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Synthesis of mesoporous silica nanosphere using different templates

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Abstract

Synthesis of mesoporous silica nanosphere were carried out using polyvinyl pyrrolidine and different templates with surfactant property, namely cetyltrimethylammonium bromide, cetyltrimethylammonium chloride, *n*-octylamine, tetrapropylammonium bromide (TPABr) and these amines give good yield except TPABr. Attempts with other amines without surfactant properties, such as *n*-propylamine, diethylamine, triethylamine, triethanolamine templates did not give any precipitate in the present reaction scheme. The above synthesis followed by sonication did not change the trend. However addition of dodeycl sodium sulfate surfactant before sonication gave precipitate in all amines, which shows particle growth is induced by surfactant.

PACS: 00: General

Keywords: A. Silica; A. Nanomaterials; A. Mesoporous; B. Synthesis

1. Introduction

There are several works in the literature on formation of spherical nanosilica materials [1–18] and many of them are mesoporous spheres [7–18]. These are widely used as small containers in drug delivery and catalysis [19,20]. Effort has been made to invent chemical routes for the synthesis of mesoporous nano spheres [7–18]. The method of using a 'hard template' to control the inner hollow core, also called the core shell technique, is probably the most effective method for this purpose [7,8]. Conventionally there are many templates, such as organic amines and quarternary ammonium salts, available in literature. Among them, cetyltrimethylammonium bromide, cetyltrimethylammonium chloride and *n*-octylamine are used for mesoporous materials synthesis. Other templates such as tetrapropylammonium bromide, *n*-propylamine, diethylamine, triethylamine and triethanolamine are not attempted. Besides, polyvinyl pyrrolidine has been used to form hollow structures [21,22]. But it is not used for mesoporous material synthesis. Further, use of ultrasonication gives hollow nanosphere.

In this paper, we report for the first time, synthesis of mesoporous silica spheres using different organic templates and polyvinyl pyrrolidine under base conditions at room temperature.

2. Experimental

2.1. Method 1

In a typical synthesis procedure 1.0 g polyvinyl pyrrolidine (Aldrich, USA) and 0.46 g NaOH (99%, Hayashi pure chemical Ind. Co. Ltd., Japan) were dissolved into 120 ml H_2O with stirring. After the solution becomes clear, 1.40 g cetyltrimethylammonium bromide (99%, Aldrich, USA) was dissolved completely, 5.6 ml TEOS (98%, Acros organics, USA) was poured into the above solution under vigorous stirring. Stirring was continued for 24 h, then sealed in Teflon-lined autoclaves and heated at 80 °C for 48 h.

2.2. Method 2

The synthesis by ultrasonication is as follows. Initially CTABr was dissolved in a NaOH solution and the resulting solution was irradiated with a high intensity ultrasound. The sonication was performed under ambient air conditions with the temperature at 25–35 °C. After 5 min of sonication, TEOS was added to the solution (0.12 CTAB:0.35 NaOH:1.0 TEOS:922 H_2O) using a syringe and the sonication was further continued

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Table 1
Influence of template on synthesis of Mesoporous silica nanosphere by Methods 1 and 2

S. no.	Synthesis	Yield (%)	Loss of weight on calcination (%)
1	Cetyl trimethyl ammonium bromide	100	54
2	Cetyl trimethyl ammonium chloride	93	40
3	Tetra propylammonium bromide	2	25
4	*n*-octylamine	50	18
5	Cetyltrimethylammonium bromide (ultrasonic)	100	50
6	Cetyltrimethylammonium chloride (ultrasonic)	95	38
7	*n*-octylamine (ultrasonic)	29	20

Table 2
Influence of template on synthesis of silica hollow sphere by Method 3

S. no.	Template	Yield (%)
1	Cetyltrimethylammonium bromide	85
2	Cetyl trimethyl ammonium chloride	100
3	*n*-octylamine	78
4	Tetrapropylammonium bromide	48
5	*n*-propylamine	72
6	Di-ethylamine	21
7	Triethylamine	16

for 1 h. A portion of the above solution was sealed inside a Teflon lined autoclave and kept at 200 °C for 48 h.

2.3. *Method 3*

Initially 3 ml sodium dodecyl sulphonate (SDS) solution (aqueous, 1%) was introduced into a centrifugal tube and irradiated in an ultrasound water bath sonicator for 5 min. The sonication was performed under ambient air conditions during the whole process. Then 0.05 g tetrapropylammonium bromide (TPABr) was dissolved into the above solution and the sonication was further continued for 5 min. Next 0.5 ml tetraethylorthosilicate (TEOS) was added to the cationic solution and sonicated for another 2 min. The final molar ratio was 0.046SDS:0.084TPABr:1.0TEOS:74H_2O. Then this reaction mixture was transferred into 100 ml Teflon lined stainless autoclave. Heat treatment on the autoclave was conducted at 180 °C in an oven for 24 h.

