

Simple preparation of monodisperse hollow silica particles without using templates†

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Received (in Cambridge, UK) 7th February 2003, Accepted 20th May 2003

First published as an Advance Article on the web 13th June 2003

Monodisperse hollow silica particles were prepared without using templates *via* a two-step method in an aqueous solution, were controlled in size and hollow diameter, and were selectively soluble in organic solvents, leading to usefulness in many applications such as coating technology, catalysis, delivery systems, nanoreactors, and composite materials.

Ceramic hollow particles have been studied in recent years because of their potential applicability to industrial and biological fields.^{1,2} The earlier literature has reported on the syntheses of ceramic hollow particles, including spray drying techniques, templating methods, and so on.^{3–8} In a typical templating procedure, hollow particles are prepared by coating of the template with a thin layer of the precursor like a sol and a dispersion and subsequent removal of the template *via* a thermal decomposition or a chemical dissolution.^{3,9–11} This process has the advantage of preparing monodisperse hollow particles, while, unfavorably, it has a cumbersome procedure for removing the template. For the preparation of hollow silica particles with a simpler and easier method that eliminates the template-removing procedure, we used a two-step method, a convenient method without using a template, in this study. The method allowed us to prepare hollow silica particles that were monodisperse in size and whose size and hollow diameter were controlled by varying the experimental conditions. The hollow silica particles as prepared are expected to be used in diverse applications including delivery systems, catalysis, coating technology, composite materials, *etc.*

It is well known that the sol–gel process has been used to prepare silica and other metal oxide particles.^{12,13} For the preparation of hollow silica particles, a two-step method based on the sol–gel process was used in this study. In the first step the hydrolysis of phenyltrimethoxysilane (PTMS) was performed under acidic conditions. Hydrolysis time plays an important role in the formation of hollow particles. In the second step the condensation of the silane progressed under basic conditions, resulting in production of monodisperse hollow silica particles. The experimental procedure is as follows: in the first step, an aqueous solution containing 0.66×10^{-2} M HNO₃ was placed in an isothermal water bath (60 °C). PTMS (0.06 M) was added to the solution, with stirring, for the hydrolysis. The mixture solution was stirred at a rate of 260 rpm for 0.5–4.0 min. In the second step, NH₄OH solution (1.44 M) was added to the resultant homogeneous solution for the condensation. The transparent mixture solution became a milky solution immediately. The solution was continuously stirred for 1 h. The resultant particles were collected with a membrane filter and washed with water and ethanol several times. The particles were dried for 2 h in a vacuum oven at 80 °C. The size and morphology of the particles were determined by scanning

electron microscopy (SEM) and transmission electron microscopy (TEM).

Fig. 1(a) shows SEM micrographs of monodisperse hollow silica particles (particle size = 780 nm, hollow diameter = 280 nm) prepared through a two-step method with PTMS. It is shown that as-prepared particles have a spherical structure with a uniform and smooth surface texture. The morphology of the particles obtained had the same appearance in all of the experimental conditions. As shown in Fig. 1(b), the particles were soluble in organic solvents. Also, they were observed with a hollow in the micrograph. Fig. 2(a) shows a TEM micrograph of the monodisperse hollow silica particles obtained. A noticeable contrast between the core and the shell of the particles was observed in the micrograph. It was also evident that the monodisperse silica particles prepared *via* the two-step method were of hollow structure consistent with the SEM result shown in Fig. 2(b). X-Ray diffraction (XRD) patterns of as-prepared particles indicate that the particles were not of crystalline structure but of amorphous structure, resulting from no observance of a remarkable peak.

As mentioned above, hydrolysis time in the first step was the crucial effect on preparation of hollow silica particles in the two-step method. The hydrolysis time used in the present study for preparation of hollow particles was in the range of 0.5–4.0

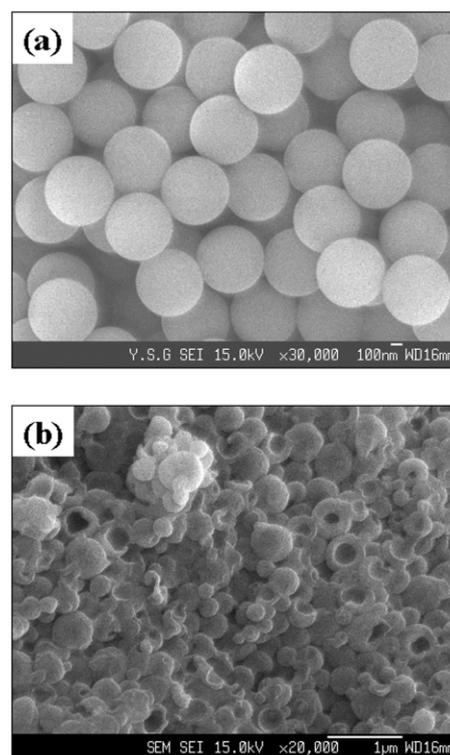


Fig. 1 SEM micrographs of (a) the monodisperse hollow silica particles obtained by the two-step method and (b) the particles dried immediately after rapidly dissolving with acetone.

