

THE CONTROL OF SIZE AND SURFACE MORPHOLOGY OF SILICA MICROSPHERES BY SOL-GEL EMULSION APPROACH

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Abstract

The influence of mixing speed and amount of solvent on the size and surface morphology of hollow silica microspheres was studied. Hollow silica microspheres were prepared via a sol-gel emulsion method. An aqueous phase of water, ammonium hydroxide and Tween 20 was emulsified in an oil phase of 1-octanol and Span 80, and stabilized by hydroxypropyl cellulose (HPC). Tetraethyl orthosilicate (TEOS) was added to the emulsion and mixed at a speed of either 400, 800, or 1200 rpm. The resulting silica particles were air-dried and calcinated at 773 K for 3 h. The characteristic bonds of silica were detected by Fourier Transform Infrared Spectroscopy and the surface morphology and size of silica microspheres were characterized by scanning electron microscopy. The particle size distribution was measured with laser diffraction and the specific surface areas and pore sizes distributions by Coulter Omnisorp 100 CX. The results indicate that the size of silica decreases from 3.1 to 2.3 μm as mixing speed increases from 400 to 1200 rpm. At constant mixing speed, the silica particles prepared from 160 ml 1-octanol exhibited the greatest specific surface area and total pore volume compared with those of 80 and 240 ml 1-octanol.

Keywords: Hollow silica microspheres, particle size, surface morphology, sol-gel emulsion

Introduction

Hollow silica microspheres exhibit substantial properties due to their low density, large specific surface area, high dopant storage capacity, thermal and chemical stability and biological compatibility. The interests in the function of silica as capsules in the field of encapsulation is increasing from both

academy and industry. Various core compounds can be entrapped into the silica shells, for example, drugs, bacteria, proteins, catalysts, fillers and artificial cells. The resulting core-shell structure permits its main application of controlled release in pharmaceutical, cosmetics, food and coating industries (Park

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et al., 2003; Chung *et al.*, 2004; Fuji *et al.*, 2007; Lee *et al.*, 2007; Singh and Garg, 2007; Peng *et al.*, 2008; Yoon *et al.*, 2009; Teng *et al.*, 2010; Ciriminna *et al.*, 2011; Chen *et al.*, 2012).

A variety of methods exist for fabricating hollow spheres of different compositions. These include spray drying (Caruso, 2000; Chung *et al.*, 2004; Singh and Garg, 2007), sol-gel/emulsion method (Park *et al.*, 2003; Lee *et al.*, 2007; Singh and Garg, 2007; Fuji *et al.*, 2007; Yoon *et al.*, 2009; Ciriminna *et al.*, 2011), sacrificial core techniques (Park *et al.*, 2003; Singh and Garg, 2007; Yoon *et al.*, 2009), and layer-by-layer deposition (Dai *et al.*, 2005). Among these approaches, hollow silica spheres prepared by sol-gel/emulsion method present distinctive advantages. First, the reaction takes place at mild condition (low temperature, atmospheric pressure), enabling the encapsulation of temperature-sensitive materials, such as organic and biological materials. Second, the method provides a cost effective solution as it does not require sophisticated facilities. Third, the versatile particle sizes, shape and surface properties can be easily controlled by adjusting both emulsion parameters (solvents, surfactants and mixing speed) and sol-gel processing parameters (solvents, precursors, molar ratio of reactants and catalysts, etc.) (Finnie *et al.*, 2006; Singh and Garg, 2007; Ciriminna *et al.*, 2011).

Fabrication of hollow silica microspheres can be carried out by commonly used oil-in-water (O/W) emulsion or in water-in-oil (W/O) emulsion system arising in popularity. The choice of these emulsion routes mainly depends on the targeted core materials to be entrapped. The direct encapsulation of hydrophobic molecules is permitted by O/W emulsion, whilst W/O is used for hydrophilic molecules (Lee *et al.*, 2007; Singh and Garg, 2007; Ciriminna *et al.*, 2011). Based on Cho *et al.* (2005), O/W emulsion always requires stable colloids in oil, however, W/O emulsion has much better phase stability due to chargeable surface moieties of silica in contact with water. Previously, we presented

the kinetics studies of hollow silica microspheres synthesized by W/O (1-octanol based oil phase) emulsion with inorganic silica precursor with mixed surfactants under basic condition (Chen *et al.*, 2012). As we have not been able to find systematic studies on the impact of solvent volume and mechanical mixing speed on particle size and surface morphology of hollow silica microspheres, we will in this paper focus on these factors. This investigation will bring significance to the process optimization particularly because of the high cost of 1-octanol.

