

# Synthesis of Mesoporous Silica Microsphere from Dual Surfactant

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A new procedure is reported to synthesis mesoporous silica micro sphere for the first time. In these method two surfactants namely Span 80 and Tween 80 were used. Small angle X ray diffraction and N<sub>2</sub> adsorption analysis shows the synthesized material has mesoporous property. The material has spherical morphology with 1-10 μm particle size. Beside the material found to have microcapsule property as observed from the Transmission electron microscopy. The Fourier transform Infrared spectroscopic analysis reveals that the materials are similar to other mesoporous materials. We also encapsulated an UV-absorber Ibuprofen inside the microcapsule, by mixing it before the synthesis. This shows a possibility of the materials in cosmetic applications.

**Keywords:** mesoporous silica micro sphere, Tween 80, Span 80

## 1. Introduction

Since silica based mesoporous molecular sieves using surfactant assemblies as supramolecular templates were reported in 1992<sup>1,2</sup>, mesoporous materials have opened many new possibilities for application in catalysis<sup>3</sup>, separation<sup>4</sup>, and nanoscience due to their tunable pore sizes and very large surface areas<sup>5-7</sup>. More recently, mesoporous silica with morphologies including thin films, monoliths, hexagonal prisms, toroids, discoids, spirals, dodecahedron and hollow tubular shapes have been synthesized<sup>8-12</sup>. In conventional procedures, silica spheres have been obtained using surfactants, block copolymers and recently by using colloidal suspensions<sup>13</sup>. Normally polymers are used in synthesis of hollow sphere. Only few are reported in surfactants. Tween 80 and Span 80 are commercially available surfactants. Preparation of micro sized silica spheres using Tween 80 and Span 80 surfactants have never been reported. The Tween 80's chemical name is Poly oxy ethylene sorbitan mono oleate or Sorbitan monooleate ethoxylate and Span 80's chemical name is Sorbitan oleate or Sorbitan (Z)- mono 9-octadecenoate. Their densities are 1.064 (Tween 80) and 0.986 (Span 80). They are high hydrophilic – lipophilic balance (HLB) and low HLB surfactants respectively<sup>14</sup>. They are used to control the viscosity and increase the Water-1/Oil/Water-2 emulsion structure.

This paper described a novel synthesis pathway for mesoporous silica microspheres of 1-10 μm particle size using dual surfactant. The synthesized material was characterized by various novel techniques and its storage property of a UV-absorber is studied for cosmetic applications.

## 2. Experimental

All chemicals used in this work were commercially available and were used without further purification. Na<sub>2</sub>SiO<sub>3</sub> (Samchun pure chemical co. Ltd, South Korea), Span 80 (Daejung Chemicals & metals co Ltd., South Korea), Tween 80 (Shinyo pure chemicals co. Ltd., Japan), NH<sub>4</sub>HCO<sub>3</sub> (95%, Dae-Jung chemicals and metals co. Ltd, South Korea), n-hexane (95%, Dae-Jung chemicals and metals co. Ltd., South Korea).

Mesoporous silica microsphere was obtained by interfacial reaction. There are three solutions namely, sodium silicate solution,

Surfactants (Tween 80 and Span 80) and n-hexane mixture and ammonium bicarbonate solution were used in the present synthesis. The first solution was prepared by mixing distilled water and sodium silicate (29.9 g) (4 M aqueous solution (36 mL)). Second mixture was prepared by mixing n-hexane (72 mL), Tween 80 (1.0 g) and Span 80 (0.50 g) for the stabilization of the water/oil emulsion. The last solution was made by mixing Distilled water and precipitant (NH<sub>4</sub>HCO<sub>3</sub>, 9.8 g) (2 M aqueous solution (252 mL)). First, n-hexane and surfactants were mixed by using a homogenizer (Matsushita Electric Industrial Co. Ltd., Japan, and Model No. National SSC811EA with 1000 rpm). To this solution, sodium silicate solution was added. After being emulsified for 1 minute, this mixture was poured into ammonium bicarbonate solution with stirring. After a thorough mixing, a white precipitate was formed. The mixture was stirred for another 2 hours to continue precipitation at constant temperature (298 K). The solid was filtered and washed with fresh distilled water for several times. Finally, the solid was dried at 373 K for 12 hours.

