

Interfacial Fabrication of Silica Hollow Particles in a Reverse Emulsion System

Linyong Song, Xuewu Ge,* and Zhicheng Zhang

Department of Polymer Science and Engineering, University of Science & Technology of China, Hefei, Anhui 230026, P. R. China

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Silica hollow particles were prepared at room temperature in a reverse emulsion system (W/O emulsion) via interfacial strategy. The cationic surfactant cetyltrimethylammonium bromide (CTAB) and aliphatic amine were found to be critical factors for the production of hollow structure.

Over the past decade, extensive research has been undertaken in the preparation of inorganic hollow microspheres because of their potential applications in cosmetics, coatings, inks, biomedicine, small containers for encapsulation process in catalysis, drug delivery, development of artificial cells, and other areas.^{1,2} On account of the well-controlled kinetics on hydrolysis and condensation of silicon alkoxides in aqueous solution, silica is by far the most popular inorganic matrix for hollow microspheres.

A previous method to produce silica hollow spheres is based on the utilization of core-shell type templating materials.³⁻¹⁰ In these cases, polymer latexes, inorganic spheres, oil droplets, and aggregates of polymers or surfactants are used as cores, and silica microspheres are formed on the core templates. For most processes using core templates, the templates need to be removed by calcination or solvent treatments to create vacant inner spaces. Another representative approach is to create silica hollow spheres using vesicle templates.¹¹⁻¹⁴ An acid-hydrolysis and base-condensation two-step preparation method is also claimed to be effective for silica hollow sphere preparation.¹⁵ Silica hollow spheres were also obtained at the air-water interface.^{16,17} However, this method was rather sensitive to the stirring conditions, induction time, and time delays between the dilution and neutralization steps in the preparation procedure.

In the present paper, we report a new facile and efficient one-step method for the preparation of silica hollow particles in reverse emulsion system (W/O emulsion). The procedure was based on the hydrolysis and condensation of tetraethoxysilane (TEOS) at the water/oil interface formed from a cationic surfactant cetyltrimethylammonium bromide (CTAB) and alkylphenol polyoxyethylene (*n*) ether (*n* = 4, OP-4). Because silica was deposited preferentially at the W/O interface, hollow particles were formed in situ. This method eliminates the need for any template extraction steps. As the diameter and shell thickness of hollow particles depend on the water droplet size, this can be controlled to some extent by varying the ratio of CTAB/water (see Figures 1A and 1B). The shell thickness was ca. 60 and 20 nm, respectively.

Silica transcription was carried out by the addition of the silica precursor TEOS to a reverse emulsion in the presence of aliphatic amine. Powder X-ray diffraction profiles showed a single broad peak centered at $2\theta = 22^\circ$ corresponding to the formation of hollow particles with amorphous silica shells. TEM showed the presence of a large amount of silica hollow particles

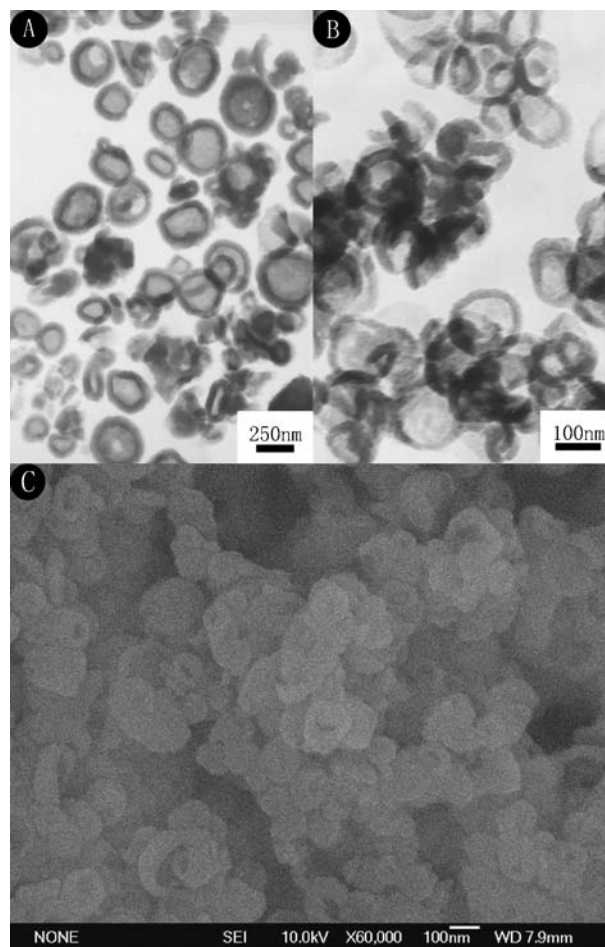


Figure 1. TEM images of silica hollow particles at different content of CTAB (A) CATB = 1×10^{-3} mol (B) CTAB = 2×10^{-3} mol (C) FESEM image of sample with CTAB = 2×10^{-3} mol.

with outer diameters ranging from about 100 up to 250 nm (see Figure 1). At the same time, few granular silica were wrapped in the hollow particles, which were due to the few hydrated silica molecules penetrated into water phase and the condensation reaction took place in the water. FESEM image showed silica particles of size similar to those observed with TEM and the fractured particles confirmed the hollow structure. Similar images were obtained after calcinations of the silica product at 873 K, confirming that the spherical structures were composed of stable silica. The diameter and shell thickness of silica hollow particles were kept almost the same (see Supporting Information). While the silica hollow particles aggregated obviously and this phenomenon was due to the irreversible condensation of adjacent surface hydroxyl groups among silica hollow particles at high