Materials and Methods

Materials

Tetraethyl orthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$, TEOS, 98%, Acros Organics) was used as a precursor, 1-Octanol ($\text{C}_8\text{H}_{18}\text{O}$, 99%, Sigma-Aldrich) as an oil phase, hydroxypropyl cellulose (HPC, average Mw ca. 100000, Acros Organics) as a stabilizer of emulsion, and Sorbitanmonooleate ($\text{C}_{24}\text{H}_{44}\text{O}_6$, Span[®]80, Fluka) as a low-HLB (hydrophilic-lipophilic balance) surfactant to disperse the oil phase. Also, Tween 20 (Acros Organics) as a high-HLB surfactant, deionized water as a reactant, ammonium hydroxide (NH_4OH , 25%, J.T. Baker) as a catalyst and ethanol ($\text{C}_2\text{H}_5\text{OH}$, 96.1 vol.%, Altia) as a washing reagent.

Sample Preparation

The hollow silica microspheres were synthesized by a sol-gel/emulsion method. Synthesis procedure of hollow silica microspheres was divided into two groups based on solvent amount and mixing speed, respectively. Figure 1 shows the general procedure of microspheres fabrication. The two groups are described in detail in the following.

Group 1: These syntheses were designed to compare the effect of solvent amount. Three syntheses were carried out by first dissolving 0.8 g HPC in 80, 160, and 240 ml 1-octanol oil phase, respectively. The mixture

was heated at 333 K and mixed by a magnetic stirrer (RCT basic IKAMAG[®] safety control, IKA[®]-Werke, GmbH & Co.KG) while heating. When HPC was completely dissolved in the oil, the temperature was decreased to 303 K. Then 3.1 ml Span 80 was added to the oil phase, and kept at 303 K for 0.5 h. The water phase was prepared by mixing 2.2 ml ammonium hydroxide in 21 ml deionized water by a magnetic stirrer (KMO 2 basic IKAMAG[®], IKA[®]-Werke, GmbH & Co.KG) for 0.5 h. Then, 0.8 ml Tween 20 was added, and the mixture was stirred for another 0.5 h. The oil phase and water phase (approximately pH 10) were then mixed for 0.5 h in order to form W/O emulsion structure. To disperse the water phase into the oil phase efficiently, constant magnetic stirring at 800 rpm and a constant temperature 303 K were performed. The sol-gel reaction for the formation of silica occurred while titrating 64.5 ml of TEOS dropwise to the emulsion. The molar ratio of TEOS: water: ammonium hydroxide was kept at (5:20:1). The silica synthesis took 6 h. After the synthesis, the samples were aged at room temperature for 14 h, then washed with ethanol and centrifuged at 3500 rpm for

10 minutes. The last two steps were repeated for three times. The resulting white powders #1, #2, and #3 (obtained by using 80, 160, and 240 ml of 1-octanol, respectively) were dried in air for 17 h, and finally calcinated in air at 773 K for 3 h.

Group 2: These syntheses were designed to compare the effect of mixing speed. Three syntheses were carried out by first dissolving 0.8 g HPC in 125 ml 1-octanol as oil phase. The mixture was heated to 333 K and stirred by a magnetic stirrer (RCT basic IKAMAG[®] safety control, IKA[®]-Werke, GmbH & Co.KG) while heating. When HPC was completely dissolved in the oil, the temperature was decreased to 303 K. Then, 3.1 ml Span 80 was added to the oil phase, and the mixture was kept at 303 K for 0.5 h. The water phase was prepared by mixing 2.2 ml ammonium hydroxide in 21 ml deionized water by a magnetic stirrer (KMO 2 basic IKAMAG[®], IKA[®]-Werke, GmbH & Co.KG) for 0.5 h. Then 0.8 ml Tween 20 was added, and the mixture was stirred for another 0.5 h. The oil phase and water phase (approximately pH 10) were mixed together with constant magnetic stirring at 400, 800, and 1200 rpm at 303 K for

