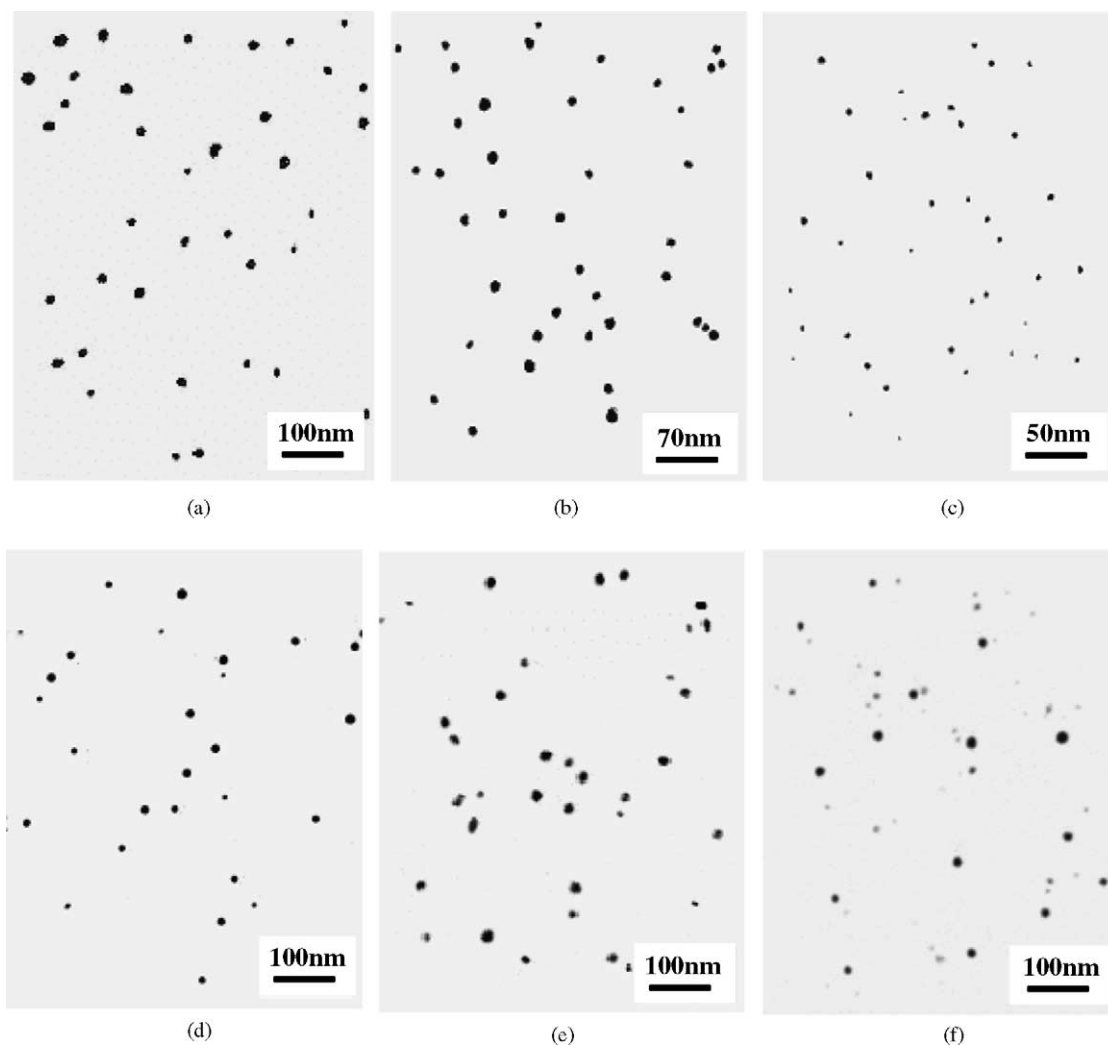


Fig. 3. TEM photographs of TiO<sub>2</sub> particles recovered from AOT reverse micelles ([AOT] = 100 mmol/l) by compressed CO<sub>2</sub> at different conditions: (a) [TIP] = 1.30 mg/ml,  $P = 5.41$  MPa,  $w_0 = 8$ ; (b) [TIP] = 0.86 mg/ml,  $P = 5.41$  MPa,  $w_0 = 8$ ; (c) [TIP] = 0.43 mg/ml,  $P = 5.41$  MPa,  $w_0 = 8$ ; (d) [TIP] = 0.86 mg/ml,  $P = 5.07$  MPa,  $w_0 = 8$ ; (e) [TIP] = 1.30 mg/ml,  $P = 5.41$  MPa,  $w_0 = 5$ ; (f) [TIP] = 1.30 mg/ml,  $P = 5.41$  MPa,  $w_0 = 2$ .

ticles were determined by transmission electron microscope (TEM) with a HITACHI H-600A electron microscope. The TEM micrographs prepared at some typical conditions are presented in Fig. 3a–f. The results show that the TiO<sub>2</sub> particles prepared at all the conditions are very small.

