Novel One-pot Sol–Gel Preparation of Amino-functionalized Silica Nanoparticles

Song Chen,[1] Akiyoshi Osaka,*[1] Satoshi Hayakawa,[1] Kanji Tsuru,[1] Eiji Fujii,[2] and Koji Kawabata[2]
[1]*Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka, Okayama 700-8530*
[2]*Industrial Technology Center of Okayama Prefecture, 5301 Haga, Okayama 701-1296*

(Received August 12, 2008; CL-080782; E-mail: a-osaka@cc.okayama-u.ac.jp)

Amino-functionalized silica nanoparticles smaller than 200 nm in diameter were directly prepared from precursor mixtures of tetraethoxysilane and aminopropyltriethoxysilane in ethanol/water solutions via a novel one-pot sol–gel procedure.

Solid, hollow, and mesoporous silica-based particles, applicable to drug-carriers or bone regenerative fillers,[1,2] have been prepared through a few synthetic routes,[3–5] including the Stöber sol–gel method. For further functionalizing the particles, surfaces were modified to introduce amino or carboxyl groups, using organosilanes with relevant groups at an end. Manzano et al.[6] and Li et al.[7] used 3-aminopropyltriethoxysilane (APTES) after treating their silica particles with piranha solution (H_2SO_4/H_2O_2) or HF–HNO_3 mixture, which in turn leads to increasing the amounts of the hydroxy groups. However, a disadvantage is the danger and toxicity of the piranha solution and nitric acid. In addition, most methods need two independent steps: preparation of silica particles and modification of the silica particles. The multistep operations are complex and disadvantageous, too. Here, we proposed a new one-step/one-pot method to prepare amino-functionalized silica particles with a narrow size distribution.

Table 1 lists the compositions of the starting materials. The ethanol/water mixtures were prepared in a 50-mL flask, before appropriate amounts of tetraethoxysilane (TEOS) and APTES were sequentially added to the above mixtures. Then the solutions were agitated and stirred for 30 min at room temperature to produce an opaque suspension. As described later, the stability of the suspension depended on the mixing ratio of the starting materials. The particles were then collected by centrifugation at 2,800 rpm for 5 min, washed with distilled water 3 times, and then dried at 105 °C overnight.

Table 1. The compositions of the starting solutions and particle sizes of the amino-functionalized silica

Sample	APTES /mmol	TEOS /mmol	Ethanol /mmol	Water /mmol	Particle size /nm
1	0.45	4.5	87	280	≈140, 30
2	0.13	0.45	87	280	≈150, 40
3	0.45	4.5	440	280	40–80

Size and morphology of the samples were observed by transmission electron microscopy (TEM; Model JEM-2010, JEOL, Japan). The IR spectra of the resultant particles were recorded on a Fourier transform infrared spectrophotometer (FTIR, Model 300, JASCO, Japan) with a KBr pellet method.

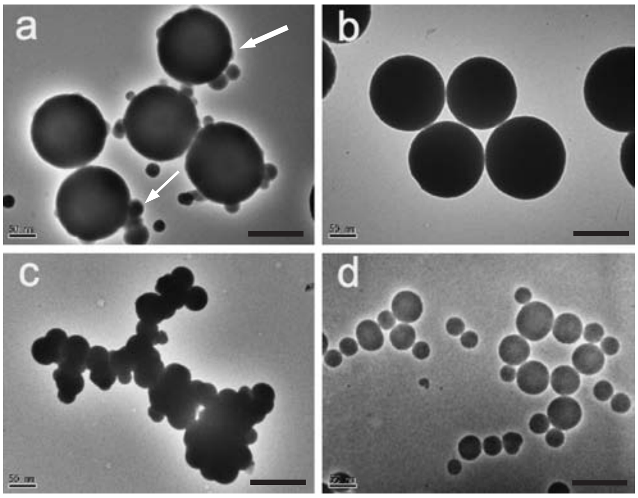

Figure 1. TEM images: Samples 1 (a), 2 (b, c), and 3 (d). Bar: 100 nm.