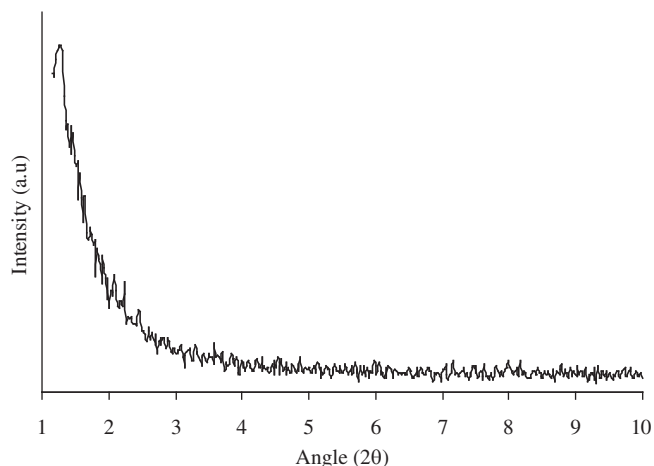
X ray diffractograms were recorded on Rigaku Multiplex diffractometer using Cu Kα radiation and a proportional counter as detector. A divergence slit of 1/328 on the primary optics and an anti-scatter slit of 1/168 on the secondary optics were employed to measure data in the low angle region. The scanning electron micrographs were taken using a Topcon, SM-300. The samples were deposited on a sample holder with an adhesive carbon foil and sputtered with gold. For transmission electron microscopy, the samples were ground and deposited on a circular disc of fine copper mesh covered with collodion. Images were taken using a JEOL JSM-2000 EX electron microscope operated at an acceleration voltage of 200 kV. The specific surface area (BET) of the samples was determined using a Micromeritics ASAP 2010 volumetric adsorption analyzer. Before N<sub>2</sub> adsorption samples was evacuated in vacuum at 573 K. The data points of p/p<sub>0</sub> in the range of about 0.05–0.3 were used in the calculations. The FT-IR spectra in the framework region were recorded in the diffuse reflectance mode (Nicolet 60SXB) using 1:300 ratio of sample with KBr, pellet. UV-spectra were analyzed using JASCO –V-530, UV-Vis spectrophotometer.

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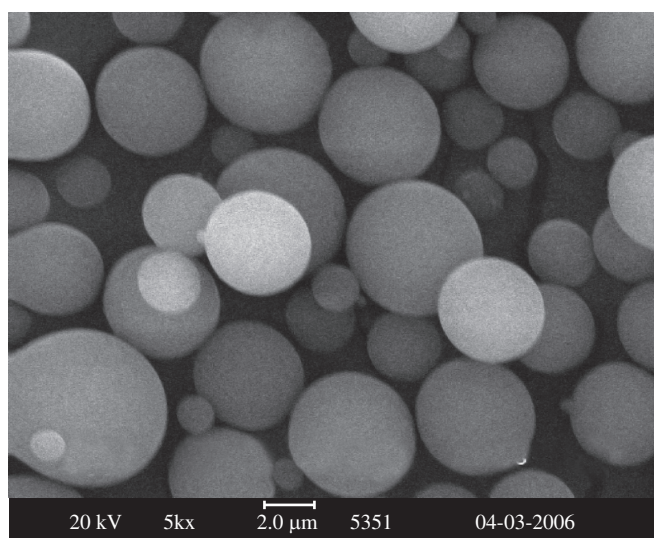
### 3. Results and Discussion

Figure 1 illustrates the low angle X ray diffraction (XRD) patterns of the as-synthesized sample. The calcined sample pattern does not vary considerably, however a small peak broadening is observed. The high intensified peak at  $2\theta = 1.25^\circ$  shows it is a mesoporous material<sup>15</sup>.

