Core/shell silica-based *in-situ* microencapsulation: A self-templating method†

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Core/shell SiO_2 and $(RSiO_{1.5})_{1-x}$–$(SiO_2)_x$ (R = alkyl) microcapsules were synthesized *via* a single-step O/W emulsion system using a self-templating method; the facile synthetic process provides an *in-situ* encapsulation route for a wide range of lipophilic functional compounds.

The use of micro/nano capsules offers greater convenience, improved physicochemical stability, and controlled release of encapsulated functional materials.[1] Applications of capsules have received considerable interest in the pharmaceutical and medical industries (*e.g.*, for drug delivery systems), in the food and cosmetic industries (*e.g.*, for flavors, fragrances, spices and nutrients), and in the agricultural industries (*e.g.*, for fertilizers, pesticides and herbicides).[2] A number of reports have appeared on the solution-based soft synthesis of ceramic hollow particles or capsules *via* templating methodologies utilizing colloidal particles, surfactants and polymers.[3] The templating methods have the advantage of controlling spherical morphology and narrow size distribution. However, they have cumbersome encapsulation procedures for removing templates, immobilizing functional target compounds, and stabilizing the compounds within the capsules by surface coating. In this connection, the *in-situ* encapsulation technique with core/shell structures using a one-pot process offers great opportunities for a wide range of application.

Herein, we report a facile *in-situ* synthesis of core/shell SiO_2 and $(RSiO_{1.5})_{1-x}$–$(SiO_2)_x$ microcapsules that contain lipophilic functional compounds. Although a few papers have reported on silica-based *in-situ* encapsulation methods to date, they have still utilized templates such as surfactants or reactive alkylsiloxanes.[4] A self-templating method without using additional organic additives can provide high-purity matrices for encapsulation of functional target compounds. It has been very difficult to synthesize the spherical particles with core/shell structures without using additional organic templates. We have solved these difficulties *via* a simple approach of chemical modification of silicon alkoxides as shell forming precursors. This strategy seems so simple, but provides a versatile and effective route for encapsulating lipophilic functional compounds. The procedure of chemical modification is as follows: The hydrolysis and condensation of tetraethoxysilane (TEOS) was performed for 12 h at 40 °C under acidic conditions. The molar composition of the mixture TEOS : EtOH : H_2O : HCl was 1 : 4 : 1 : 3×10^{-3}. Then the solvent and by-product were removed by a rotary vacuum evaporator for 1 h at 60 °C, resulting in a transparent viscous solution. The precursors for $(RSiO_{1.5})_{1-x}$–$(SiO_2)_x$ microcapsules could be prepared by a simple combination of $Si(OR)_4$ and $RSi(OR')_3$ (where, R, R′ = alkyl, $x = 0.1 \sim 0.5$) such as methyltrimethoxysilane (MTMS), phenyltrimethoxysilane (PTMS) and methacrylopropyltrimethoxysilane (MPTS), *etc*. For the core/shell *in-situ* encapsulation of lipophilic functional compounds, an oil in water (O/W) emulsion method based on sol–gel process was used in this study. The lipophilic functional compounds were mixed into the shell precursor, and emulsified into an aqueous solution using a mechanical stirrer or homogenizer. Then the resultant microemulsions containing lipophilic active compounds were solidified by adding NH_4OH or water-soluble amines for 10 min at room temperature. The final pH value of the solutions was about 12 (0.1 M NH_4OH). The resultant microcapsules were aged for 1 h without stirring, collected by centrifugation, washed with water, and dried for 24 h at room temperature.

Fig. 1 shows scanning electron microscopy (SEM) images of the core/shell SiO_2 (A) and $(CH_3SiO_{1.5})_{0.3}$–$(SiO_2)_{0.7}$ (B) microcapsules synthesized by a self-templating method. Octylmethoxycinamate (OMC) which is a well-known organic UV absorber was used as a lipophilic functional target compound. It is shown that as-prepared particles have spherical and core/shell structures with a broad particle size distributions. The choice of functional materials for this approach has no limitation as long as they are miscible with the shell forming precursors.

