

Research Letter

Synthesis and Surface Properties of Silica Spheres with Core Shell Structure by One Convenient Method

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Earlier, we have published a paper on the preparation of silica sphere using propanol as cosurfactant. We report here a highly cost-effective method of preparation of mesoporous silica spheres with core shell structure using sodium silicate as silica precursor, cetyltrimethyl ammonium bromide (CTAB) as surfactant, and methanol as cosurfactant. Thus after removal of the template by dissolutions or/and activation at higher temperature, mesoporous silica spheres with core shell structure were obtained. The products prepared with methanol to CTAB molar ratio 8.5 : 1 were confirmed to give best results. All the spherical products have very large surface area ($\sim 589\text{--}1044\text{ m}^2/\text{g}$), pore volume ($\sim 0.98\text{--}1.41\text{ cm}^3/\text{g}$), and ordered pore structure.

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1. Introduction

The synthesis of ordered mesoporous metal oxide using surfactant templating was first reported by Kresge et al. and Beck et al. in 1992 [1, 2]. Since then, ordered mesoporous metal oxides have been the topic of rapid discovery in material chemistry, catalysis, chemical sensing, and separations [3, 4]. Silica spheres have almost been obtained by using a biphasic system of a quaternary ammonium surfactant [5–7], that recently has been synthesized using the nonionic polyethylene-oxide-based surfactant by Boissière et al. [8] and dual templates by Yang et al. [9]. Silica spheres of hollow morphologies have attracted much attention due to their potential applications in drug-delivery, adsorption, and catalysis [10]. Hollow spheres may also provide some immediate advantages over their solid counter parts because of their relatively low densities [11]. Several chemical and physicochemical methods have been used to synthesize hollow spheres, including emulsion phase separation techniques, emulsion interfacial polymerization, and templating colloidal particle techniques [12]. Li et al. [13] reported the isolation of hollow silica spheres taking calcium carbonate nanoparticles as templating agent and sodium silicate as silica source for drug delivery applications. Very recently, Zhang et al. [14] prepared hollow monodispersed silica

spheres from TEOS by varying water to ethanol molar ratio under sonication environment. Naik and Sokolov [15] reported the preparation of nanoporous silica spheres at room temperature using sodium metasilicate as silica precursor and CTACl as structure directing agent.

The present work is an extension of our previous work reported elsewhere [16] to get hollow silica spheres. We report here a cost effective, simple, and convenient method for the preparation of well-ordered hollow mesoporous silica spheres taking CTAB and methanol as templating agents and sodium silicate as silica source. The materials were characterized by small-angle X-ray diffraction (SAXRD), N_2 adsorption-desorption, pore size distribution, BET-surface area (Brunauer-Emmett-Teller), particle size distribution, scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HRTEM).

2. Experimental

2.1. Material Synthesis. In a typical synthesis, 10.76 mmol of cetyltrimethyl ammonium bromide (CTAB) was dissolved in 50 mL of double distilled water. Methanol was added to the above solution maintaining the molar ratio of methanol to CTAB in the range of 7 : 1 to 10 : 1. A solution containing 4 g