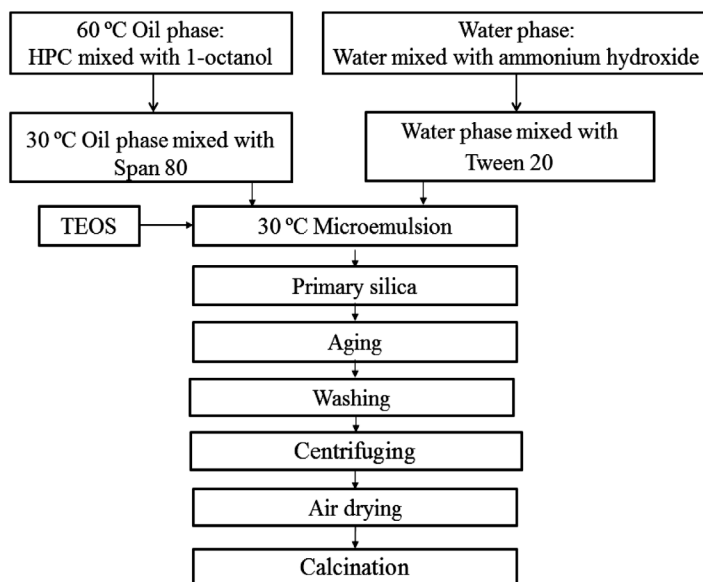


Figure 1. Schematic diagram of fabricating silica powders

0.5 h, respectively. The following steps were the same as for Group 1. The resulting white powders #4, #5, and #6 (obtained at 400, 800, and 1200 rpm, respectively) were air dried for 17 h, and finally calcinated in air at 773 K for 3 h.

FTIR Measurement

The characteristic functional groups of silica were identified by Fourier Transform Infrared Spectroscopy (Nicolet™ 380 FT-IR). Each powder sample (approximately 0.1 mg) was pressed in the pure disc and the IR spectra were analyzed by OMNIC software.

Scanning Electron Microscopy

Surface morphology of silica particles was investigated by field emission scanning electron microscopy (SEM, Hitachi-S4700 FEG-SEM). A small amount of silica particles was first diluted with ethanol, and mixed in an ultrasonic mixer (Ultrasonic M03, FinnSonic) for 3 min and then dropped onto a silicon wafer. After the evaporation of the ethanol, the dried sample was placed onto a carbon tape. The samples were coated with gold by sputtering for 90 sec (Leica EM SCD050). The FE SEM was operated at 10 kV accelerating voltage and 15 μ A current. The chemical composition of the spheres was studied by energy-dispersive X-ray spectroscopy in SEM (Hitachi-S4700 FEG-SEM EDS) with INCA Microanalysis system.

Particle Size Distributions

Particle size distributions of the silica powders were determined by the laser diffraction size analyzer (Malvern Mastersizer 2000 equipment with Hydro 2000MU). Measurement model was general purpose (spherical). For the measurement the powder was inserted into distilled water to form dispersion. Adding powder was continued until right obscuration range was reached. Continuous ultrasound was used to break agglomeration of particles. Sample was measured for three times with one minute intervals to ensure stable dispersion. If dispersion was not stable additional five

minutes were waited and the procedure was repeated until dispersion was stable. The particle size distribution was calculated by applying Mie theory (Hickey, 2004) by adopting the refractive index of 1.45 and absorption of 0.1 for silica (Yablon, 2005).

Surface Area and Porosity Measurements

Specific surface areas and porosity of the silica particles were calculated using nitrogen adsorption and desorption isotherms (Gregg and Sing, 1982) measured by Coulter Omnisorp 100CX instrument. Samples were dried in vacuum at 623 K as a pretreatment, and adsorption and desorption measurements were performed with nitrogen at liquid nitrogen temperature (77 K). Specific surface areas were calculated from adsorption data using BET equation (Brunauer *et al.*, 1938) from the range where nitrogen forms monomolecular layer on the surface of the particles. The pore volume and pore size distribution were determined from the nitrogen desorption isotherms using the Barrett-Joyner-Halenda (BJH) method (Barrett *et al.*, 1951).