The solid product was recovered by filtration, then washed with distilled water and dried under vacuum at room temperature. A portion of the as-synthesized product was calcined in air at 550 °C for 10 h to remove the templates.

The other templates used in all the above synthesis were cetyltrimethylammonium chloride, tetrapropylammonium bromide, *n*-octylamine (99%, Aldrich, USA), *n*-propylamine, diethylamine (Osaka Hayashi Pure Chemical Industries Ltd., Japan), triethylamine and triethanolamine. The results are given in Tables 1 and 2.

X-ray diffraction analysis was carried out using a Mac Science Co. Ltd., MO3XHF22 instrument in the range 1.5°–10°. BET surface area analysis was carried out using a Micromeritics Tristar surface area and porosity analyzer. The particle size and shape were analyzed by a Topcon, SM-300 scanning electron microscope. The copper disc was pasted with carbon tape and the sample was dispersed over the tape. The disc was coated with gold in an ionization chamber. 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).

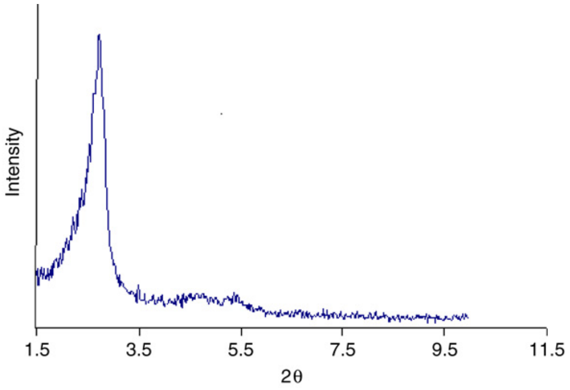

Fig. 1. Low angle X-ray diffraction of samples synthesized by Method 1 using templates of cetyl trimethylammonium bromide.

3. Results and discussion

The results of various templates on hydrothermal crystallization by Method 1 & 2 were given in Table 1. In Method 1, cetyl trimethylammonium bromide, cetyl trimethyl ammonium chloride, tetrapropyl ammonium bromide and *n*-octylamine gave solid precipitate. However other amines such as *n*-propylamine, diethylamine, triethylamine and triethanolamine did not give any solid product. Calcination of these four products gave a huge loss (55%) for cetyltrimethylammonium bromide products. N-octylamine gave less loss (18%). Method 2, gave a similar trend except tetrapropylammonium bromide did not give any residue. It has to be noted that in Method 3 we got precipitate when we used all the above templates (Table 2). This reveals the importance of surfactants in aqueous phase reaction. Long chain amines have hydrophilic and hydrophobic ends (surfactant). The synthesis involves two phases namely aqueous and organic phase (TEOS). They are not miscible with each other. To carry out the reaction in such a condition, the surfactant will facilitate one end in aqueous phase and another in organic phase. As tetrapropylammonium bromide is a weak surfactant, it gave little yield.

The low angle X-ray diffraction pattern (Fig. 1) shows a high intensity peak around 2.5° for the samples synthesized using cetyltrimethylammonium bromide, cetyltrimethylammonium chloride and *n*-octylamine by Method 1. So they are found to be mesoporous. Other samples synthesized with different templates did not show such a peak.

SEM analysis (Fig. 2) reveals the sample synthesized by Method 1 from CTABr has particle size 500 nm–2 μm with spherical shape, CTACl also having spherical shape with 100–300 nm size and the sample synthesized with *n*-octylamine has spherical platelets with 200–400 nm size. TEM analysis (Fig. 3) shows that the samples synthesized by Method 1