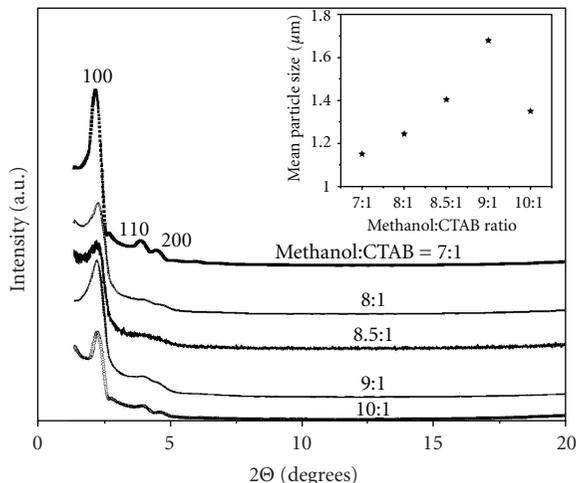
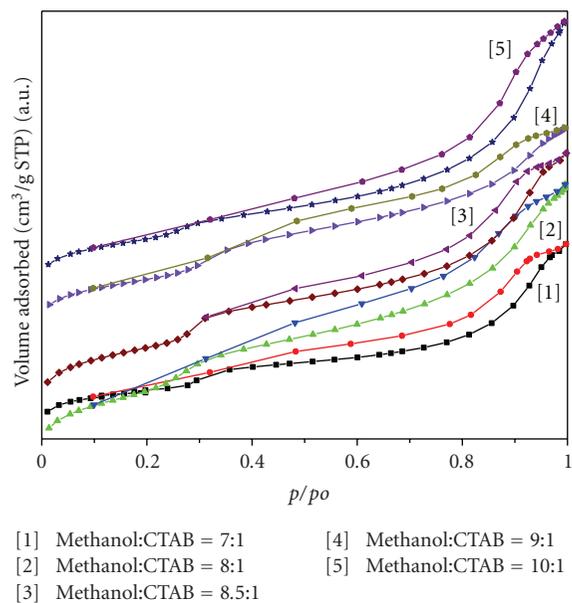


FIGURE 1: SXR D of mesoporous silica at different molar ratios of methanol to CTAB (inset particle size distribution).



[1] Methanol:CTAB = 7:1 [4] Methanol:CTAB = 9:1
 [2] Methanol:CTAB = 8:1 [5] Methanol:CTAB = 10:1
 [3] Methanol:CTAB = 8.5:1

FIGURE 2: N₂ adsorption profile of mesoporous silica at different molar ratios of methanol to CTAB.

of sodium silicate, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, was added to the above mixture with constant stirring at room temperature. The total volume of the solution was kept at 140 mL. About 10 mL of ethyl acetate was added to the above solution and was continuously stirred for 5 hours. After complete hydrolysis, the mixture containing the gel was kept in the oven at 80°C for 72 hours. The resulting product was recovered by filtration followed by washing with double distilled water and ethanol. The washed particles were kept at 80°C and further activated at 540°C for 6 hours to get the hollow structure.

2.2. Methods of Characterization. X-ray diffractograms were recorded on a Rigaku Miniflex (set at 30 kV and 15 mA) powder diffractometer using Cu K α radiation within the 2θ

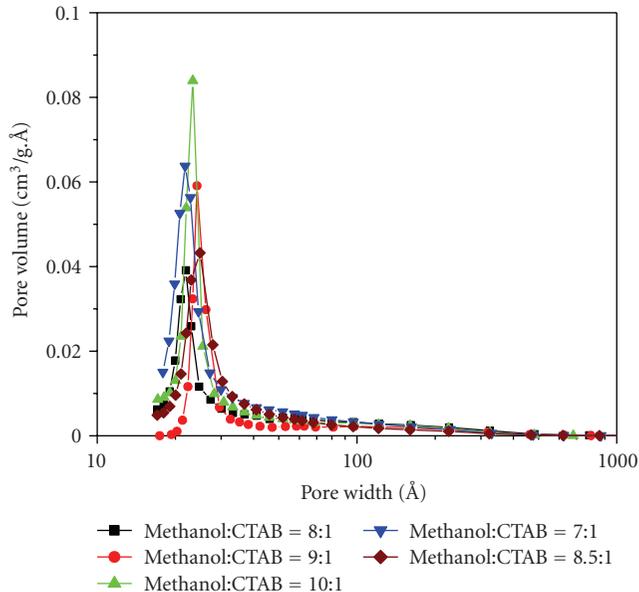


FIGURE 3: Pore size distribution of mesoporous silica at different molar ratios of methanol to CTAB.