† Electronic supplementary information (ESI) available: TEM showing effects of hydrolysis time, reaction temperature and calcination on the particles. TGA of hollow particles, BET measurements of hollow and calcined hollow particles. See <http://www.rsc.org/suppdata/cc/b3/b301521a/>

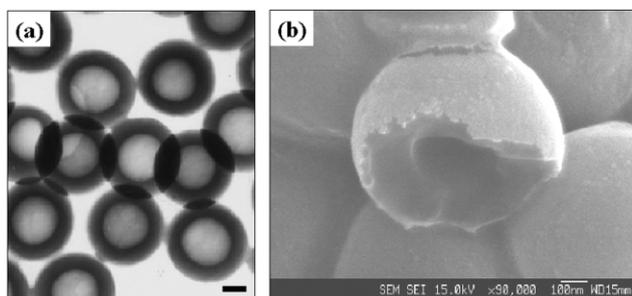


Fig. 2 TEM micrograph of (a) monodisperse hollow silica particles (scale bar: 200 nm) and SEM micrograph of (b) the broken hollow particle after mechanically fracturing.

min, in which all the resultant particles were observed as hollow particles. Outside this range no hollow silica particles were obtained. The particle size and hollow diameter of the particles were controlled by the hydrolysis time. In the range of hydrolysis time, the particles were obtained in the size of 300–800 nm (Table 1). The hollow diameter of the particles was observed in a range of 40–500 nm, which was estimated by measuring the diameter of the bright circular part of the particle in the TEM micrograph. The ratio of hollow diameter to particle size obtained experimentally was in the range of 0.10–0.67. The particle size decreased with increasing hydrolysis time. In addition, the particle size and hollow diameter of the particles can also be controlled by other variables such as PTMS concentration, reaction temperature, and so on. The thermal property and BET measurements of the particles are shown in the ESI.†

The mechanism of the formation of the hollow structure is not clear. However, it may be supposed as follows. When PTMS is added to the acidic solution in the first step, PTMS is immiscible with the aqueous solution and phase separation (silane–water) occurs in the mixture solution. Under stirring conditions, droplets of PTMS are formed and become smaller gradually due to miscibility of hydrolyzed PTMS with the aqueous solution as the hydrolysis progresses. In the second step, NH_4OH solution is added to the resultant homogeneous solution and then the condensation is commenced immediately. After a second to minutes, the turbidity of the mixture solution increases rapidly and monodisperse hollow silica particles are prepared ultimately. The production of methanol caused by hydrolysis has an effect on the solubility of the unhydrolyzed PTMS, existent in the interior of droplets, in the aqueous solution. The release of the unhydrolyzed PTMS with methanol from the droplets coincides with the formation of silica particles. In general, hydrolysis occurs continuously in basic conditions as well as in acidic conditions, although the rate of condensation is faster than that of hydrolysis in basic conditions.⁹ The released PTMS monomers are used for the growth of particles. Consequently, hollow silica particles are prepared in this system. Hydrolysis time plays an important role in the preparation of hollow silica particles, because it strongly relates to the solubility of PTMS.

Solid-state ^{29}Si nuclear magnetic resonance (NMR) spectroscopy provides information about the condensation reaction. The ^{29}Si NMR spectra of monodisperse hollow silica particles

Table 1 The particle size and hollow diameter of monodisperse hollow silica particles with hydrolysis time (condition: PTMS 0.06 M, 60 °C)

	Hydrolysis time/min			
	0.5	1.0	2.0	4.0
Particle size ^a /nm	800	780	575	300

^a The hollow diameter of the particles can be controlled by other variables such as PTMS concentration, reaction temperature and HNO_3 concentration. When particle size is 600 nm, the hollow diameter can be controlled in a range of 50–400 nm.

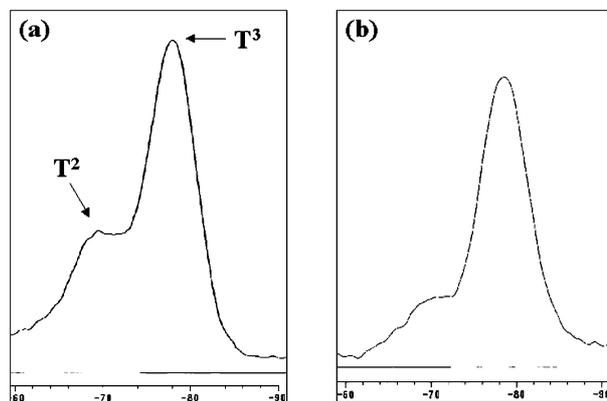


Fig. 3 Solid-state ^{29}Si NMR spectra of monodisperse hollow silica particles. (a) The spectra of particles obtained after washing only with water. (b) The spectra of particles obtained after washing with ethanol three times.

prepared *via* the two-step method are shown in Fig. 3. These spectra show two peaks at -78.1 and -69.4 ppm, which can be assigned to T^3 ($\text{C}_6\text{H}_5\text{SiO}_3$) and T^2 ($\text{C}_6\text{H}_5\text{SiO}_2(\text{OH})$) silicon sites. In the particles washed only with water, both T^3 and T^2 peaks were shown in their spectra. However, a decrease of the intensity of the T^2 peak was evident in the spectra of the particles obtained after washing with ethanol three times. This can be explained by the fact that ethanol, which is permeable through the particle, released linear oligomers (T^2) from the interior of the particles during the washing procedure.

Characteristically, the as-prepared monodisperse hollow silica particles are soluble in organic solvents including acetone, chloroform, tetrahydrofuran, *etc.* This feature of the particles can be used in application fields including delivery systems, nanoreactors, coating technology, catalysis, and so forth.

In conclusion the present paper has demonstrated a two-step method to prepare monodisperse hollow silica particles, which is a simple and easy method without using organic templates such as surfactants, polymer latex cores, *etc.* The particle size and hollow diameter of the particles can be controlled by the variation of the hydrolysis time: the particle size was in a range of 300–800 nm and the ratio of hollow diameter to particle size was in a range of 0.10–0.67. The particle size and hollow diameter can also be controlled by other variables such as PTMS concentration, reaction temperature, *etc.* Moreover, the particles are soluble in some organic solvents and may be useful in many application fields.

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