Results and Discussion

The FTIR transmittance spectra of all the calcinated samples are shown in Figure 2. The peaks corresponding to presence of characteristic bands at 1041-1050, 800 cm^{-1} indicate the stretching and bending of Si-O-Si bonds, respectively (Hase, 1992). The bonds O-H (3500-3600, intramolecular) and C-H (3000) disappeared after calcination. Therefore, the presence of silanol (Si-OH) and silicon ethoxy (Si-OC₂H₅) group was not seen. Furthermore, EDS analysis suggested the presence of only Si and O, corroborating the FTIR observations that the phase of the particles is silica.

Figures 3 and 4 visualizes the structure of the silica samples by varying the amount of 1-octanol and mixing speed, respectively. The micrographs showing the empty interior of the silica spheres in all samples confirm their hollow structure. The reaction system is W/O emulsion, in which the water as internal

phase is dispersed in the external oil phase, and the formation of emulsion droplets provides “micro-reactors (reverse micelles)” where sol-gel reaction takes place. The internal water phase contains ammonium hydroxide as a catalyst and hydrophilic surfactant Tween 20, whereas oil phase includes 1-octanol as solvent, amphiphilic surfactant HPC and lipophilic surfactant Span 80. The water phase was added to the oil phase, and mixed by magnetic stirrer at a constant speed and stabilized with multiple nonionic surfactants, in this case, HPC, Tween 20 and Span 80. Figures 3–4 shows the morphology of silica particles, all have regular spherical shape due to the addition of HPC polymer. It increases the viscosity of the oil phase, hence restricting the mobility of water droplets and coalescence between them. The concentration of Tween 20 and Span 80 in the emulsion affects the pore diameter and pore size distribution due to the solubilization of surfactants (Lee, 2005). When TEOS precursor is added into the emulsion, it preferably orients itself towards

the non-polar 1-octanol oil due to their hydrophobic properties. As its nonpolar alkyl chains slowly diffuse into the polar water droplets surrounded by the surfactants, hydrolysis of TEOS occurs followed by subsequent polycondensation, in which water and ethanol are produced from hydrolyzed molecules of silicic acid $\text{Si}(\text{OH})_4$ or $\text{Si}(\text{OH})_x(\text{OR})_{4-x}$ (where x lies between 1 and 3) (Brinker, 1990). As a result, the primary silica shells were obtained. During the washing process, 1-octanol and some surfactants were removed. Later, water and ethanol inside the silica shell, as well as remaining surfactants, were evaporated during calcination. This led to a hollow structure of silica particles.

Figure 5(a) depicts the particle size distributions of the microspheres from three samples with different volumes of 1-octanol, #1 (80 ml), #2 (160 ml), and #3 (240 ml). The mean size of the silica powders is in the range of 2.4–4.8 μm (Table 1, Figure 5(a)). The particle size distribution of the sample #1 (80 ml) is broad, varying from 1 to 79 μm , while in the sample #2 (160 ml) 0.8–6.6 μm ,