range from 1 to 20° at a rate of 2°/min in steps of 0.01°. Nitrogen sorption isotherms were recorded at liquid nitrogen temperature (−196°C) on ASAP 2020 (Micromeritics, USA). Prior to analysis, the particles were subjected to vacuum (5×10^{-3} torr) at 200°C in order to ensure a clean surface. Surface areas were calculated using Brunauer-Emmett-Teller (BET) method. The pore volumes were taken at relative pressure p/p_0 of 0.95. Pore size distributions were analyzed using Barrett-Joyner-Halenda model. Specimens for SEM were prepared by placing the particles on the carbon tape and coated with gold by sputtering. The sample grids were examined by SEM (Hitachi S-3400N). Particle size analysis of all the mesoporous materials was carried out by Nanotracs 150 (Microtrac Instruments) with sodium hexametaphosphate as dispersant. High-resolution transmission electron microscopic (HRTEM) images were obtained on JEOL JEM 2100, in which samples were prepared by dispersing the powdered samples in 2-propanol by sonication for 20 minutes and then drop-drying on a copper grid coated with carbon film.

3. Results and Discussion

3.1. Characterization by Small-Angle XRD, N₂ Sorption at −196°C and Particle Size Analysis. The SXR D pattern shows three diffraction peaks indexed as (100), (110), and (200) (Figure 1). This indicates that the pore structure of the mesoporous silica is in a hexagonal array as was reported by Lin and Mou [17]. The interplanar distance and the distance between pore centers, represented by the d -values of (100) diffraction peak and the a -values ($a = 2d_{100}/\sqrt{3}$), respectively, were listed in Table 1. The a -values increase with increasing molar ratio of methanol to CTAB. Since the mesoporous silica spheres were synthesized using