Figure 1 shows the TEM images of Sample 1 (a), Sample 2 (b) and (c), and Sample 3 (d). All gave spherical particles with the diameter less than 200 nm; the particle size and size distribution depended on the mixing ratios of the starting materials. Sample 1 consisted of particles in two different particle size ranges, or showed a bimodal size distribution: the larger one was 140 nm in diameter and the smaller was ≈30 nm. The smaller particles (arrows) tended to attach on or be aggregated around the larger particles. Sample 2 also indicates a bimodal particle size distribution; it consisted of larger particles (b) 150 nm in diameter and smaller ones (c) about 50 nm. The particles, either larger or smaller, of Sample 2 were slightly larger than those of Sample 1. The smaller ones of Sample 2 were likely to agglomerate themselves to form aggregates. The APTES/TEOS molar ratios for Sample 1 and Sample 2 are 0.1 and 0.28, respectively. A comparison between Sample 1 and Sample 2 indicates that the increase in the APTES/TEOS molar ratio led to more serious agglomeration and that their reaction conditions were not optimum.

Moreover, the reactions in the precursor solutions for Samples 1 and 2 were so vigorous that the solutions, transparent at the beginning, rapidly became opaque (turbid) within a few minutes. White sediment precipitated from the opaque suspensions onto the bottom of the reaction vessel. Thus, such vigorous reaction of APTES and TEOS under larger water content, or a small ratio of ethanol/water (Table 1), seemed unfavorable to obtain the particles with a narrow size distribution. Solution systems dilute in the reactant concentration retard the reaction. Then, the amount of water was reduced and the ratio ethanol/water was increased to 1.57 as the ratio APTES/TEOS was fixed at 0.1 (Sample 3). The reaction in this precursor solution was much milder than that for Samples 1 and 2, and no precipitates were detected within 30 min. Figure 1d shows that the particles of Sample 3 were spherical in shape less than 100 nm in diameter,

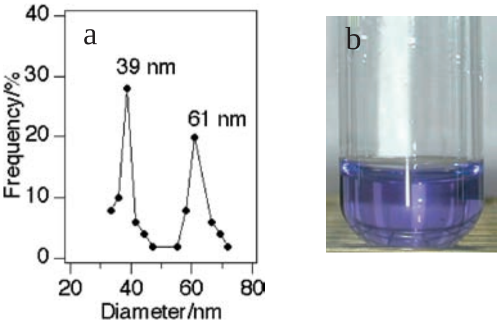

Figure 2. Particle size distribution of (a) and a micrograph of ninhydrin solution incubated with (b) Sample 3.

and in contrast to those of Sample 1 and Sample 2, they are only slightly agglomerated. Its size distribution was thus obtained by directly measuring the diameter of particles from TEM images and plotted in Figure 2a. The particles showed a bimodal distribution, with peaks at ≈39 and 61 nm. The increased molar ratio ethanol/water, i.e., dilution in terms of water, led to mild reactions and contributed to decrease in the particle size and better dispersion.

Sample 3 was then characterized first in terms of FTIR spectrum to confirm involvement of amino or other functional groups. Sample 1 and Sample 2 gave a similar IR spectral profile. In Figure 3, the 2941 and 2873 cm^{-1} bands are two typical bands for $-CH_2$ groups, while the 1552 cm^{-1} band is attributed to the $-NH_2$ groups, both of which were associated with the APTES skeleton. The strong, sharp peak at 1070 cm^{-1} ($\nu(SiO_4)_{asym}$) as well as the small, sharp peak at 798 cm^{-1} peak ($\nu(SiO_4)_{sym}$) were assigned to the –Si–O–Si– bonds constructing the silicate network.[8,9] The absorption peaks around 565 and 460 cm^{-1} were attributed to the Si–O–Si bending vibration.[9] The weak shoulder peak at 960 cm^{-1} was attributed to the Si–OH groups and the 1645 cm^{-1} peak was assigned to the adsorbed water. The wide, bulky peak at 3500 cm^{-1} is an envelope of the bands for adsorbed water, the hydroxy groups of silanol groups (Si–OH), and the amino groups ($-NH_2$). Thus, the silica particles rich in amino groups were obtained. In addition, after Pryce and Hench,[10] the surface amino groups could be confirmed and quantified with a ninhydrin reagent that reacts with the primary amino groups to produce Ruhemann's purple.[11] The purple solution in Figure 2b confirms that some primary amino groups were present on the particle surface (0.04 mmol/g particles).