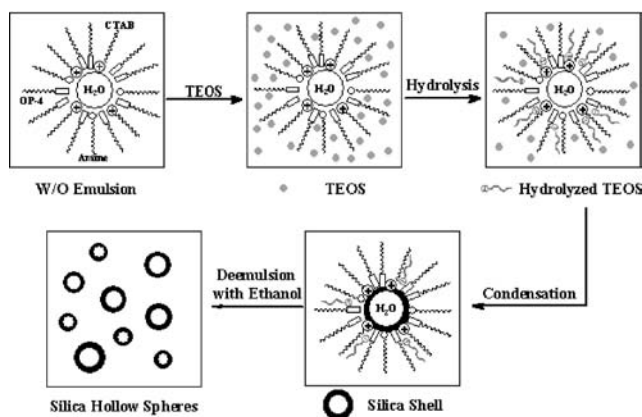


Figure 2. Schematic representation of the formation of silica hollow particles in W/O emulsion system.

temperature. The porosity of the shell was investigated using nitrogen adsorption–desorption isotherms (see Supporting Information). Typical value for the specific surface area according to the BET method is $652.8 \text{ m}^2/\text{g}$ (Micromeritics ASAP2020). The high special surface area of hollow particles may originate from mesophases formed by the precursors and the mixed surfactants.

We proposed a formation mechanism as shown in Figure 2 to explain the hollow structure formation. The precursors of TEOS, initially dissolved in the oil phase, penetrated slowly into the surfactant membrane. Hydrolysis of TEOS occurred as a consequence of contact with the aqueous phase and catalysis by dodecylamine. The hydrolyzed TEOS molecules were then condensed at the W/O emulsion interface, leading to the formation of silica hollow particles.

CTAB and the dodecylamine were found to play critical role in the formation of stable silica hollow particles. To investigate the role of cationic surfactant (CTAB) and aliphatic amine (dodecylamine) and the proposed reaction mechanism, four recipes were examined (see Table 1). Experiments Entries (1–3) resulted in the exclusive formation of solid or granular silica (as observed with TEM, see Supporting Information), indicating that indeed both positively charged surfactant CTAB and aliphatic amine need to be present in order to obtain silica hollow particles. The silica shell structure was a result of steady self-assembly of negatively charged silicates and the ammonium cation of CTAB at the W/O interface. In the base-catalyzed hydrolysis of TEOS, the OH^- ion displaces of $\text{C}_2\text{H}_5\text{O}^-$ and the higher pH value would favor the hydrolysis reaction. It has been observed that the hydrolysis of TEOS was obviously slower using dodecylamine than NaOH as catalyst (by comparing the time of the reverse emulsion from transparent to turbid), so the silicates were attracted by the cationic surfactant and the condensation was mainly proceed at the W/O interface. In the end, the silica

Table 1. Results and conditions for the silica transcription

Entry ^a	Surfactants	Base	Silica structure
1	OP-4+OP-10	NaOH	solid silica
2	OP-4+OP-10	dodecylamine	granular silica
3	OP-4+CTAB	NaOH	granular silica
4	OP-4+CTAB	dodecylamine	hollow partilce

^aIn Entries 1 and 3, NaOH is 0.002 mol; in Entries 2 and 4, dodecyl amine is 0.002 mol.

shell structure was formed in suit. In Entries 1 and 3, when NaOH was used as catalyst, the hydrolysis of TEOS was so fast that SiOH-based molecule will become water-soluble and the condensation will take place in the aqueous phase. On the other hand, without cationic surfactant CTAB, the adsorption of non-ionic surfactant on silicates was weaker than that of the CTAB and the interface membrane of nonionic surfactant cannot prevent the silicates from penetrating into the inner aqueous phase, hence granular silica was also obtained.

In conclusion, we have demonstrated a new facile and efficient sol–gel approach to create silica hollow particles at a W/O interface. The diameter and thickness of the silica hollow particles can be controlled by varying the ratio of CTAB/water. The porous shell wall of the spheres could have potential applications as controlled release capsules for drugs, dyes, cosmetics, inks, artificial cells, catalysts, and fillers. Furthermore, this approach could be extended to the synthesis of other oxide composite hollow spheres such as Ti–Si, Zr–Si, et al., as currently being investigated in our laboratory.

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- 18 Experiments and Characterizaion: Reverse emulsion was prepared by mixing 5 mL of aqueous solution of 0.37 g of CTAB with 25.0 mL of kerosene solution of 2.0 g of OP-4 and 0.37 g of dodecylamine under continually stirring. Hollow silica particles were then prepared at room temperature by adding 9.32 g of TEOS to the reverse emulsion and the reaction was continually stirred 24 h. Finally, ethanol was added into the reverse emulsion to precipitate the silica particles. The morphology of silica particles was studied by FESEM (JEOL JSM-6700) and TEM (Hitachi H-800). The control experiments (Entries 1–3 in Table 1) were conducted under the same conditions except the use of different surfactants and basic catalysts.