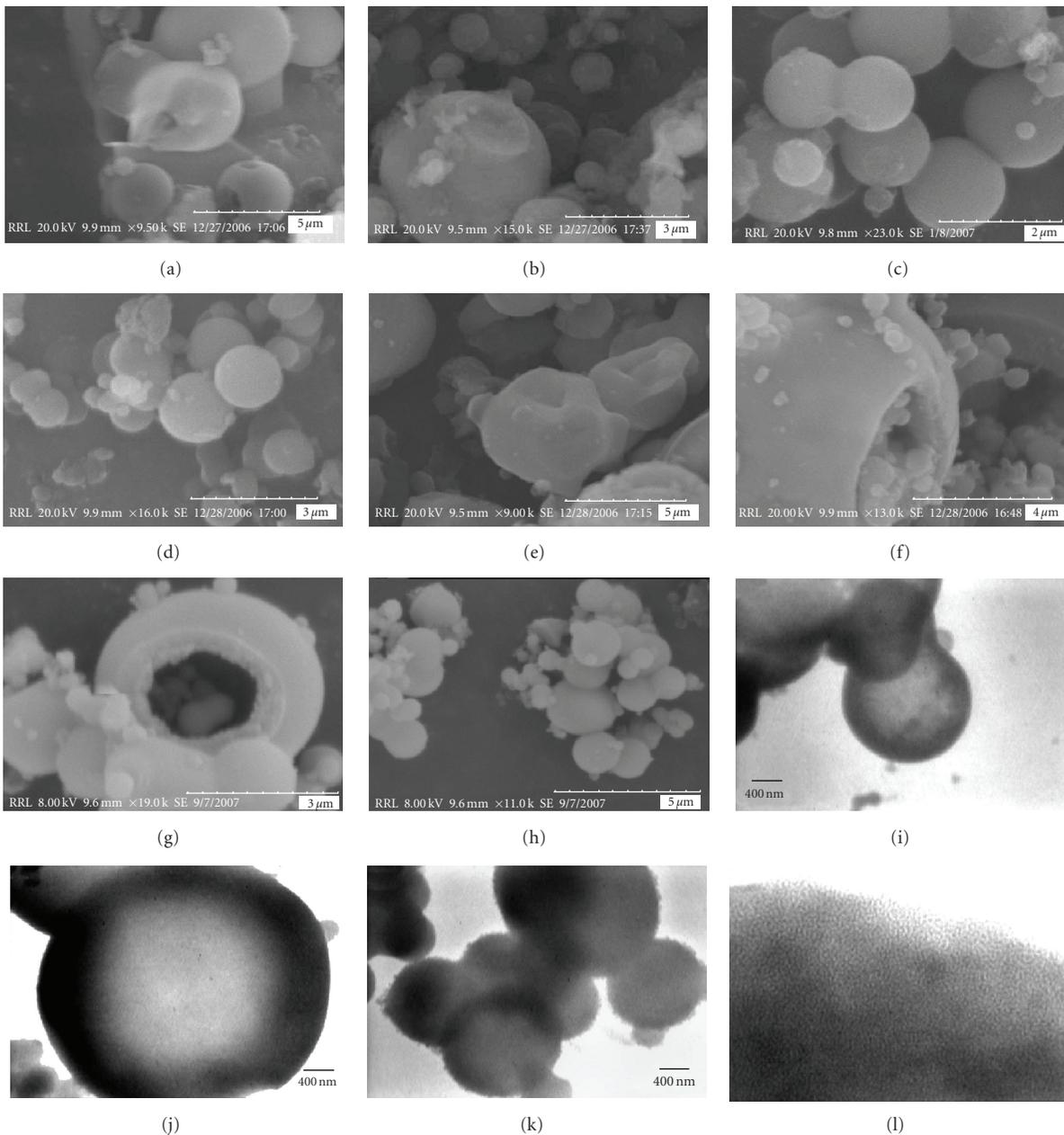


FIGURE 4: SEM micrographs of mesoporous silica molar ratios of methanol to CTAB: (a) 7 : 1, (b) 8 : 1, (c) 8.5 : 1, (d) 9 : 1, (e) 10 : 1, (f) cracked silica particle of 9 : 1 molar ratio, (g) cracked silica particle of 8.5 : 1 molar ratio, (h) 600°C calcined silica particles of molar ratio 8.5 : 1, (i) and (j) TEM micrographs of 600°C activated silica with molar ratio 8.5 : 1 at different magnification, (k) TEM, (l) HRTEM micrographs of silica with molar ratio 8.5 : 1 activated at 540°C.

the micelles as templates, we believe that the size of the micelles increased with increase in the amount of methanol. This is also expected, as methanol could only be solubilized in the palisade layer of the micelles [18]. As a consequence there is an increase in the distance between two adjacent pore centers.

From Figure 2, all the samples were observed to follow the type IV isotherm, H1 hysteresis loop. From Figures 2[1] and 2[3]–[5] for molar ratios 8.5 : 1, 8 : 1, 7 : 1, and 9 : 1, respectively, clear adsorption steps of capillary

condensation were observed indicating the larger mesopore diameter and uniformity of framework mesoporosity. The materials are observed to be of not exactly MCM 41, rather MCM 41 type. The isotherm in Figure 2[2] for the product obtained with methanol to CTAB ratio 10 : 1 exhibits no such clear steps. The result indicates that the pore size of the synthesized silica was found in the range of mesoscale which is in agreement with Sing et al. [19]. Specific surface area and total pore volume were listed in Table 1. All the samples have very high surface area (~ 589–1044 m²/g) and pore volume

TABLE 1: Effect of molar ratio of methanol to CTAB on d_{100} , surface area, pore volume, and mean pore size of mesoporous silica.

Methanol : CTAB	d_{100}^a (nm)	a (nm)	Pore size with BJH diameter ^b (nm)	Specific surface area ^c (m ² /g)	Total pore volume (cm ³ /g)
7 : 1	3.89	4.5	2.178	589	0.98
8 : 1	3.96	4.57	2.194	904	1.027
8.5 : 1	3.99	4.61	2.486	1044	1.41
9 : 1	4.05	4.68	2.422	699	1.33
10 : 1	3.91	4.51	2.33	696	1.32

^a Calculated from SXRD.

