

# Synthesis and Characterization of Silica Nanosphere from Octadecyltrimethoxy Silane

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Amorphous silicate nanoparticles are used in many applications including ceramics, catalysis, pharmaceutical, electronic packaging and chemical-mechanical polish.<sup>1-5</sup> In particular, special attention has recently been paid to methods for controlling the nanospheres, size and distribution, because they exhibit peculiar and desirable properties in the wafer polishing process. Monodisperse silica nanospheres were first synthesized by Stober *et al.* using sol-gel method which induces high purity in the resulting particles.<sup>6</sup> Bogush and Zukoski reported the influence of reaction parameters such as ammonia and water contents on the particle size and distribution.<sup>7</sup>

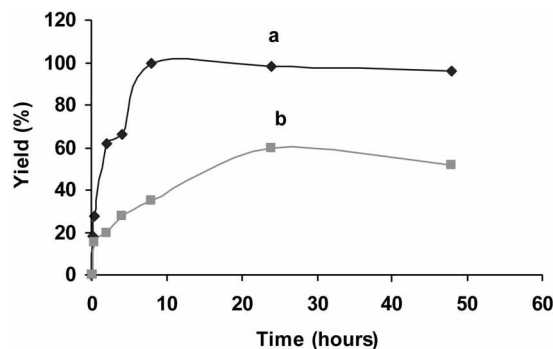
Recently silica nanospheres have been considered effective candidates for chemical-mechanical polishing materials, so several investigators have reported ways to control particle size by using reactor type and varying the concentrations of ammonia, water and alcohol solvent.<sup>8-10</sup> They also examined the influence of reaction method (such as semi-batch reaction and batch reaction) on particle size and 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.<sup>9</sup>

The mechanism of the silica nanospheres was generally suggested to be via hydrolysis of silica source to form the hydrolyzed monomer. Subsequently, this intermediate reaction product condenses and eventually forms silica. There are several problems occurs during the silica nanosphere synthesis. They include, low rate of particle growth and yield, uneven particle size and larger particle size. There are several attempts to avoid these problems by varying the reaction constituents. However, only a least success on their attempt.<sup>11</sup> Here we have attempted and overcome most of the problems by adding a new silicon source (octadecyltrimethoxy silane).<sup>12</sup> Earlier it was used as porogen in solid core/mesoporous shell silica spheres synthesis. In this communication, we report, it also acts as a particle size normalizer and efficient catalyst. One of the drawbacks in the present synthesis is the cost of octadecyltrimethoxy silane. However, we use a minimum quantity. The materials were characterized by conventional physicochemical techniques such as Scanning electron microscopy, Electron diffraction and X-ray emission analysis and Transmission electron microscopy.

3.14 mL of aqueous ammonia (28-30%, Aldrich, USA) was added to a solution containing 74 mL of ethanol (99%, Aldrich, USA) and 10 mL of deionized water. Six milliliters of tetraethoxysilane (TEOS, 98%, Aldrich, USA) was added to the above mixture at 298 K and stirred for another 1 h to yield uniform silica spheres. A mixture solution containing 5 mL of TEOS and 2 mL octadecyltrimethoxy silane (C18TMS, 90%, Aldrich, USA) was added to the solution containing the silica spheres resulting molar gel composition is, 11.4 SiO<sub>2</sub>: 6 NH<sub>4</sub>OH: 1 C18TMS: 149 H<sub>2</sub>O: 297.5 EtOH. The gel was stirred for another 1 h. The resulting octadecyl group incorporated silica nanocomposite was retrieved by centrifugation, and calcined at 823 K for 6 h under an air atmosphere to produce silica nanosphere. Another material was prepared in same procedure without octadecyltrimethoxy silane.

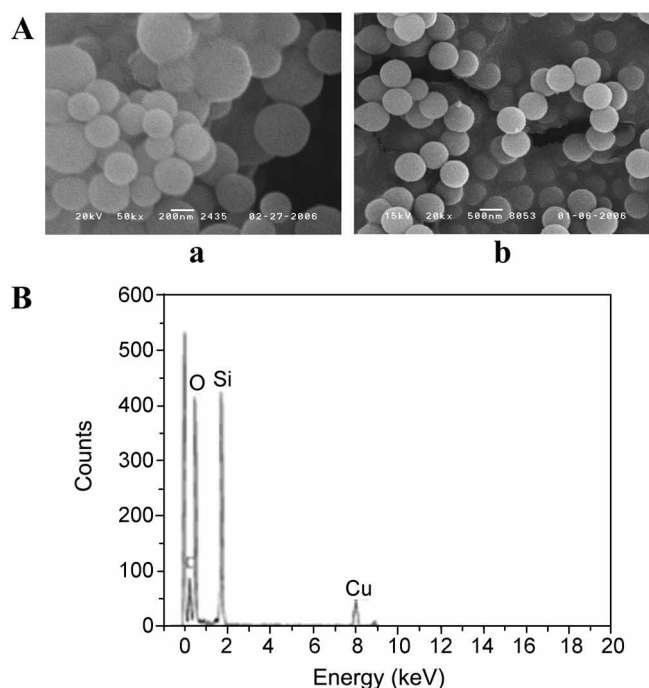
The particle size and shape were analyzed by a Topcon, SM-300 scanning electron microscope. The copper disc pasted with carbon tape and the sample was dispersed over the tape. The disc was coated with gold in ionization chamber before microscopic analysis. E-DAX analysis was also carried out by the same instrument. Transmission electron microscopic (TEM) studies were performed on a JEOL JSM-2000 EX electron microscope operated at 200 kV. The TEM sample was prepared by dipping a Cu grid coated with carbon films in sample suspension with water as solvent (solution was sonicated for 20 min).

