Novel Synthesis of Submicrometer Silica Spheres in Non-alcoholic Solvent by Microwave-assisted Sol–Gel Method

Kaoru Adachi, Takeru Iwamura, and Yoshiki Chujo*
Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University,
Katsura, Nishikyo-ku, Kyoto 615-8510

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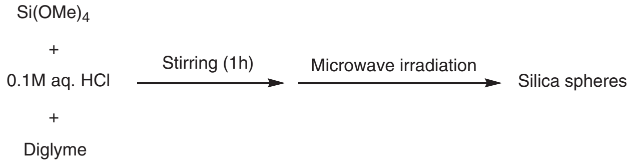
Monodisperse submicrometer silica spheres in the range of 200–700 nm diameter were rapidly prepared in less than 3 min by sol–gel reaction of tetramethoxysilane with assistance of 2.54 GHz, 500-W microwave irradiation in non-alcoholic diglyme solution in the presence of an acidic catalyst.

Nanometer and submicrometer metal oxide spheres have been attracting a lot of attention in many fields, such as optical materials, catalysts, and other nanotechnologies.[1] Regarding such applications, a monodisperse size distribution and an easy surface modification are desirable. The sol–gel method[2] is one of the most useful methods to prepare such metal oxide spheres. In most cases such as Stöber method, these materials have been prepared in alcoholic solutions.[3] However only a few investigations were reported about the use of non-alcoholic solvent.[4] In non-alcoholic solvents, the surface modification using silane coupling agents or chlorosilanes would become easier and the effect should be improved. In the present research, non-alcoholic solvent was used.

Microwave technology has been applied to various chemical reactions.[5] Generally, the microwave method is fast, simple, and highly energy efficient. We have been investigating a preparation of hybrid materials from an organic polymer and a silica-gel utilizing the microwave-assisted sol–gel method.[6] Recently, the microwave method has been applied to the preparation of metal oxide nanoparticles. For example, using a microwave-assisted polyol method, TiO_2 nanocrystallites,[7] SnO_2 sols[8] and $BaTiO_3$, $Ba_6Ti_{17}O_{40}$, $BaZrO_3$, $PbTiO_3$ nanoparticles[9] have been prepared. In this communication, a novel rapid synthesis of submicrometer silica spheres is reported. Bis(2-methoxymethyl) ether (diglyme) was used as a non-alcoholic solvent and the silica spheres were prepared by the microwave-assisted sol–gel reaction of tetramethoxysilane (TMOS) with an acidic catalyst.



Scheme 1. Synthetic scheme of microwave-assisted sol–gel method in non-alcoholic solvent.

Microwave irradiation experiments were performed using a microwave oven (Matsushita NE-NS70), equipped with a magnetron (2.45 GHz, 500 W). The reaction was carried out in a PTFE beaker at the center of the microwave oven. Into 50 mL of sealed glass bottle, diglyme (40 mL) was poured and TMOS (1 mL) and acidic water (0.1 M aq HCl) were added. For the hydrolysis of TMOS, the mixture was stirred at ambient temperature for 1 h. Then, the solution was poured into 50 mL of PTFE beaker. The beaker was put at the center of the microwave oven and to the solution, microwave was irradiated. To evaluate the effect of microwave irradiation time, the experiments were carried out with different irradiation time (Table 1). Only 2-min microwave irradiation gave a white precipitation and, as a result, turbid solution was obtained. More than 3-min irradiation led some evaporation of the solvent. The solution temperature was found to be 128, 133, and 136 °C after 2-, 2.5-, and 3-min microwave irradiation, respectively. This reaction time is extraordinary short even compared with other methods to prepare such silica spheres. The solution was subjected to dynamic light scattering (DLS) analysis, which was performed by Otsuka FPAR-1000 system. For comparison with microwave treatment, conventionally heated (140 °C, 12 h) turbid solution was also prepared. The white precipitates were separated by centrifuging at 2500 rpm for 10 min (60 min for conventional heating). For all samples, the obtained precipitates were washed with tetrahydrofuran twice under ultrasonication and centrifuged at 2500 rpm for 10 min (60 min for conventional heating) and dried under vacuum, then subjected to scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses. SEM measurements were conducted using a JEOL JSM-5600 system. XRD was performed by a Rigaku Miniflex system.

