doi:10.1246/cl.2012.943

Synthesis of High-purity Spherical Silica Nanoparticles from Powder Quartz by Improved Sol–Gel Method

Jinhui Lin,[1] Hui Dan,[1,2] and Yi Ding*[1,3]
[1]*College of Materials and Chemistry and Chemical Engineering, Chengdu University of Technology, Chengdu 610059, P. R. China*
[2]*Mianyang Normal University, Mianyang 621000, P. R. China*
[3]*College of Materials Science and Engineering, Sichuan University, Chengdu 610064, P. R. China*

(Received May 4, 2012; CL-120386; E-mail: linjinh@cdut.edu.cn)

High-purity spherical silica nanoparticles have been successfully synthesized using powder quartz as silica sources in an improved sol–gel method. The effects of the modulus (molar ratio SiO_2/Na_2O) of sodium silicate and poly(ethylene glycol) (PEG) on the properties of silica nanoparticles were investigated. The results suggested that with the increase of modulus, the purity of silica nanoparticles increased. The higher purity (99.92 wt %) products can be obtained from the modulus of 3. Moreover, it was also found that the particle size, distribution, and dispersion significantly depend on the concentration of PEG. The silica nanoparticles with average size of 60 nm are well-dispersed and show a narrow size distribution when the PEG concentration is 2 wt %. The results suggest that it is feasible to prepare high-purity spherical silica nanoparticles using powder quartz as silica sources.

Silica nanoparticles have received extensively study due to their utility in various industrial applications, such as thermal insulators, composite fillers, enzyme and catalytic carriers, and insulation adiabatic fillers,[1–3] which highly depend on the purity and morphology of silica nanoparticles. Usually, tetraethyl orthosilicate (TEOS)[4–6] is used as silica source to synthesize silica nanoparticles. However, a high production cost is incurred by using this precursor. Currently, silica nanoparticle materials are prepared using several methods, including chemical vapor deposition,[7] chemical precipitation,[8] and sol–gel.[9] Among these methods, the sol–gel method is widely applied due to low cost and ease of controlling particle size and morphology. It is a good inspiration for us that there have been several reports on the preparation of silica nanoparticles from rice husk.[10–12] An alternative silica source, the powder quartz is cheap and has higher silica content than mineral. Thus, it is a good candidate for preparing silicon-based materials. To the best of our knowledge, the preparation of high-purity spherical silica nanoparticles has received little attention. A cheap approach to synthesize high-purity spherical silica nanoparticles is still a challenge.

Here, we report for the first time the successful synthesis of high-purity spherical silica nanoparticles from powder quartz by a novel sol–gel method in the presence of PEG, ethanol, and ammonia. By using an improved sol–gel method, the silicate was polymerized under the same conditions through simultaneously adding sodium silicate solution and HCl into the mother solution with certain pH value. In this way, the as-synthesized materials with well-dispersion and narrow size distribution were obtained, because the rate and way of silicate polymerization were uniform. In this paper, we discuss the effects of the modulus and PEG on the properties of products. Noticeably, it is a cheap route to synthesize high-purity spherical silica nanoparticles from powder quartz.

The natural powder quartz (PQ) mineral was leached using mixed acid H_2SiF_6 and HCl before use. A detailed process of acid leaching carried out was as follows: powder quartz and mixed acid solution (3% (v/v) H_2SiF_6 and 10% (v/v) HCl) were mixed under stirring in a glass beaker at 80 °C for 0.5 h. After leaching, the powder quartz was thoroughly washed with distilled water and then dried in an air oven at 110 °C. The acid-leached powder quartz (APQ) and sodium carbonate (Na_2CO_3) were mixed at the molar ratio of X:1 ($X = 1$–3) and then heated at 1450 °C for 2 h to obtain solid sodium silicate, followed by dissolving it using deionized water in a high-pressure reactor to obtain sodium silicate solution. In a typical synthesis procedure, 1 g of PEG was dissolved in 392 mL of deionized water. When the PEG was completely dissolved, 75 mL of ethanol and 33 mL of aqueous ammonia (25–28% ammonia) were added to obtain solution A. The pH value of the solution A was adjusted to 9 using 2 M HCl. Then, 50 mL of 0.2 M APQ derived sodium silicate solution and 2.4 M HCl were simultaneously added to the solution A under vigorous stirring at room temperature. The pH value of the system was maintained at 9 by adjusting the addition speed of HCl and sodium silicate solution. The resulting gel was aged at room temperature under static conditions for 2 h. After aging, the silica gel was filtered, washed with deionized water, and dried at 80 °C for 6 h. The as-synthesized samples were calcined at 550 °C for 6 h. The silica nanoparticles were obtained finally. The silica nanoparticle samples obtained from the different modulus of sodium silicate were designated as S-X where X refers to the modulus of sodium silicate.