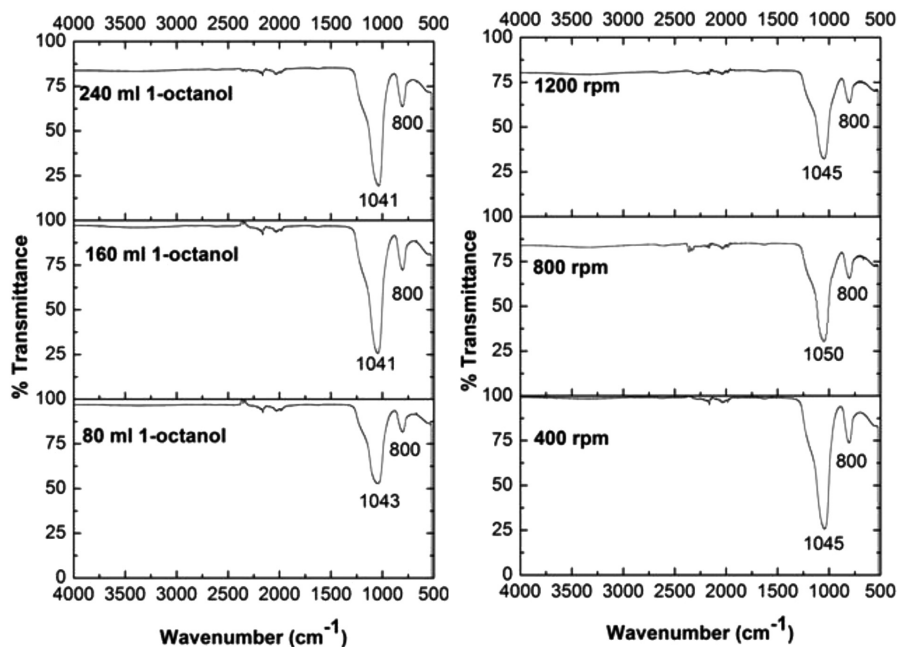


Figure 2. FTIR spectra (ranging 4000–500 cm^{-1}) of calcined spheres prepared by sol-gel / water-in-oil emulsion

and in the sample #3 (240 ml) 0.1–17 μm . There seems to be a narrow size distribution in the sample #2 (160 ml) in comparison with #1 and #3. Samples #1 and #3 exhibit similar high peaks at about 7 and 8 μm , respectively. It can be seen that, at a constant stirring speed, the particle sizes of microspheres are increased with decreasing the amount of nonpolar solvent. At the increase of solvent from 43

to 60 wt% (80 to 160 ml, respectively), the particle sizedecreasedfrom 4.8 to 2.4 μm as the water amountwasdecreased from 14 to 10 wt% in correspondence with a decrease of HPC from 0.5 to 0.4 wt%. Higher water content reduces rigidity of the surfactant protective layer and enhances particle aggregation upon collision and the formation of larger particles. This is in accordance with

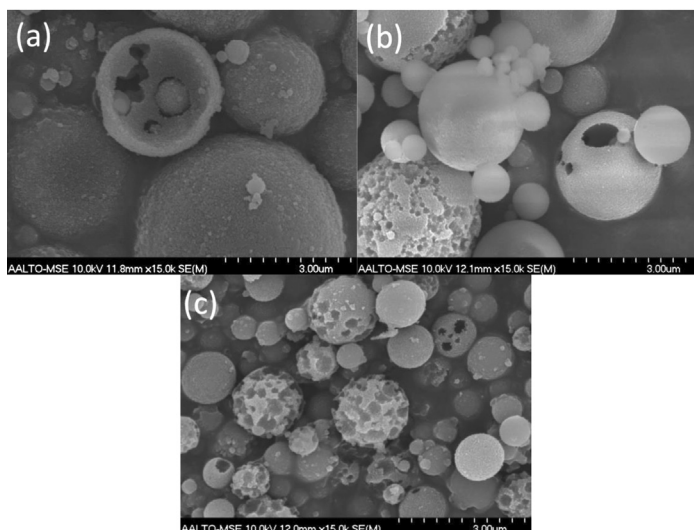


Figure 3. SEM images of silica powders prepared by using different amount of 1-octanol: (a) 80 ml (#1); (b) 160 ml (#2); (c) 240 ml (#3)