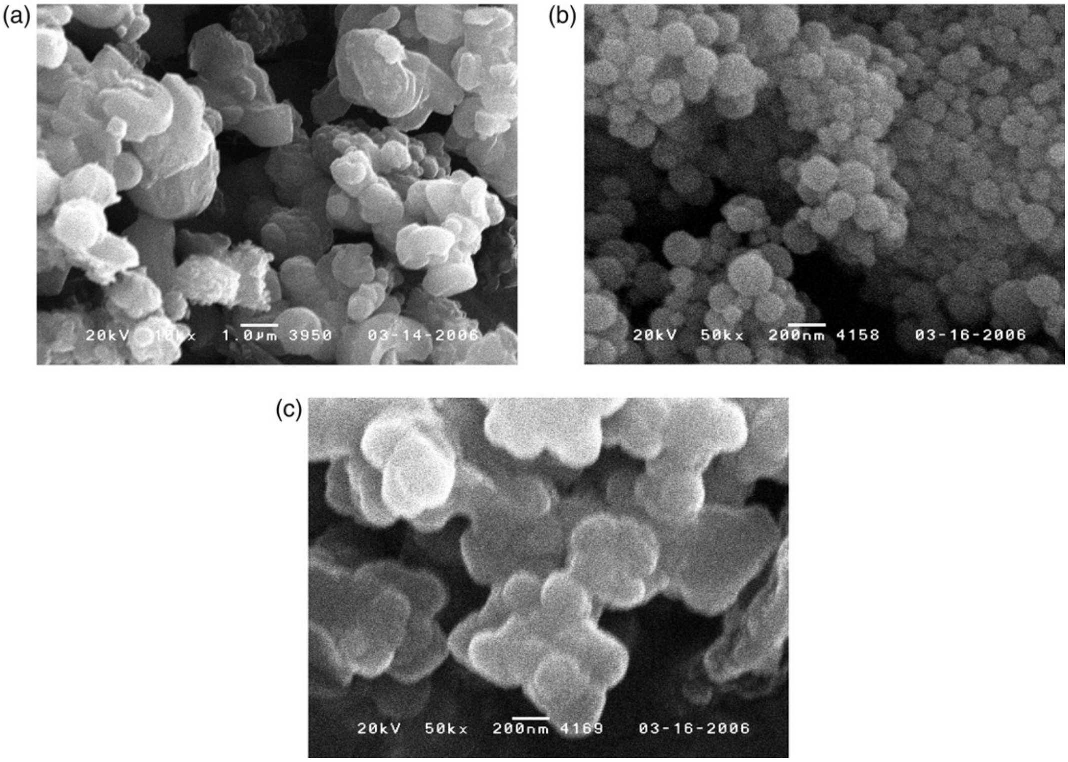

Fig. 2. SEM photograph of as-synthesized form of sample from (a) cetyl trimethylammonium bromide, (b) cetyl trimethyl ammonium chloride and (c) *n*-octylamine by Method 1.

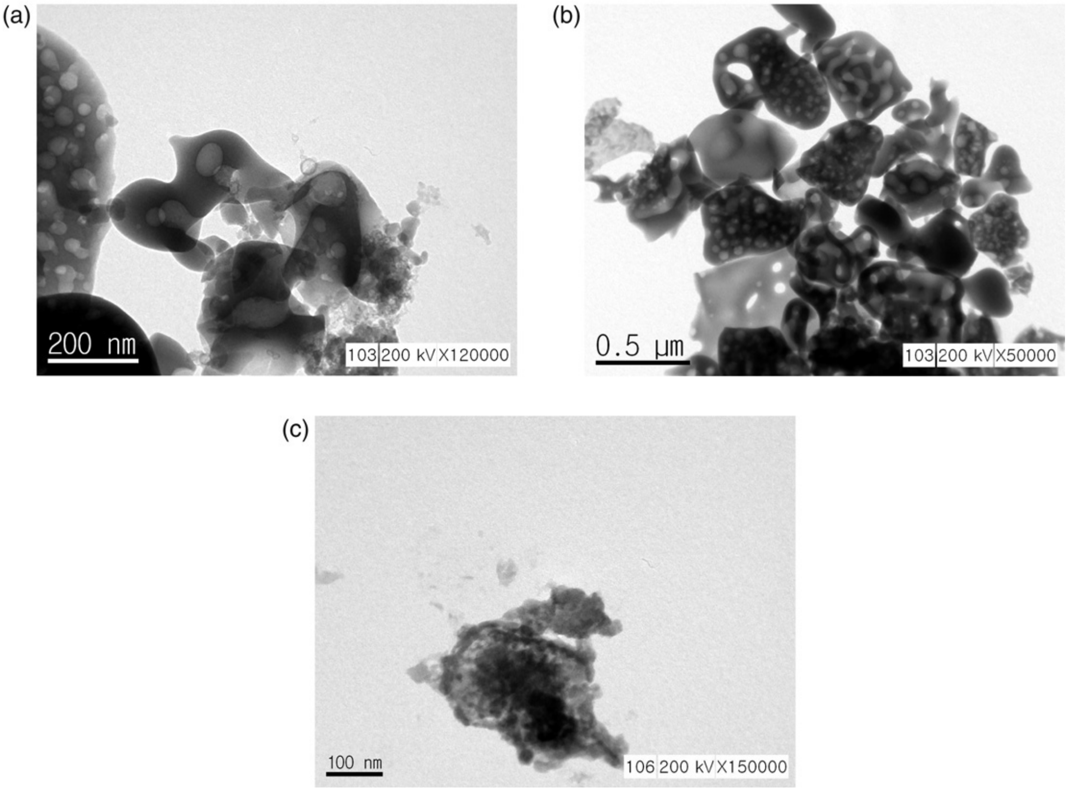

Fig. 3. TEM photograph of calcined form of sample from (a) cetyl trimethyl ammonium bromide, (b) cetyl trimethyl ammonium chloride and (c) *n*-octylamine by Method 1.