Figure 1 shows the SEM images of the prepared precipitates. In all the cases of the microwave heating (Figures 1a–1c), the observed particles were spherical with narrow dispersion of the

Table 1. Preparation of silica spheres via microwave heating and conventional heating

Run	TMOS /mL	Diglyme /mL	0.1 M HCl aq/mL	Stirring Time/h	Heating	Temperature[b] /°C
1	1	40	1	0.5	Microwave[a] 120 s	128
2	1	40	1	0.5	Microwave[a] 150 s	133
3	1	40	1	0.5	Microwave[a] 180 s	136
4	1	40	1	0.5	Oil bath (140 °C) 12 h	—

[a] 2.45 GHz 500 W.
[b] Solution temperature after microwave irradiation.

Table 2. Prepared silica particles and their diameters

Run	Heating	Shape[a]	Diameter[b]/nm	Diameter[c]/nm	
					Std[d]
1	Microwave 120 s	Sphere	222.2	546	65
2	Microwave 150 s	Sphere	240.3	607	39
3	Microwave 180 s	Sphere	351.7	667	50
4	Oil bath (140 °C) 12 h	Random	N/D	N/D	N/D

[a] Observed in SEM image.
[b] Determined by DLS analysis.
[c] Determined by SEM image.
[d] Standard deviation.

particle size in the range of 200–700 nm diameter. With the increase of microwave irradiation time, the size of the particle was increased. Surprisingly, only few aggregated particles were obtained and the particle surfaces were smooth. In the case of conventional heating (Figure 1d), various shapes and various sizes of the particles were observed. And most of the particles were aggregated.

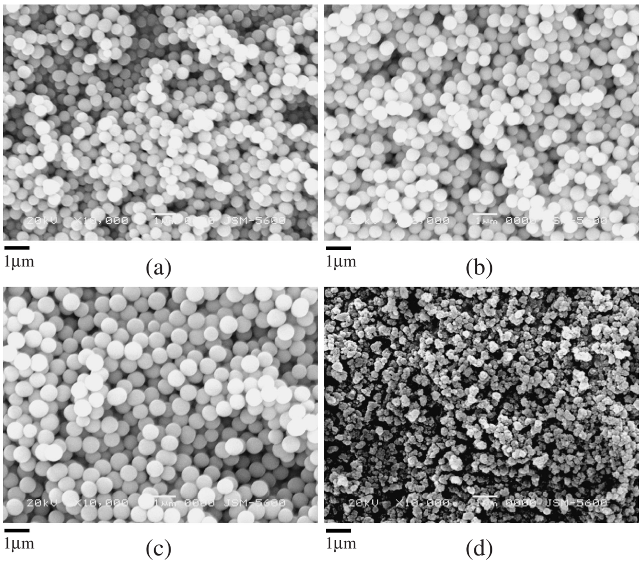


Figure 1. SEM images of the precipitates. (a)–(c) Spherical silica particles prepared by microwave heating (2.45 GHz, 500 W): 120, 150, 180 s irradiated respectively. (d) Random shape silica particles prepared by conventional heating (oil bath, 140 °C, 12 h).

Table 2 shows the results of the obtained particle shapes and their average diameters. The average diameters of the samples prepared by 120-, 150-, and 180-s microwave irradiation were 222.2, 240.3, and 351.7 nm from DLS analyses, respectively. From the SEM images, the particle sizes were found to be 546, 607, and 667 nm, respectively. In all cases, the results by DLS were smaller than that observed in the SEM images. It may be due to the difference of refractive index depending on the solute such as partially hydrolyzed TMOS, methanol, and water. From these results, the particle sizes were increased with the increase of microwave irradiation time and it can be concluded that the particles grew by the microwave irradiation.