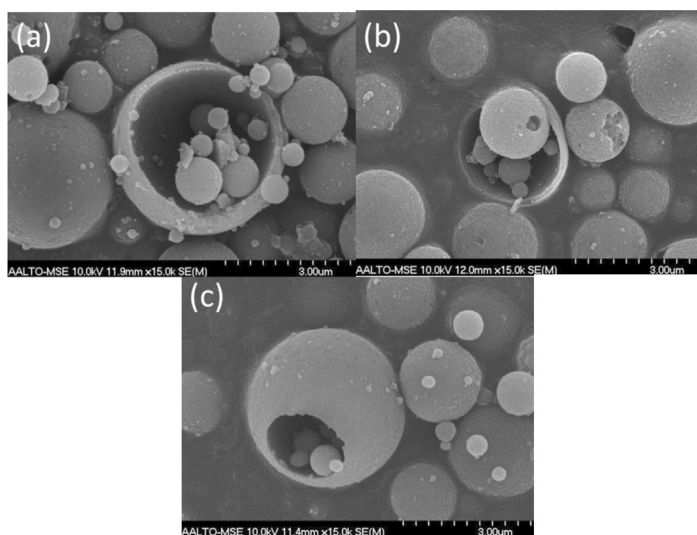


Figure 4. SEM images of silica powders prepared by using different mixing speed: (a) 400 rpm (#4); (b) 800 rpm (#5); (c) 1200 rpm (#6)

the BET measurement, where a smaller specific surface area of 140 m²/g of sample #1 was detected compared with 164 m²/g of sample #2. As the amount of solvent was increased to 69 wt% (corresponding to 240 ml), water dropped to 7 wt%, and no visible difference was detected in particle size. This suggests that the particle size of microspheres is not affected at the range of

7–10 wt% water content in the emulsion. Sample #3 (Figure 3(a)) tends to form also more sponge-like structures in addition to hollow spheres. This observation is also supported by the BET measurement, which gave a specific surface area of 115 m²/g for Sample #3. The pore size distribution curve of the silica particles #1, #2, and #3 (Figure 6(a-b)) indicates the presence of both

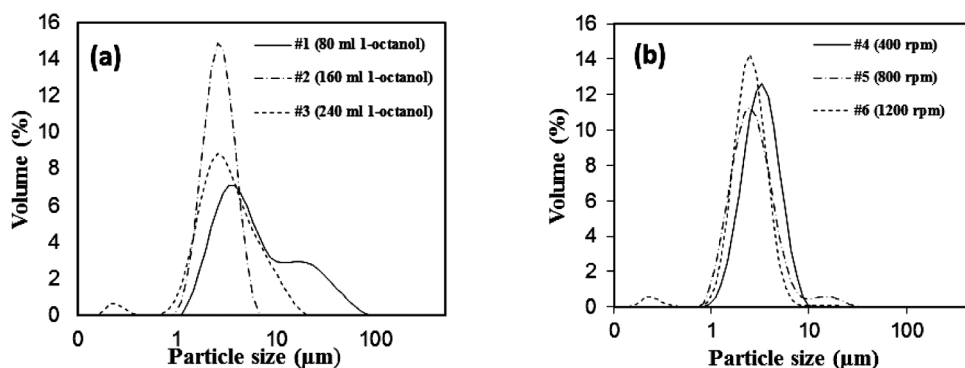


Figure 5. Particle size distributions: (a) different amount of 1-octanol solvent; (b) different mixing speed

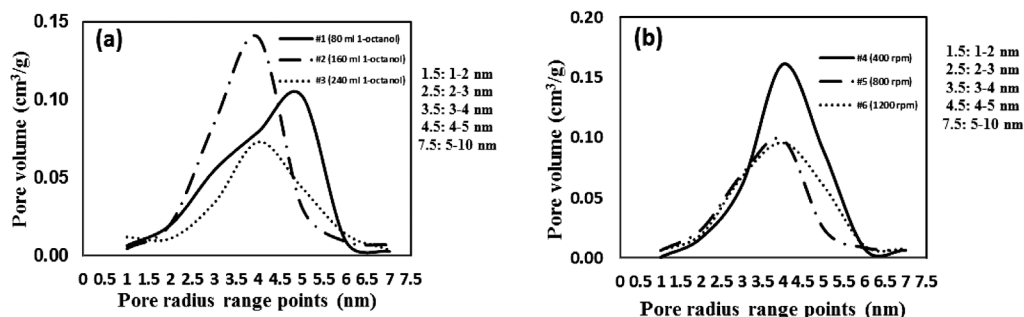


Figure 6. Pore size distribution for silica prepared with (a) different amount of 1-octanol solvent; (b) different mixing speed

Table 1. Properties of hollow silica microspheres prepared by different amount of 1-octanol