The silica nanosphere synthesized with and without octadecyltrimethoxy silane gave yield at different time (in hours) intervals were presented in Figure 1. It follows a half S type curve. The yields were calculated in comparison with



**Figure 1.** Time (hours) vs. Yield (%) plot of silica nanosphere synthesized a) with octadecyltrimethoxy silane and b) without octadecyltrimethoxy silane.

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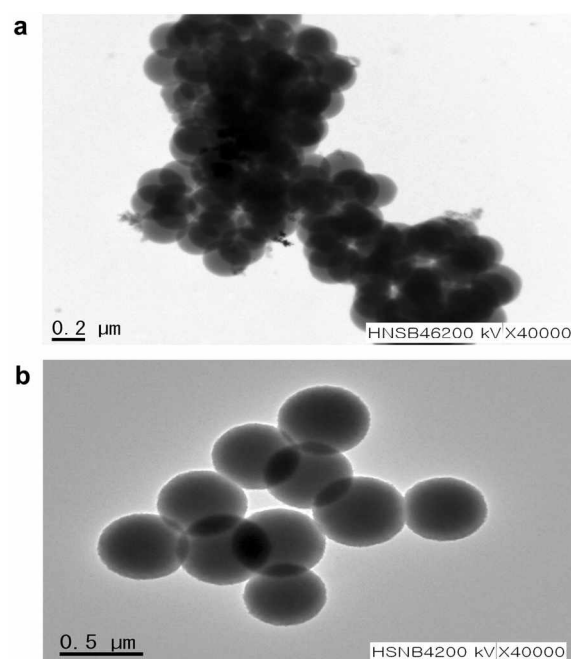
**Figure 2.** A) Scanning electron micrograph of silica nanosphere synthesized a) without octadecyltrimethoxy silane and b) with octadecyltrimethoxy silane and B) E-DAX analysis of sample synthesized with octadecyltrimethoxy silane.

the theoretical silica yield from the total input. Maximum yield occurs at 8 h. After this peak maximum, a decrease in yield is occurred. It may be due to partial dissolution in precipitated silica at higher pH from the liberated alcohol. The time required for maximum yield is high for octadecyltrimethoxy silane free batches.

Figure 2A shows the morphology and particle size. The sample synthesized without octadecyltrimethoxy silane shows bimodal particle size. The smaller particles are huge (100 nm, 80%) in amount. But the bigger particles (300 nm) are smaller (20%). However on addition of octadecyltrimethoxy silane the particle size is normalized (400 nm, 100%). Octadecyl group in trimethoxy silane molecule increase the electron density around the silane atom. So the basicity in oxide group is increased on link to silanol groups from tetraethoxy silane. So the reactivity of the modified silanol groups are slower than others and result in increased particle size. E-DAX spectrum of the as-synthesized sample shows (Fig. 2B) a peak for Si, C and O and no other impurities occur.

The TEM analysis of samples with and without octadecyltrimethoxy silane is given in Figure 3. The samples synthesized without octadecyltrimethoxy silane are normal. However the sample synthesized with octadecyltrimethoxy silane shows a core shell type structure. The shell width is 50 nm. It is known from the results that the octadecyltrimethoxy silane create core shell.

The mechanism of synthesis is as follows. Tetraethyl orthosilicate monomers were hydrolyzed to hydroxides and ethyl alcohol is liberated. Hydrolyzed silicates were conden-



**Figure 3.** Transmission electron micrograph of silica nanosphere synthesized a) without octadecyltrimethoxy silane and b) with octadecyltrimethoxy silane.

sed to form polymeric silica. Octadecyltrimethoxy silane forms a spongy thin layer around the nuclei. The resulting silica sphere was even in size.

In conclusion a bimodal synthesis of silica nanosphere was observed in conventional silica nanosphere synthesis. The particle size is normalized on addition of octadecyltrimethoxy silane. Yield with respect to time give an S type curve.

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## References

- Iler, R. K. *The Chemistry of Silica*, Wiley: New York, 1979.
- Sacks, M. D.; Tseng, T. Y. *J. Am. Ceram. Soc.* **1984**, *67*, 526.
- Masuda, R.; Takahashi, W.; Ishii, M. *J. Non-Cryst. Solids* **1990**, *121*, 389.
- Yamashita, Demiya, M.; Mori, H.; Maekawa, T. *J. Ceram. Soc. Jpn.* **1992**, *100*, 1444.
- Taira, M.; Yamaki, M. *J. Mater. Sci. Mater. Med.* **1995**, *6*, 197.
- Stober, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.
- Bogush, G. H.; Zukoski, C. F. *J. Non-Cryst. Solids* **1988**, *104*, 95.
- Park, S. K.; Kim, K. D.; Kim, H. T. *Colloids Surfaces A: Physicochem. Eng. Aspects* **2002**, *197*, 7.
- Kim, K. D.; Kim, H. T. *J. Sol-Gel Sci. Tech.* **2002**, *25*, 183.
- Sadasivan, S.; Rasmussen, D. H.; Chen, F. P.; Kannabiran, R. K. *Colloids Surfaces A: Physicochem. Eng. Aspects* **1998**, *132*, 45.
- Yun, D. S.; Kim, H. J.; Yoo, J. W. *Bull. Korean Chem. Soc.* **2005**, *26*, 1.
- Buchel, G.; Unger, K. K.; Matsumoto, A.; Tsutsumi, K. *Adv. Mater.* **1998**, *10*, 1036.