Fabrication of Hollow Silica Microspheres through the Self-assembly Behavior of Polymers in W/O Emulsion

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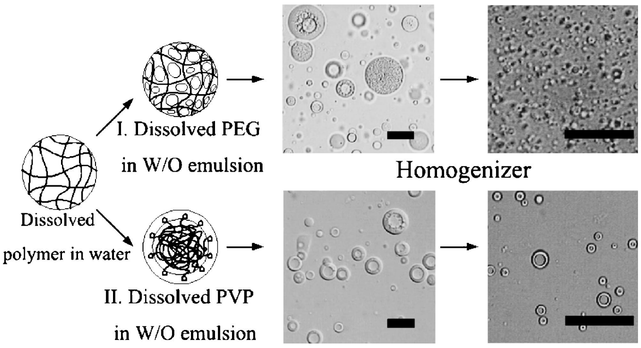
The major focus of this study is on understanding the mechanism of formation of the hollow silica microspheres through the self-assembly behavior of polymers (PEG and PVP) in W/O emulsion and studying their particle morphology, particle size, and pore structure depending on the experimental conditions.

Recently, there has been intense interest about the fabrication of micro and nanometer-sized hollow particles. These hollow particles often exhibit properties that are substantially different from general particles (for example, low density, large specific surface area, stability and surface permeability), which make them attractive from both a scientific and a technological viewpoints.[1] Applications for such particles are cosmetics, including capsule agents for drug delivery system (DDS), catalysis, coatings, composite materials, dyes, inks, artificial cells, fillers and protecting sensitive agents such as enzymes and proteins.[1–3]

However, in case of hollow silica microspheres fabricated in emulsion which has a lot of reaction factors and thermodynamic instability, the yield of hollow silica microspheres is generally low.[4–6] In this paper, we report a method to synthesize hollow silica microspheres by sol-gel process of tetraethyl orthosilicate (TEOS) in W/O emulsion containing polymers and surfactants at high yield.

The overall procedure for the preparation of hollow particles in W/O emulsion with polymers is represented in Scheme 1. External oil phase was prepared by dissolving hydroxypropyl cellulose (HPC, average Mw ca. 370000) as a stabilizer of emulsion structure in octanol (45 g), then held at 80 °C for 4 h. Then oil phase was kept at 40 °C. After 30 min, sorbitan monooleate (3 wt% Span 80) was added into oil phase. Water phase was prepared with polymers: polyethylene glycol (PEG, average Mw. 20000, 18 wt%) in Scheme 1-I or polyvinylpyrrolidone (PVP, average Mw. 40000, 28 wt%) in Scheme 1-II.

The polyoxyethylene(20) sorbitan monolaurate (5 wt% Tween 20) and NH_4OH as a catalyst were added in the water phase. Water phase was added to an external oil phase to make W/O emulsion. The weight ratio of water to oil phases in emulsion was kept as 1:9. To obtain a narrow and small droplet size distribution, the mixtures were pulverized by using a homogenizer at a rate of 12000 rpm for 5 min. Samples were prepared in the experimental beakers with flat bottom and kept for 12 h with soft agitation using small magnet stirrers. The sol–gel reaction for the formation of silica particles was initated by adding TEOS into oil phase. The molar ratio of water to TEOS was kept as 10. After reaction was completed, the samples were centrifuged at 2500 rpm for 15 min to obtain hollow silica particles. In order to remove the unreacted materials such as polymers, octanol and surfactants, the particles obtained by centrifugation were washed with ethanol. After this procedure was repeated three times, the hollow silica particles were collected. Then, particles were dried in an incubator at 40 °C for 1 day and were finally calcined in air at 600 °C for 6 h to remove the remaining polymers and water inside particles.



Scheme 1. Schematic illustrations of the key stages in the formation of the W/O emulsion with polymers and optical microscopic images of each stages. I) The molecular behavior of PEG in W/O emulsion. II) The molecular behavior of PVP in W/O emulsion. (the scale bar in images corresponds to 10 µm.)

The morphologies of particles preparaed through the Scheme 1-I and Scheme 1-II are shown in Figure 1. SEM and TEM images of particles shows the completely different morphologies; mesoporous (Figures 1a and 1b) and hollow structures (Figures 1c and 1d). In case of using PEG, both the surface of silica particle and the inside have the mesoporous structure (Figures 1a and 1b). The inset in Figure 1b is an expanded TEM image of a single hollow microsphere with mesoporous structure. But, the yield of hollow silica particles with mesoporous shell was below 10%.

The morphologies of particles prepared using PVP are different from the those of using PEG in that they evidently have hollow structure. Some broken microspheres are observed in the SEM image (Figure 1c), which indicates that they have hollow structure. This is further proven by the sharp contrast between the dark surface and the pale core in the TEM image (Figure 1d). The shell wall thickness of particles had a broad distribution in the range of 100 to 400 nm, independent of the particle size. This variable thickness of the shell wall could be the reason for the formation of a closed structure below 400 nm particle size resulting in solid spheres. But, the particles prepared using PVP have hollow structure more than 80%.