The H_2O/Si ratio and evaporation procedure played major roles in the core/shell *in-situ* encapsulation. The H_2O/Si ratio used in the present study was in the range of $0.8 \sim 1.5$, in which all the resultant microcapsules were observed as core/shell structures showing high encapsulation yields of over 90%.[5] Outside this range no core/shell microcapsules were obtained. The evaporation procedures to remove alcohol were needed to

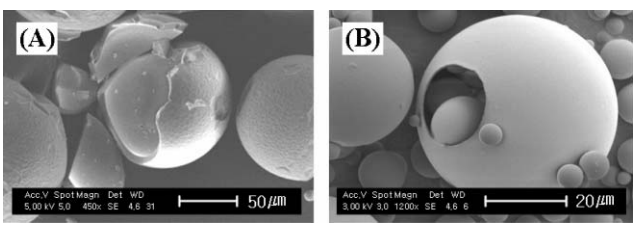

Fig. 1 Scanning electron microscopy (SEM) images of the microcapsules synthesized by an *in-situ* encapsulation process using a self-templating method: (A) SiO_2, (B) $(CH_3SiO_{1.5})_{0.3}$–$(SiO_2)_{0.7}$.

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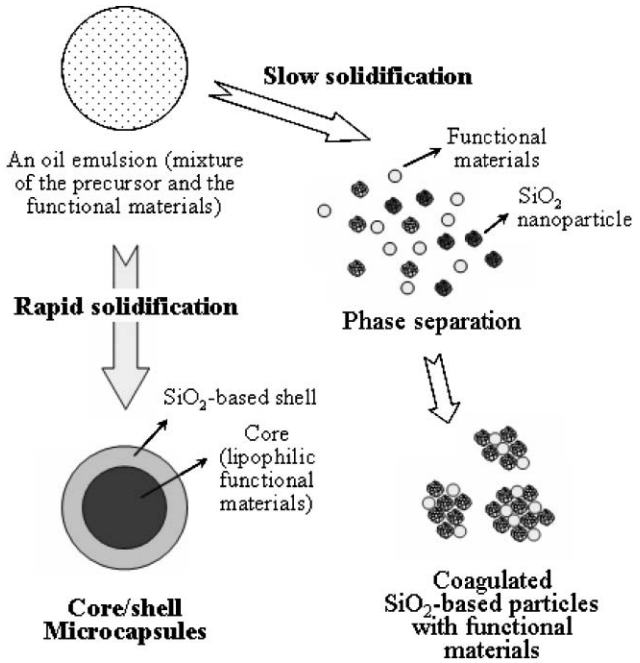

Scheme 1 Schematic representation of the silica-based core/shell *in-situ* microencapsulation process *via* a self-templating method.

enhance encapsulation yield. Without removing alcohol, the encapsulation yield decreased due to the diffusion phenomena of the lipophilic functional compounds toward aqueous solutions. The average particle size distribution, shell thickness, and porosity of the microcapsules were controllable by adjusting processing parameters. The average particle size decreased with increasing agitation speed due to the smaller emulsion size. The shell thickness decreased as the loading of the lipophilic functional compounds was increased. The average pore size of the pure silica microcapsules was 17 nm in the mesoporous range and it decreased to several nanometers with increasing the portion of R groups in $(RSiO_{1.5})_{1-x}$–$(SiO_2)_x$.[6] SEM images also show that the alkyl-modified silica has smoother surface texture. The supporting data of SEM and BET are given in the ESI.†

The mechanism of the core/shell *in-situ* microencapsulation process using a self-templating method is not clear. However, it may be proposed as follows (Scheme 1). The mixture solution of silicon alkoxides as precursors and lipophilic functional compounds form oil emulsions in an aqueous solution. However, the emulsions undergo phase separation during the solidification step because the silicon alkoxides become soluble in aqueous solution, while the lipophilic functional compounds maintain their nature unchanged, resulting in coagulated particles *via* particle growth from hydrolysed silicon alkoxides. The SEM supporting data are shown in the ESI.† For this reason, surfactants or polymers have been used as templates to prevent the phase separation phenomena. The rates of solidification played an important role in the core/shell *in-situ* encapsulation, and they were simply controllable by modifying the nature of the silicon alkoxides as a function of H_2O/Si molar ratio. The rate of solidification increased with increasing H_2O/Si ratio.[7] The supporting data are shown in the ESI.† In the rapid solidification system, the mixture solution of the modified precursors and the lipophilic functional compounds form emulsions in an aqueous solution, followed by solidification reaction from the outer surface toward the center of the emulsions. Once the outer surface of the emulsion is solidified, it may serve as a self-template. Then the un-reacted precursor within the emulsion becomes solidified onto the external shell, while the lipophilic functional compounds become phase-separated in the center of the shell, resulting in a core/shell microcapsule containing the lipophilic functional compounds as a core. Therefore, the highlight of the core/shell *in-situ* microencapsulation was to design it so that the solidification rate of the precursors was fast enough that they served as self-templates rather than dissolved into the aqueous medium. The core/shell structures were obtained only from the modified precursor systems. Although the rates of solidification were also increased with increasing the concentration of gelling agents such as NH_4OH or water-soluble amines, core/shell microcapsules were not obtained.

