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Synthesis of silica nanosphere from homogeneous and heterogeneous systems

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Abstract. **Silica nanosphere was synthesized using homogeneous and heterogeneous systems, respectively. In homogeneous system, silica spheres were synthesized without cetyltrimethylammonium bromide (CTABr), which gave bimodal particle size and lower yield (77%). To improve the yield, CTABr was added and found that the yield was very high (100%). The particle was in nm range, but the particle sizes are bimodal. To avoid it, reaction in heterogeneous system using CTABr was carried out. Nanosized silica sphere with uniform size (yield, 94%) was observed. Homogeneous system contains a mixture of ethanol, water, aqueous ammonia and tetraethylorthosilicate (TEOS). In the case of heterogeneous system, only ethanol was absent.**

Keywords. **Silica nanosphere; homogeneous; heterogeneous.**

1. Introduction

Amorphous silica nanoparticles are used in many applications including ceramics, catalysis, pharmaceutical, electronic packaging, photonic and chemical–mechanical polishing (Iler 1979; Sacks and Tseng 1984; Masuda *et al* 1990; Yamashita *et al* 1992; Taira and Yamaki 1995). In particular, special attention has recently been paid to methods for controlling the size and distribution of nanospheres, because they exhibit peculiar and desirable properties in the wafer polishing process. Monodisperse silica nanospheres were first synthesized by Stober *et al* (1968) using sol–gel method which induces high purity in the resulting particles. Bogush and Zukoski (1988) reported the influence of reaction parameters such as ammonia and water contents on the particle size and distribution.

Recently, silica nanospheres have been considered as effective candidates for chemical–mechanical polishing materials. So several investigators have reported ways to control particle size by using reactor type and varying the concentrations of ammonia, water and alcohol solvent (Sadasivan *et al* 1998; Kim *et al* 2000; Kim and Kim 2002; Park *et al* 2002). They also examined the influence of reaction methods (such as semi-batch reaction and batch reaction) on particle size and its distribution. A relatively slow rate of hydrolysis of TEOS occurred during the semi-batch process, which resulted in larger silica particles and a narrower size distribution (Kim and Kim 2002).

The mechanism of silica nanospheres formation was generally suggested to be via hydrolysis of silica source to form the singly hydrolyzed monomer. Subsequently, this intermediate reaction product condensed and eventually formed nanosphere.

2. Experimental

2.1 *Synthesis by homogeneous system without CTABr*

Tetraethylorthosilicate, 1·06 ml (98%, Aldrich, USA) was mixed with 5 ml of ethanol (98%, Aldrich, USA). To this mixture, 0·215 ml of aqueous ammonia (26–30%, Aldrich, USA) was added. Then 1·08 ml of distilled water was added. Finally 5 ml of ethanol was added. The total mixture was stirred continuously for 2 h. The product was centrifuged and washed with distilled water several times.

2.2 *Synthesis by homogeneous system with CTABr*

Cetyltrimethylammonium bromide, 2·5 g (surfactant, Aldrich, USA) was dissolved in 50 ml of deionized water, and 13·2 ml of aqueous ammonia and 60 ml of absolute ethanol were added to the surfactant solution. The solution was stirred for 15 min (250 rpm) and 4·6 ml of TEOS was added once resulting in a gel with the following molar composition: 1 TEOS: 0·3 C_{16}TMABr: 11 NH_3: 144 H_2O: 58 EtOH. After stirring for 2 h, the white precipitate was filtered and washed with distilled water several times.

2.3 *Synthesis by heterogeneous system with CTABr*

Cetyltrimethylammonium bromide (2·405 g) was dissolved in 120 ml of distilled water and 9·5 ml of aqueous

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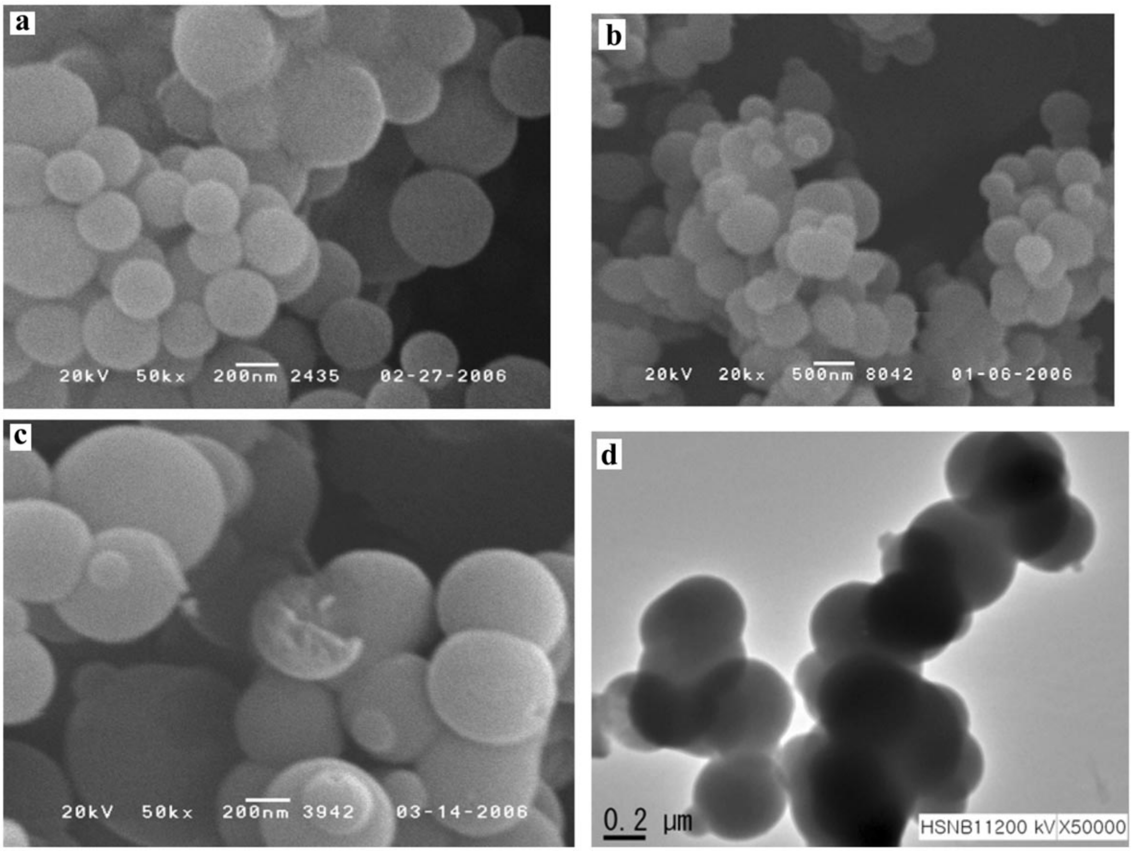