Samples	Volume of 1-octanol (ml)	Mean sphere size (μm)	Surface area (m ² /g)	Total pore volume* (cm ³ /g)
#1	80	4.8	140	0.277
#2	160	2.4	164	0.299
#3	240	2.8	115	0.193

*above pore radius 1 nm

micro- and mesopores, however, macropores were not detected. Sample #2 with the greatest surface area exhibited a sharp peak centered at 4–5 nm, having also the biggest value in total pore volume

Compared with the hollow silica particles shown in Figure 3, more uniformed silica shells were obtained by employing different mixing speeds with a fixed volume of 125 ml 1-octanol (Figure 4). The mean size of the silica powders #4, #5 and #6 (corresponding to a mixing speed of 400, 800, and 1200 rpm) is in the range of 2.3–3.1 μm (Table 2, Figure 5(b)). In overall, the trend of decreasing particle size was observed, when increasing the mixing speed from 400 to 1200 rpm. Moreover, all samples exhibit a narrow particle size distribution up to 13 μm . The particle size of the silica spheres is strongly dependent on the size of the reverse micelles (emulsion droplets), in which the primary silica is produced (Ciriminna *et al.*, 2011). Furthermore, the size of droplets is controlled by the viscosity and surface tension of the sol-gel solution as well as the operation parameters, such as temperature and flow rate (Park *et al.* 2003; Baudonnet *et al.* 2007). An increasing stirring speed promotes the dispersion and decreases the viscosity of the emulsion (Baudonnet *et al.*, 2007), causing a decrease in the size of water droplets, thus leading to smaller silica spheres. It is noteworthy that the high mixing speed may deteriorate the generation of pores. That may be because the liquid core failed to endure enormous shear force at vigorous mixing speed (Baudonnet *et al.*, 2007). This is illustrated by the highest specific surface

area and total pore volume of 173 m^2/g and 0.341 cm^3/g , respectively, at a mixing speed of 400 rpm compared to silica particles resulting from 800 and 1600 rpm mixing speed (Table 2). And this is also consistent with the pore size distribution depicted in Figure 6(b). In spite of largest mean particle size, the largest surface area of 173 m^2/g was measured for silica particles mixed at 400 rpm, when compared to those for 800 and 1200 rpm. This is because the greatest pore volume resulted from the lowest mixing speed. BET measurement counts all the pore surfaces into the surface area. When mixing speed was increased from 800 to 1200 rpm, the difference in particle size, surface area and total pore volume was small, and in overall the influence of the amount of 1-octanol on surface morphology and sizes of silica particles was stronger than that of the mixing speed.

Conclusions

Hollow silica microspheres were prepared by a sol-gel emulsion method. The emulsion system consists of water as internal phase, 1-octanol as external oil phase, multiple surfactants HPS, Tween 20 and Span 80, and TEOS as silica precursor. The influence of solvent volume (80, 160, and 240 ml 1-octanol) and mixing speed (400, 800, and 1200 rpm) on the size and surface morphology of silica was investigated. Hollow particles were found in all samples, moreover, the structure also exhibited mesoporous feature. The results revealed that particle size decreased as the solvent increased from 80

Table 2. Properties of hollow silica microspheres prepared by using different mixing speeds

Sample	Mixing speed (rpm)	Mean sphere size (μm)	Surface area (m^2/g)	Total pore volume* (cm^3/g)
#4	400	3.1	173	0.341
#5	800	2.4	149	0.237
#6	1200	2.3	154	0.266

*above pore radius 1 nm

to 160 ml due to the decreased size of reverse micelles, and there was no significant difference in particle size when the solvent increased from 160 to 240 ml. Silica particles prepared by 160 ml 1-octanol also presented the greatest specific surface area and total pore volume. This met our goal successfully on the process optimization in aspect of saving the high cost of 1-octanol. When the mixing speed was increased from 400 to 800 rpm, a clear decrease in particle size was observed. When the mixing speed was further increased from 800 to 1200 rpm only a minor decrease in the particle size occurred. Similarly, this is also due to the decreased size of reverse micelles caused by decreased viscosity of the emulsion. Vigorous mixing speed may collapse the pore formation and results in a lower specific surface area and pore volume.

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