In conclusion, the present paper has demonstrated a core/shell silica-based *in-situ* microencapsulation using a self-templating method with a one-pot process. The solidification rate of precursor played the major role in controlling the core/shell structures. In the rapid solidification systems, the precursor emulsions served as self-templates, and the resultant microcapsules showed high encapsulation yield over 90%. The self-templating process is so simple, but provides a versatile and effective route for encapsulating lipophilic functional compounds into silica-based matrices with high purity.

Notes and references

1 G. Ibarz, L. Dähne, E. Donath and H. Möhwald, *Adv. Mater.*, 2001, **13**, 1324; H. Ai, S. A. Jones, M. M. Villiers and Y. M. Lvov, *J. Controlled Release*, 2003, **86**, 59.

2 R. V. Parthasarathy and C. R. Maetin, *Nature*, 1994, **369**, 298; A. G. Skirtach, A. A. Antipov, D. G. Shchukin and G. B. Sukhorukov, *Langmuir*, 2004, **20**, 6988; M. T. Morgan, M. A. Carnahan, C. E. Immoos, A. A. Ribeiro, S. Finkelstein, S. J. Lee and M. W. Grinstaff, *J. Am. Chem. Soc.*, 2003, **125**, 15485.

3 J. J. L. M. Cornelissen, E. F. Connor, H. C. Kim, V. Y. Lee, T. M.agibitang, P. M. Rice, W. Volksen, L. K. Sundberg and R. D. Miller, *Chem. Commun.*, 2003, 8, 1010; T. Coradin, E. Mercey, L. Lisnard and J. Livage, *Chem. Commun.*, 2001, 23, 2496; A. Dong, Y. Wang, Yi Tang, Nan Ren, Y. Zhang and Z. Gao, *Chem. Mater.*, 2002, **14**, 3217; C. E. Fowler, D. Khushalani and S. Mann, *Chem. Commun.*, 2001, 19, 2028; C. I. Zoldesi and A. Imhof, *Adv. Mater.*, 2005, **17**, 924; M. S. Wong, J. N. Cha, K. S. Choi, T. J. Deming and D. Stucky Galen, *Nano Lett.*, 2002, **2**, 583; H. J. Hah, J. I. Um, S. H. Han and S. M. Koo, *Chem. Commun.*, 2004, 8, 1012; Y. Wang and F. Caruso, *Chem. Commun.*, 2004, 13, 1528; Q. Sun, P. J. Kooyman, J. Grossmann, P. H. H. Bomans, P. M. Frederik, P. C. M. M. Magusin, T. P. M. Beelen, R. A. van Santen and N. A. J. M. Sommerdijk, *Adv. Mater.*, 2003, **15**, 1097; Q. Sun, P. C. M. M. Magusin, B. M. Mezari, P. Panine, R. A. van Santen and N. A. J. M. Sommerdijk, *J. Mater. Chem.*, 2005, **15**, 256.

4 R. S. Underhill, A. V. Jovanovic, S. R. Carino, M. Varshney, D. O. Shah, D. M. Dennis, T. E. Morey and R. S. Duran, *Chem. Mater.*, 2002, **14**, 4919; A. V. Jovanovic, R. S. Underhill, T. L. Bucholz and R. S. Duran, *Chem. Mater.*, 2005, **17**, 3375.

5 The encapsulation yield was determined by UV-VIS spectroscopic measurement (Simadzu, UV-2401-PC). The samples were prepared by eluting 1 g of microcapsules with 20 ml of absolute ethyl alcohol for 1 h at 60 °C.

6 The pore characteristics of the microcapsules were measured by the BET system (ASAP 2010, Micromeritics) after removing the lipophilic functional compounds completely by eluting them with ethyl alcohol.

7 Some criterion was needed to determine the solidification rate of the liquid phase oil emulsions in aqueous solutions. We used the solidification time at the point that the pre-solidified emulsions sustain their spherical shapes without deformation after drying.