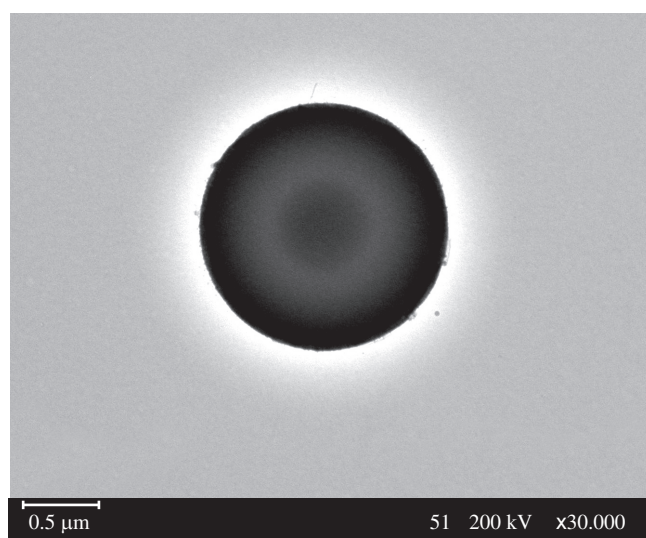
The Scanning electron microscopic image of the material posse's spheroid and the particle size is in between 1 to 10  $\mu\text{m}$  (Figure 2a). The sample synthesized without surfactants namely, Tween 80 and Span 80 shows irregular flakes morphology (Figure 2c). The Transmission electron microscopic picture shows presence of microcapsule property (Figure 2b). The wall thickness of the shell was found to be 0.25  $\mu\text{m}$  and the diameter of the silica particle is about 1.5  $\mu\text{m}$ . Therefore the shell wall was considerably thin, and its thickness was estimated to be about 20% of the total size of the particle, although most of the other reported silica hollow sphere has thicker shell walls. Similar reports are available in the literature<sup>15</sup>. The sample synthe-



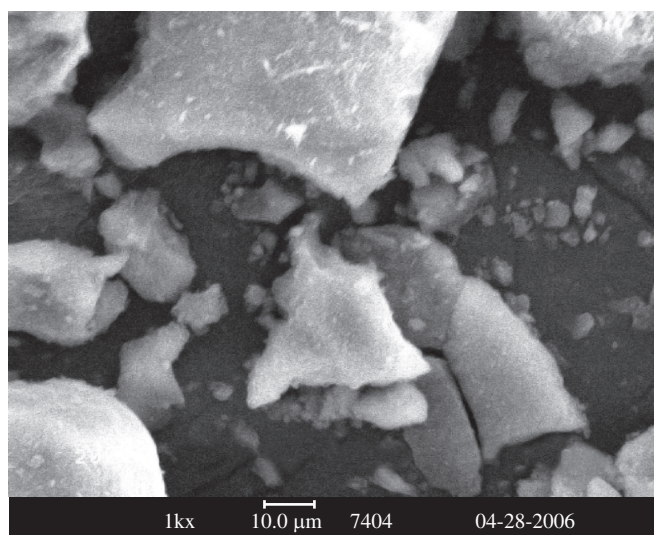
**Figure 1.** X ray diffraction pattern of as synthesized sample prepared from Tween 80 and Span 80 surfactant mixture.



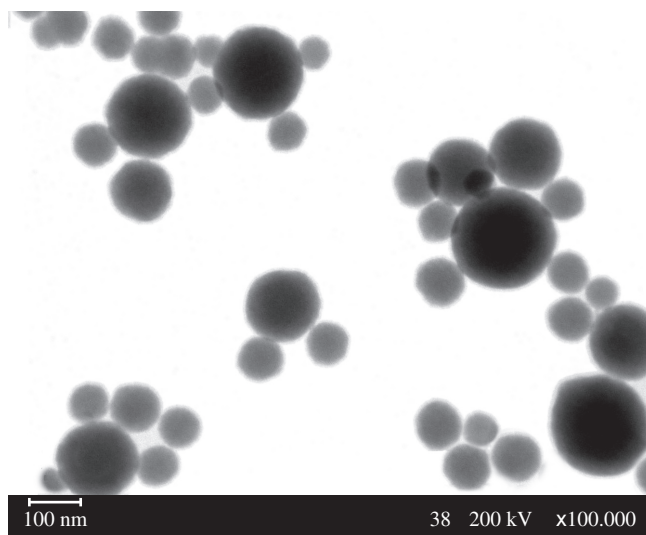
(a)