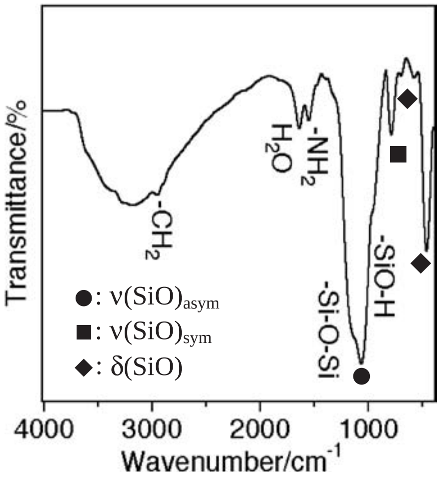

Figure 3. A FTIR spectrum of Sample 3.

As reported by Hüsing, Schubert, et al.[12] the amino groups in APTES could catalyze the hydrolysis and condensation of TEOS and showed a catalytic ability. Moreover, Ottenbrite, Wall, and co-worker[13] further pointed out that an increase in APTES concentration resulted in an increase in the pH of the solution. When APTES was added to the mixture of ethanol/water/TEOS, the pH rapidly increased (>11) owing to the strong protonation of $-NH_2$ groups and produced a large amount of OH^- ions that initiated the sol–gel reaction in the precursor mixture of water/ethanol/TEOS/APTES.

In addition, as mentioned above, the FTIR spectrum of Sample 3 showed the presence of fewer silanol groups and a larger amount of Si–O–Si groups in the particles, indicating that most of the Si–OH groups were condensed to form the Si–O–Si skeletal network of silica and that both TEOS and APTES have a high reactivity in the precursor system.

In conclusion, we developed a novel one-pot sol–gel process to prepare amino-functionalized silica nanoparticles within a few hours without the use of toxic and corrosive treating agents. The particle size and morphology could be well controlled by adjusting the compositions of the starting solutions, and the resultant particles with few agglomerations were spherical in shape less than 100 nm in diameter. The surface amino groups were confirmed and quantified with a ninhydrin reagent. Although the role of APTES in the particle formation mechanism is still under investigation, such amino-functionalized silica particles have a potential application as the carriers of enzymes, drugs, and DNA for biomedical applications.

References

1 Y. Aburatani, K. Tsuru, S. Hayakawa, A. Osaka, *J. Ceram. Soc. Jpn.* **2003**, *111*, 318.
2 S. Angelos, M. Liong, E. Choi, J. I. Zink, *Chem. Eng. J.* **2008**, *137*, 4.
3 M. Pirouzmand, M. M. Amini, N. Safari, *J. Colloid Interface Sci.* **2008**, *319*, 199.
4 W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.* **1968**, *26*, 62.
5 T. Shiomi, T. Tsunoda, A. Kawai, H. Chiku, F. Mizukami, K. Sakaguchi, *Chem. Commun.* **2005**, 5325.
6 M. Manzano, V. Aina, C. O. Arean, F. Balas, Vauda, M. Colilla, M. R. Delgado, M. Vallet-Regi, *Chem. Eng. J.* **2008**, *137*, 30.
7 X. Li, Y. He, M. T. Swihart, *Langmuir* **2004**, *20*, 4720.
8 V. G. Pol, D. N. Srivastava, O. Palchik, V. Palchik, M. A. Slifkin, A. M. Weiss, A. Gedanken, *Langmuir* **2002**, *18*, 3352.
9 S. Hayakawa, L. L. Hench, *J. Non-Cryst. Solids* **2000**, *262*, 264.
10 R. S. Pryce, L. L. Hench, *J. Mater. Chem.* **2004**, *14*, 2303.
11 M. Friedman, *J. Agric. Food Chem.* **2004**, *52*, 385.
12 N. Hüsing, U. Schubert, R. Mezei, P. Fratzl, B. Riegel, W. Kiefer, D. Kohler, W. Mader, *Chem. Mater.* **1999**, *11*, 451.
13 R. M. Ottenbrite, J. S. Wall, J. A. Siddiqui, *J. Am. Ceram. Soc.* **2000**, *83*, 3214.

Published on the web (Advance View) October 25, 2008; doi:10.1246/cl.2008.1170