The mechanism of formation of the hollow structure microspheres can be explained as follows. First, the water–PEG interaction and the quantities of PEG dissolved in water have the important role in the mechanism of Scheme 1-I. The water–PEG interaction was believed to be through a hydrogen bonding between the isolated hydroxyl groups of water and the ether oxygen in PEG polymer. Hydrogen bonding has generally been assumed to be a ubiquitous mechanism of polymer adsorption on hydrophilic surfaces.[7,8] Also, in case of the addition of PEG in aqueous phase, unstable multiple emulsion droplets are observed, and both Ostwald ripening and release of the internal oil phase into the outer oil phase occur. This is the coalescence between the smaller inner oil gloubles within the water droplet and coalescence of the small inner oil droplets with the outer droplets interface.[5] Thus, the molecular behavior of PEG in the aqueous droplet is just the same as shown in Scheme 1-I.

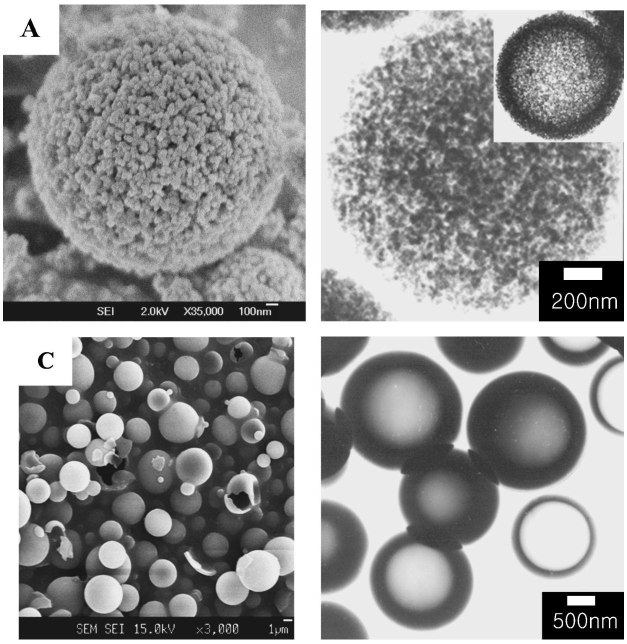


Figure 1. SEM(A,C) and TEM(B,D) images of silica particles produced from W/O emulsions containing PEG (A,B) and PVP (C,D) in aqueous phase; The inset of figure B is an expanded TEM image of a single hollow microsphere with mesoporous shell wall.

Second, the molecular behavior of PVP is different from that of PEG in that PVP polymer has a specific character of partially amphiphilic property. The hydrophilic part in PVP is arranged toward the aqueous layer in droplet and the hydrophobic part in PVP is arranged toward inner oil phase in aqueous droplets. Thus, the molecular behavior of PVP in the aqueous droplet is just the same as shown in Scheme 1-II.

Because water-soluble PVP molecules have partially hydrophobic properties, their molecular behavior is different rather than other general hydrophilic polymers in emulsion. To confirm the molecular behaviors of PVP and PEG in W/O emulsion, the experiment using two polymers simultaneously was attempted in W/O emulsion. Figure 2 shows the images of emulsion droplets by optical microscope and those of particles by SEM. In Figure 2a, the water droplets are divided into PEG and PVP regions because the molecular behaviors of polymers are mutually different. Inset magnified illustration indicated droplets structures. The upper part of droplets consist of PVP region and water layer, while the lower part of droplets consist of PEG and water. After the reaction with TEOS, the lower part of the droplet was only remained (Figure 2b). But, due to the thin water layer, the shape of the upper part was disrupted. By means of this experiment, it was inferred that the particles of different mophology were formed by the different molecular behavior of PEG and PVP in water.

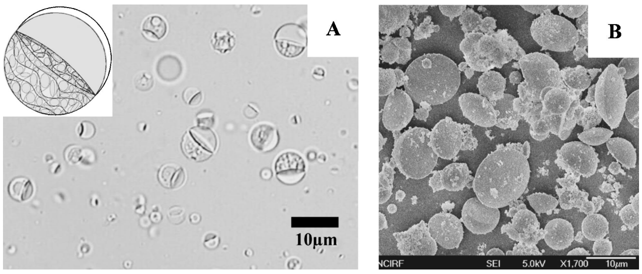


Figure 2. A) optical microscopic image of emulsion droplets; Inset modified illustration indicated droplets structures. B) SEM image of silica particles produced from W/O emulsions containing PEG and PVP in aqueous phase.

In conclusion, we have succeeded in preparation of hollow microspheres through the self-assembly behavior of polymers in W/O emulsion. The molecular behavior of PVP led to the formation of emulsion droplets possessing a hydrophobic part of PVP core surrounded by a hydrophilic part of PVP shell with aqueous layer. The central layer, composed of alkyl chain in PVP, fix the inner oil droplets to core. Also, the molecular behavior of PEG led to the formation of multiple emulsion possessing a hydrogen bonding with aqueous phase. Because this route is based on common and nonexpensive polymer products and the processing is simple, it may have great potential for further applications in fabricating supramolecuar materials for various fields such as cosmetics, catalysis, composite materials, drug encapulation and controlled release.

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