^b Calculated from the desorption portion of N₂ adsorption-desorption isotherm.

^c BET-method.

(~ 0.98–1.41 cm³/g). The average pore size increases with increase in the methanol to CTAB ratio (Figure 3). From Figure 3, the pore size of all the materials was observed to be unimodal in character. This is in agreement with SXRD. At the same time, total pore volume also increases with increase in the molar ratio of methanol to CTAB (see Table 1). This shows that an optimum amount of methanol is required for the formation of a more ordered pore structure and also helps in increasing the total pore volume. This is in support of particle size analysis (inset of Figure 1).

3.2. SEM and TEM Observations. From Figure 4, the spherical particles with multiple of micrometer size were observed by varying the molar ratio of methanol to CTAB (from 7 : 1 to 9 : 1). Also, it is clearly visible from Figures 4(a), 4(f), and 4(g) that the particles have core shell structure. This structure has been destroyed at molar ratio of 10 : 1 (Figure 4(e)). Again, one can clearly notice from Figures 4(h), 4(i), and 4(j) that the particles are still spherical and hollow at 600 °C for the molar ratio 8.5 : 1. The wall thickness was found to be ~ 200–800 nm from TEM micrographs. This is not clearly observed from Figure 4(k) due to the incomplete removal of the template at 540 °C. Again, Figure 4(l) shows the close packed hexagonal structure of mesoporous silica as well as the existence of uniform pores in the wall of hollow silica sphere. As the formation of particles is templated by micelles, the morphology changes with the molar ratio of methanol to CTAB. Above the critical micelle concentration (CMC), the size and the shapes of micelles changed in response to increase in the CTAB concentration. Again, with excess of methanol the shape of the micelles could be transformed to spheres [20]. Ethyl acetate was added to control the solution pH. It is soluble in the palisade layer of the CTAB micelles. Its hydrolysis is catalyzed by cationic micelles to form acetic acid:



The acetic acid formed during hydrolysis may possibly be neutralized by sodium silicate on the CTAB micelle surface. Therefore the pH value of the solution decreased gradually from basic to neutral conditions, and finally silica is formed. Furthermore, the morphology of mesoporous silica is also dependent on the hydrophobic interactions between CTAB and methanol which were self-assembled onto mesoporous silica. It has been observed by Zana [21]

that with increase in methanol concentration (above 9 : 1 molar ratio) the hydrophobic interactions between the molecules of adsorbed methanol and CTAB on the surface of colloidal seeds get weakened. For this reason we believe that the pore structure of the resulting silica spheres became less ordered. However, correlating our previous work [16] with present investigation, a question might be raised why propanol/CTAB system gives solid SiO₂ spheres whereas methanol/CTAB system gives core shell structures? Previous investigations have shown that the self-assembly of organic-inorganic hybrid system can be explained in terms of surfactant packing parameter/critical aggregation parameter, $g(V/(a_o l))$ [22], where “V” is the total volume of the surfactant chain plus any cosolvent molecules between the chains, “ a_o ” is the effective head group area at the organic-inorganic interface and “ l ” is the surfactant chain length. Depending on the cosolvent or swelling agent chain length, the “V” will vary and consequently “ g ”. Hence, we change the $C_{\text{cosolvent}}^{-3}$ to $C_{\text{cosolvent}}^{-1}$, which causes a transformation from solid to core shell structure.

4. Conclusions

The synthesized silica particles with methanol : CTAB molar ratio below 10 : 1 show core shell structure which was evidenced from SEM and TEM micrographs. The sizes of the particles were in the range of 1 to 1.7 micron with very large surface area (~ 658–1110 m²/g) and pore volume (~ 1.17–1.74 cm³/g) and exhibit ordered pore structure. There existed a type IV adsorption isotherm and H1 hysteresis loop according to IUPAC classification. The most probable pore size increased with increase in the molar ratio of methanol to CTAB. This is in agreement with the small-angle X-ray diffraction data. The small angle XRD patterns reveal that the materials are MCM 41 type.

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