(b)



(c)



(d)

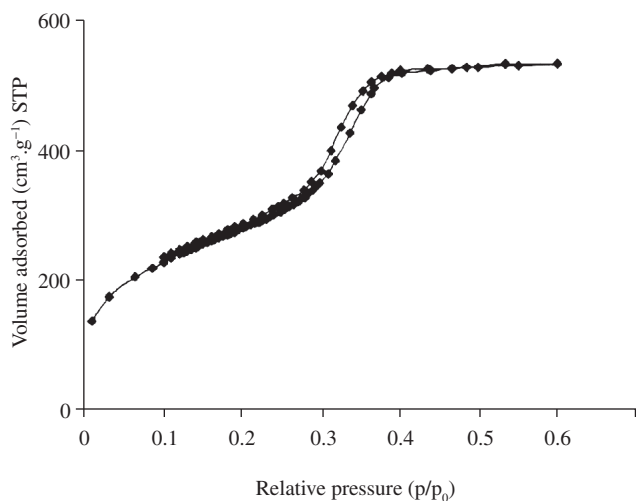
**Figure 2.** Scanning electron microscopic photograph of sample prepared from a) Tween 80 and Span 80 surfactant mixture and c) without surfactant and Transmission electron microscopic photograph of sample prepared from b) Tween 80 and Span 80 surfactant mixture and d) Tween 80/Span 80 surfactant.

sized with any one of the surfactant give nanosphere, but the hollow sphere property lost (Figure 2d). The physicochemical nature of the two surfactants in combine plays a major role in hollow formation. Yield was 99% with respect to the theoretical yield of precipitated silica. The total weight of silica ( $\text{SiO}_2$ ) present in whole sodium silicate was taken as the theoretical yield. This silica microcapsule was not mechanically fragile. When this microcapsule was pounded hard in a mortar, no parts of the microcapsule were broken. The thermo gravimetric analysis shows that the sample loss about 10% of its total weight on calcinations. EDX analysis of the sample after calcinations indicates the presence of only silicon other than oxygen.

Typical nitrogen sorption isotherms at 77 K and the corresponding pore size distribution are shown in Figure 3. The nitrogen isotherms indicate a linear increase of the amount of adsorbed nitrogen at low pressures ( $P/P_0 = 0.35$ ). The resulting isotherm can be classified as a type IV isotherm with a type H2 hysteresis, according to the IUPAC nomenclature<sup>15-18</sup>. The steep increase in nitrogen uptake at relative pressures in the range between  $P/P_0 = 0.40$  and  $0.60$  is reflected in a narrow pore size distribution. Thus, the variation of the catalyst in the solution during the growth process enables one to adjust and to control pore structural parameters such as the specific surface area ( $900 \text{ m}^2/\text{g}$ ), the specific pore volume ( $1.29 \text{ cm}^3/\text{g}$ ), and the average pore diameter ( $31 \text{ \AA}$ ).

The FT-IR spectrum of as-synthesized sample (Figure 4) shows peaks around  $1700$  and  $3430 \text{ cm}^{-1}$  corresponding to the carboxyl and hydroxyl groups<sup>19</sup> respectively. The adsorption peak belonging to the Si-O stretching vibration of Si-OH bond appears<sup>20</sup> at  $960 \text{ cm}^{-1}$ . The weak peaks at  $2855$  and  $2920 \text{ cm}^{-1}$  belong to the stretching vibrations of C-H bonds, which show a few organic groups are adsorbed on the spheres. The strong peaks near  $1100$ ,  $802$  and  $467 \text{ cm}^{-1}$  agree to the Si-O-Si bond which implies the condensation of silicon source<sup>21</sup>.