From the above results, this spherical growth by microwave heating could be assumed by the followings. At first, the silica seeds were produced during the stirring at ambient temperature. Then, during the microwave irradiation, the energy of microwave was absorbed at the surface of the seeds directly because of the polarized silanol groups. This direct heating might increase the reactivity of the surface. Due to the low microwave absorption of the solvent, however, the solution temperature might be low and the vibration of the seeds should be slow. Then, the seeds would react faster with dissolved alkoxysilanes than aggregation with other seeds. Repeating this reaction grows the spherical silica particles. In the case of conventional heating, on the other hand, energy was transferred slowly through the vibration of the solvent molecules and the particle formation was slow. Then the seeds were aggregated and the random shape silica particles were obtained.

The phase of the obtained silica spheres was examined by XRD analysis. Figure 2 shows XRD patterns of the silica spheres prepared by microwave heating (Run 3 in Table 2) and conventional heating (Run 4 in Table 2). In both patterns, only broad amorphous halos ($2\theta = 20$–30) derived from homogeneously amorphous silica matrix are shown. These results suggest that the microwave heating gave amorphous silica gel similar to the conventional heating.

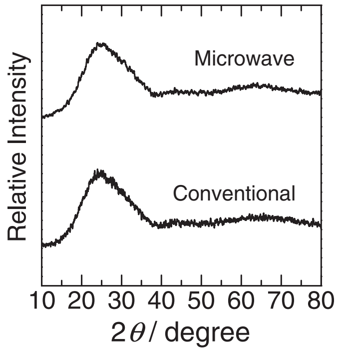


Figure 2. XRD patterns of the silica spheres prepared by microwave heating and conventional heating.

In conclusion, the amorphous submicrometer silica spheres were prepared rapidly by the microwave-irradiated sol–gel reaction of TMOS with an acidic catalyst in diglyme as a solvent. The particle sizes were increased by the microwave irradiation time. In contrast, random shape silica particles were obtained by the conventional heating at 140 °C. The characters of the obtained spheres should be different from the silica spheres prepared by other methods because of the following three different factors: (1) acidic condition, (2) non-alcoholic solvent, and (3) under microwave irradiation. Further investigation concerning the mechanism of particle growth and applications of the silica particles is now ongoing.

References

1 W. Wang, B. H. Gu, L. Y. Liang, and W. A. Hamilton, *J. Phys. Chem. B*, **107**, 12113 (2003); J. E. G. J. Wijnhoven and W. L. Vos, *Science*, **281**, 802 (1998); P. Jiang, J. F. Bertone, and V. L. Colvin, *Science*, **291**, 453 (2001); O. D. Velev and E. W. Kaler, *Adv. Mater.*, **12**, 531 (2000); Y. N. Xia, B. Gates, and Z. Y. Li, *Adv. Mater.*, **13**, 409 (2001).

2 C. J. Brinker and G. W. Scherer, "Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing," Academic Press Inc., San Diego, CA (1990).

3 W. Stöber and A. Fink, *J. Colloid Interface Sci.*, **26**, 62 (1968).

4 S. Roy, S. Bandyopadhyay, and D. Chakravorty, *J. Mater. Sci. Lett.*, **15**, 1872 (1996).

5 K. J. Rao, B. Vaidhyanathan, M. Ganguli, and P. A. Ramakrishnan, *Chem. Mater.*, **11**, 882 (1999); S. Deshayes, M. Liagre, A. Loupy, J. L. Luche, and A. Petit, *Tetrahedron*, **55**, 10851 (1999); N. Kuhnert, *Angew. Chem., Int. Ed.*, **41**, 1863 (2002); P. Lidstrom, J. Tierney, B. Wathey, and J. Westman, *Tetrahedron*, **57**, 9225 (2001).

6 K. Adachi and Y. Chujo, *Polym. Prepr. Jpn.*, **52**, E254 (2003).

7 T. Yamamoto, Y. Wada, H. B. Yin, T. Sakata, H. Mori, and S. Yanagida, *Chem. Lett.*, **2002**, 964.

8 E. Michel, D. Stuerga, and D. Chaumont, *J. Mater. Sci. Lett.*, **20**, 1593 (2001).

9 O. Palchik, J. J. Zhu, and A. Gedanken, *J. Mater. Chem.*, **10**, 1251 (2000).

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