Figure 1. SEM picture of silica nanosphere synthesized from **a**. homogeneous system without CTABr, **b**. homogeneous system with CTABr, **c**. heterogeneous system with CTABr, and **d**. TEM picture of heterogeneous system sample with CTABr.

Table 1. Molar gel compositions of various processes to synthesize silica nanosphere.

Sl. no.	Gel composition	Growth period	Yield (%)	Particle size
1.	0·5 TEOS: 0·7 NH_3: 6 H_2O: 85 EtOH	2 h	77	100 and 300 nm
2.	1 TEOS: 0·3 C_{16}TMABr: 11 NH_3: 144 H_2O: 58 EtOH	2 h	100	200–500 nm
3.	1 TEOS: 0·152 CTABr: 2·8 NH_3: 141·2 H_2O	1 h	94	200 nm

Conditions: temperature = 25°C; pressure = ambient.

ammonia was added to the solution. While stirring, 10 ml of tetraethylorthosilicate was added slowly to the surfactant solution over a period of 15 min resulting in a gel with the following molar composition: 1 TEOS: 0·152 CTABr: 2·8 NH_3: 141·2 H_2O. The mixture was stirred for 1 h, then the white precipitate was filtered and washed with 100 ml of deionized water.

After drying at 363 K for 12 h, the samples were heated to 823 K (rate, 1 K/min) in air and kept at this temperature for 8 h to remove the template.

The particle size and shape were analysed by a Topcon, SM-300 scanning electron microscope. The copper disc was pasted with carbon tape and the sample was dispersed over the tape. The disc was coated with gold in ionization chamber before microscopic analysis.

3. Results and discussion

The SEM pictures of the sample synthesized (table 1) from homogeneous and heterogeneous systems are given in figure 1. Initially, silica nanosphere was synthesized in homogeneous system which involves TEOS, ethanol, aqueous ammonia and water, for 2 h. We found the particle size to be bimodal (100 and 300 nm). The yield also was less (77%). To avoid this, a calculated amount of cetyltrimethylammonium bromide was added, which increased the yield considerably (100%). Yield was calculated based on the theoretical yield from the total silica input. Here the particle sizes are not even 200–400 nm. To avoid the multiple size of particles, we changed the system into heterogeneous, where the reaction was carried out in absence of ethanol. Water and TEOS did not mix with each other. To avoid this, cetyltrimethylammonium bromide surfactant was added. Now in lesser time (1 h) of particle growth, good yield and even particle size (200 nm) occurred. The even particle size of heterogeneous system is also supported by TEM (figure 1d). No any hollow sphere nature in its TEM picture was observed, even though it shows a high surface area (>1000 m^2/g) after calcination.

4. Conclusions

Silica nanosphere with uniform size and higher yield was synthesized by modified procedure, which employs CTABr in heterogeneous system. Earlier, in our attempt with homogeneous system, with and without cetyltrimethylammonium bromide, we obtained less yield with multiple particle sizes.

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References

Bogush G H and Zukoski C F 1988 *J. Non-Cryst. Solids* **104** 95

Iler R K 1979 *The chemistry of silica* (New York: Wiley)

Kim K D and Kim H T 2002 *J. Sol–Gel Sci. Technol.* **25** 183

Kim K S, Kim S S, Kim S K, Kim J K and Kim W S 2000 *Hwahak Konghak* **38** 817

Masuda R, Takahashi W and Ishii M 1990 *J. Non-Cryst. Solids* **121** 389

Park S K, Kim K D and Kim H T 2002 *Colloids Surfaces A: Physicochem. Eng. Aspects* **197** 7

Sacks M D and Tseng T Y 1984 *J. Am. Ceram. Soc.* **67** 526

Sadasivan S, Rasmussen D H, Chen F P and Kannabiran R K 1998 *Colloids Surfaces A: Physicochem. Eng. Aspects* **132** 45

Stober W, Fink A and Bohn E 1968 *J. Colloid Interface Sci.* **26** 62

Taira M and Yamaki M 1995 *J. Mater. Sci. Mater. Med.* **6** 197

Yamashita D M, Mori H and Maekawa T 1992 *J. Ceram. Soc. Jpn* **100** 1444