Table 1 exhibits the chemical composition of the samples obtained in this study. The purity of sample PQ and that of APQ were 98.55 and 99.95 wt %, respectively. This result indicates

Table 1. Chemical composition of the samples[a]

Sample	Composition/wt %						
	SiO_2	Al	Fe	Ca	Mg	Na	Cl
PQ	98.55	0.220	0.310	0.009	0.051	0.010	N.D.
APQ	99.95	0.008	0.003	0.001	0.001	0.002	N.D.
S-1	99.89	0.0003	0.001	0.0005	0.0003	0.043	0.051
S-2	99.91	0.0004	0.002	0.0004	0.0002	0.028	0.036
S-3	99.92	0.0002	0.001	0.0006	0.0002	0.023	0.030

[a]The impurity content of the products was measured by X-ray fluorescence spectroscopy (XRF, X-ray spectrometer PW2400, Philips).

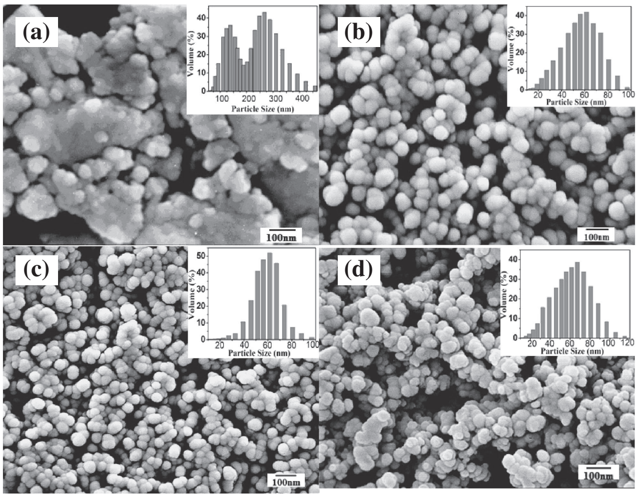

Figure 1. SEM images of silica nanoparticles obtained with different PEG concentrations: a, 0; b, 1; c, 2; d, 3 wt %. Inset represents particles size distribution curves of representative examples.

that the acid-leaching treatment can remarkably reduce the total content of metal oxide impurities and resulted in a high-content of silica in sample APQ. The purity of the silica nanoparticles obtained from the modulus of 3 was the best (99.92 wt %).

As shown in Table 1, with the increasing of the modulus of sodium silicate, the purity of silica nanoparticles improved. This may have resulted from the following two aspects. On the one hand, the amount of Na^+ ions increased with the decrease of the modulus, the purity of silica nanoparticles becomes lower because more Na^+ ions were encapsulated by silica nanoparticles. Consequently, the encapsulated Na^+ ions were hard to wash out completely. On the other hand, with the decrease of the modulus of sodium silicate, the pH value increased. The concentration of Cl^- ions in the synthesis mixtures is higher due to the greater amount of HCl needed to reduce the pH value of the system, it was also difficult to wash out completely and resulted in the purity of the silica nanoparticles decreasing.