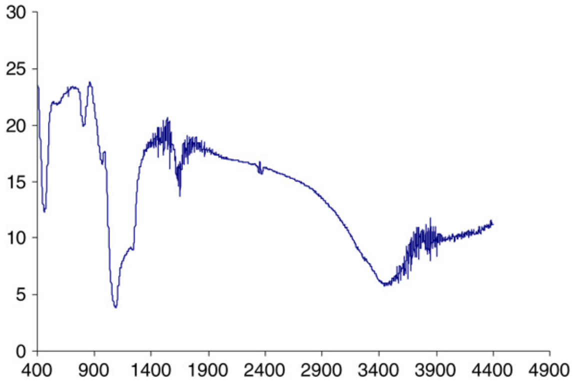

Fig. 4. FT-IR spectrum of sample synthesized by Method 1 using cetyl trimethyl ammonium bromide.

using CTABr and CTACl are of spherical hollow type with 20–50 nm size and the sample synthesized from *n*-octylamine has spherical hollow type sizes with size 300 nm with 25 nm wall size.

The FT-IR spectrum of as-synthesized mesoporous nanosphere samples from Method 1 shows a pattern simillar to Fig. 4, which reveals peaks around 1700 cm^{-1} and 3430 cm^{-1}, corresponding to the carboxyl and hydroxyl groups [23], respectively. The carboxyl peak appeared from atmospheric carbon dioxide. The adsorption peak belonging to the Si–O stretching vibration of the Si–OH bond appears at 960 cm^{-1} [24]. The weak peaks at 2855 and 2920 cm^{-1} belong to the stretching vibrations of C–H bonds, which show that a few organic groups are adsorbed on the spheres. The strong peaks near 1100, 802 and 467 cm^{-1} agree with a Si–O–Si bond, which implies the condensation of silicon alkoxide [25].

Nitrogen adsorption–desorption isotherms of the samples synthesized using CTABr, CTACl and *n*-octylamine by Method 1 show a curve simillar to the pattern given in Fig. 5. They show a type IV hysteresis characteristic of mesoporous materials. The BET surface area of the sample was found to be 900, 850 and 630 m^2/g and the average pore diameter was found to be 40, 32 and 26 Å.

It is found that polyvinylpyrrolidine (PVP) has a key influence on the formation of hollow core structures in hydrothermal mesoporous nanosphere particle growth. Without using PVP or using a lower amount of PVP, partially hollow mesoporous silica spheres or mesoporous silica spheres could form. It is believed that PVP as a co-template plays a crucial role in the formation of hollow mesoporous nanosilica spheres.

4. Conclusions

In summary, mesoporous silica spheres with uniform size and morphology have been successfully synthesized in a facile route using polyvinyl pyrrolidine and cetyltrimethylammonium bromide, cetyltrimethylammonium chloride and *n*-octylamine. Use of tetrapropylammonium bromide gave less yield. Ultrasonication followed by hydrothermal crystallization gave a similar trend except TPABr did not give precipitate. Addition of dodecylsulfonate surfactant followed by ultrasonication and hydrothermal growth give precipitate in all templates irrespective of its nature. So, it was found that the surfactant property of the template or surfactant is essential for precipitation. Calcination followed by TEM analysis gives hollowspheres with mesoporous properties in CTABr, CTACl and *n*-octylamine containing products. However these properties change depend on the template.

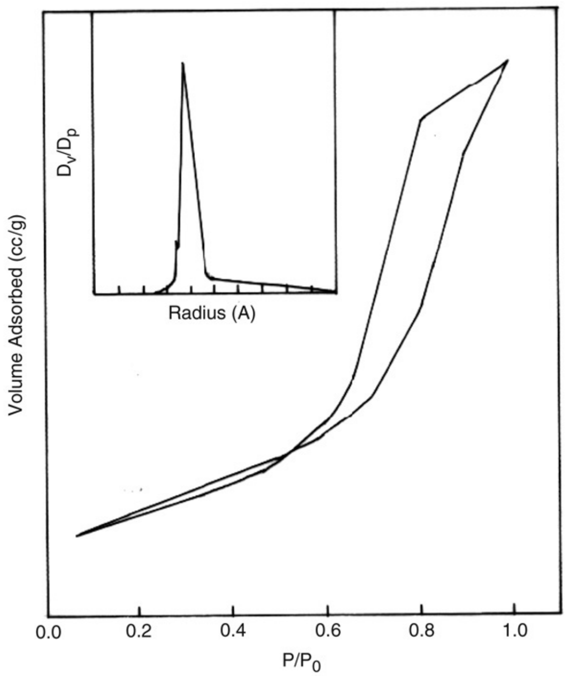

Fig. 5. N_2 adsorption and desorption isotherm of sample synthesized by Method 1 using cetyltrimethylammonium bromide template.

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