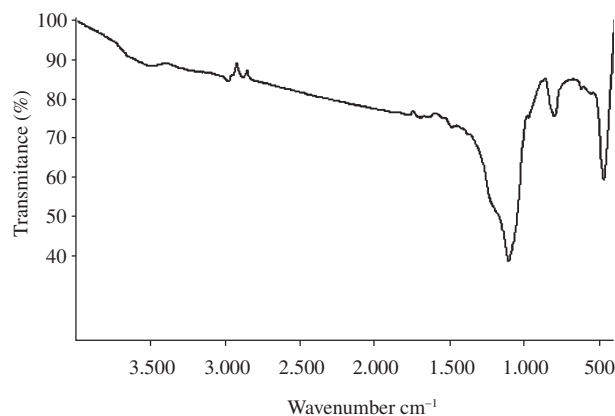
Ibuprofen with the molecules size of  $1.0 \times 0.6 \text{ nm}$  was used to examine the UV-absorbing capacity<sup>22,23</sup>. The UV-absorber was introduced inside the shell by mixing prior to synthesis. Figure 5 shows the UV absorbance spectra of ibuprofen encapsulated silica micro capsule, pure ibuprofen and ibuprofen adsorbed on silica microcapsule. Pure ibuprofen shows highest intensity followed by ibuprofen adsorbed silica microcapsule. The UV absorbance intensity of ibuprofen encapsulated samples decrease marginally. This illustrates that the capsule could hold more UV-absorber molecules.



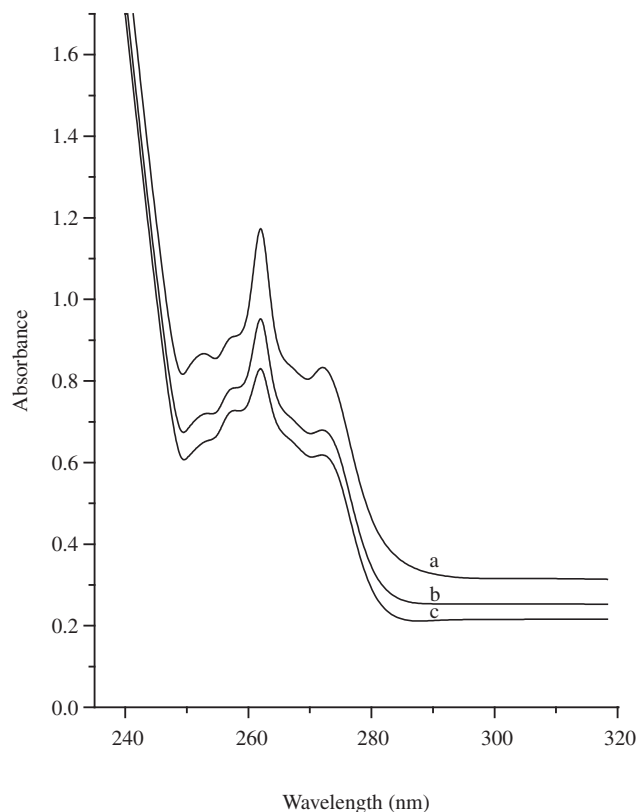
**Figure 3.** Nitrogen sorption isotherms at 77 K for calcined sample prepared from Tween 80 and Span 80 surfactant mixture.

## 4. Conclusions

A novel procedure brought out for synthesis of mesoporous silica microcapsule from dual surfactant. Mono and surfactant free synthesis leads different material. It can hold good number of an UV absorber say Ibuprofen by presynthesis modifications. It can be used in cosmetics applications.



**Figure 4.** Fourier transform Infrared spectroscopic analysis of the as-synthesized sample prepared from Tween 80 and Span 80 surfactant mixture, in the framework region (Bands =  $467 \text{ (s)}$ ,  $802 \text{ (m)}$ ,  $960 \text{ (vw)}$ ,  $1100 \text{ (vs)}$ ,  $1700 \text{ (vw)}$ ,  $2855 \text{ (w)}$ ,  $2920 \text{ (w)}$  and  $3430 \text{ (w)}$ ).



**Figure 5.** UV-Vis spectra of a) pure Ibuprofen, b) Ibuprofen dispersed silica microsphere and c) Ibuprofen encapsulated silica microsphere prepared from Tween 80 and Span 80 surfactant mixture.

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