The effect of the reactant concentration on the size of the TiO<sub>2</sub> nanoparticles can be seen in Fig. 3a–c. Evidently, the particle size decreases with the decreasing TIP concentration. The main reason is that the amount of TiO<sub>2</sub> in each micelle is smaller at the lower concentration, which is favourable to producing smaller particles. Fig. 3b and d compare the TiO<sub>2</sub> nanoparticles recovered at different CO<sub>2</sub> pressures. Size of particles recovered at 5.41 MPa is smaller and more uniform than that at 5.07 MPa. This may be due to the reduced viscosity and enhanced diffusivity of the CO<sub>2</sub>-expanded solutions at higher pressure. Fig. 3a, e and f demonstrate the effect of  $w_0$  on particle size. The particles recovered at  $w_0 = 8$  and 5 are similar both in size and size distribution. The products obtained at  $w_0 = 2$  contains very smaller particles, and the size of the larger ones are similar to those produced at  $w_0 = 8$  and 5. The main reason is that the particles in the reverse micelles synthesized at  $w_0 = 2$  are much smaller. Some of them aggregate to form the larger particles during the recovery process.

### Acknowledgements

The authors are grateful to the National Natural Science Foundation of China (20133030) and Ministry of Science and Technology for the financial support (G2000078103).

### References

- [1] S. Vemury, S.E. Pratsinis, *J. Am. Ceram. Soc.* 78 (1995) 2984.
- [2] T.A. Ring, *Fundamentals of Ceramic Powder Processing and Synthesis*, Academic Press, San Diego, 1996.
- [3] Y. Paz, Z. Luo, L. Rabenberg, A. Heller, *J. Mater. Res.* 10 (1995) 2842.
- [4] A. Corma, *Chem. Rev.* 97 (1997) 2373.
- [5] V. Swayambunathan, D. Hayes, K.H. Schmidt, Y.X. Liao, D. Meisel, *J. Am. Chem. Soc.* 112 (1990) 3831.
- [6] S.M. Oh, D.W. Park, *Thin Solid Films* 386 (2001) 233.
- [7] G.L. Messing, W.T. Minehan, *J. Ceram. Soc. Jpn.* 99 (1991) 1036.
- [8] R. van Grieken, J. Aguado, M.J. López-Muñoz, J. Marugán, *J. Photochem. Photobiol. A* 148 (2002) 315.
- [9] K. Chhor, J.F. Bocquet, C. Pommier, *Mater. Chem. Phys.* 32 (1992) 249.
- [10] M.E. Tadros, C.L.J. Adkins, E.M. Russick, M.P. Youngman, *J. Supercrit. Fluids* 9 (1996) 172.
- [11] T.H. Kim, D.Y. Lim, B.S. Yu, J.H. Lee, M. Goto, *Ind. Eng. Chem. Res.* 39 (2000) 4702.
- [12] T. Hirai, H. Sato, I. Komazawa, *Ind. Eng. Chem. Res.* 32 (1993) 3014.
- [13] E. Stathatos, D. Tsiourvas, P. Lianos, *Colloid Surf. A* 149 (1999) 49.
- [14] H. Sakai, H. Kawahara, M. Shimazaki, M. Abe, *Langmuir* 14 (1998) 2208.
- [15] P.K. Dutta, M. Jakupca, K.S.N. Reddy, L. Salvat, *Nature* 374 (1995) 44.
- [16] M.L. Steigerwald, A.P. Alivisatos, J.M. Gibson, T.D. Harris, R. Kortan, A.J. Muller, A.M. Thayer, T.M. Duncan, D.C. Douglass, L.E. Brus, *J. Am. Chem. Soc.* 110 (1988) 3046.
- [17] D.H. Chen, S.H. Wu, *Chem. Mater.* 12 (2000) 1354.
- [18] M.A. Winters, D.Z. Frankel, P.G. Debenedetti, J. Carey, M. Devaney, T.M. Przybycien, *Biotechnol. Bioeng.* 62 (1999) 247.
- [19] F. Favari, A. Bertucco, N. Elvassore, M. Fermeglia, *Chem. Eng. Sci.* 55 (2000) 2379.
- [20] D. Li, Z.M. Liu, G.Y. Yang, B.X. Han, H.K. Yan, *Polymer* 41 (2000) 5707.
- [21] M. Muller, U. Meier, A. Kessler, M. Mazzotti, *Ind. Eng. Chem. Res.* 39 (2000) 2260.
- [22] M. Yoshida, M. Lal, N. Deepak Kumar, P.N. Prasad, *J. Mater. Sci.* 32 (1997) 4047.
- [23] E. Reverchon, *J. Supercrit. Fluids* 15 (1999) 1.
- [24] P. Chattopadhyay, R.B. Gupta, *Ind. Eng. Chem. Res.* 39 (2000) 2281.
- [25] J.L. Zhang, B.X. Han, J.C. Liu, X.G. Zhang, J. He, Z.M. Liu, *Chem. Commun.* (2001) 2724.
- [26] H.F. Zhang, Z.M. Liu, B.X. Han, *J. Supercrit. Fluids* 18 (2000) 185.