To evaluate the influence of PEG on the products, experiments were performed by varying its concentration from 0 to 3 wt % of total mass of solution A. Figure 1 exhibits that the particle size, distribution, and dispersion can be significantly affected by the amount of PEG. Figure 1a shows that the products displayed serious aggregation and wide size distribution without PEG. The shape of particles is irregular and the particle size distribution ranged from dozens of nanometers to several hundred nanometers. The following reasons might account for the above phenomenon. Usually, in wet silica colloid, water molecules interact with the free hydroxyl groups on the surface of the silica colloid particles through hydrogen bonds. When particles get close, these molecules will draw neighboring particles together to form big particles. Obviously, the addition of PEG could effectively prevent the aggregation of silica particles (Figures 1b–1d). We considered a possible reason: the degree of adsorption of OH^- on silica particles and the interface energy of silica particles were reduced by the adsorption of PEG molecules, which could weaken the self-aggregation process; furthermore, the silica particles was wrapped by PEG molecules, which leads to electrostatic repulsion increasing because the same kind of charges were taken on the surface of silica particles, the aggregation of silica particles were prevented. When there is insufficient PEG to fully cover the surface of particles, the slight aggregation cannot be avoided. As can be seen in Figure 1b, the particle size distribution is wide, ranging from 20 to 90 nm. However, with the increase of the amount of PEG, the particle size with narrow distribution, good dispersion, and the average size of 60 nm can be observed in Figure 1c. It indicates that the appropriate concentration PEG could effectively prevent the aggregation of silica nanoparticles. But, with further increasing the concentration of PEG, the entangled PEG chains were formed in the synthesis system. Sodium silicate molecules, precursors for the silica nanoparticles, could penetrate into the entangled PEG chains. Therefore, the silica particle clusters could be formed inside the PEG matrix after the silicate polymerization. The slight aggregation and clusters of silica nanoparticles are observed in Figure 1d. It was found that the right concentrations of PEG can effectively prevent the aggregation of silica particles.

In summary, the high-purity spherical silica nanoparticles can be successfully synthesized using powder quartz as silica source by an improved sol–gel method. The purity of nano-silica powder increased with the modulus of sodium silicate solution. Narrow size distribution and well-dispersed silica nanoparticles can be formed at appropriate PEG concentrations. This shows that the powder quartz has the potential to be used as an alternative and cheap silica source in the production of silica nanoparticle materials.

The authors express thanks to the education department of Sichuan province for its financial support under key project (No. 2004A147).

References

1 L. Sun, K. Gong, *Ind. Eng. Chem. Res.* **2001**, *40*, 5861.
2 J. Pang, Y. Luan, F. Li, X. Cai, Z. Li, *Mater. Lett.* **2010**, *64*, 2509.
3 S. W. Shang, J. W. Williams, K.-J. M. Söderholm, *J. Mater. Sci.* **1992**, *27*, 4949.
4 R. Masuda, W. Takahashi, M. Ishii, *J. Non-Cryst. Solids* **1990**, *121*, 389.
5 C. R. Silva, C. Airoldi, *J. Colloid Interface Sci.* **1997**, *195*, 381.
6 W. Yan, L. Shi, S. Yuan, Y. Zhao, J. Fang, J. Zhao, *Mater. Lett.* **2010**, *64*, 1208.
7 N. Awaji, S. Ohkubo, T. Nakanishi, T. Aoyama, Y. Sugita, K. Takasaki, S. Komiya, *Appl. Phys. Lett.* **1997**, *71*, 1954.
8 T. Jesionowski, *Powder Technol.* **2002**, *127*, 56.
9 J. R. Martínez, S. Palomares-Sánchez, G. Ortega-Zarzosa, F. Ruiz, Y. Chumakov, *Mater. Lett.* **2006**, *60*, 3526.
10 T.-H. Liou, *Mater. Sci. Eng., A* **2004**, *364*, 313.
11 N. Yalçin, V. Sevinç, *Ceram. Int.* **2001**, *27*, 219.
12 J. Umeda, K. Kondoh, *Ind. Crops Prod.* **2010**, *32*, 539.