Hollow hybrid spheres with silica inner shell for non-deformable, core exchangeable properties†

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Core exchangeable polymer–silica hybrid capsules with solvent-selective permeability were fabricated, in which the internal silica layer, formed from pre-included precursors, has the role of a framework to prevent irreversible deformation of the hollow capsules.

Fabrication of polymer hollow spheres and core–shell capsules has been considered as an important research field due to their potential uses in a wide range of applications. These spheres have been developed to have various shapes and properties to allow them to function as nano/micro-containers for controlled release, transportation, storage, and reactions of substances.[1] To obtain functional hollow polymer spheres, various methods have been reported, which are categorized as self-assembled formation,[2] template approaches,[3] and complex approaches, such as emulsion polymerization,[4] where use of a soft template coexists with self-assembled layer formation. Based on these synthetic approaches, hybrid types of capsules have also been extensively developed.[5] The major routes for fabrication are inorganic layer formation on hard and soft templates or starting with an inorganic particle template on which to form the organic layer.

Through layer-by-layer (LbL) adsorption of polyelectrolytes and inorganic particles onto colloidal templates, followed by core dissolution, desirable functionalities for nano/micro-containers have been obtained. These allow control of permeability and refillability of substances, including organic compounds and inorganic nanoparticles.[6] Although excellent control of shape and functionality is now available, for practical usage as micro-containers and reactors, there is still a need for more control of structural stability and tolerance for various circumstances and processes (such as drying, isolation, and medium changing). On the other hand, stable core–shell spheres have been produced by interfacial polycondensation to give oil encapsulated polymers and inorganic shells by relatively simple steps of emulsion polymerization, and a variety of these fabrication methods have been developed.[7] However, for tailoring properties for specific applications, methods to afford functionality control, such as control of incoming and outgoing core substances, or to make modifications to the shell interior, still need to be developed, which do not limit the core substances and compositions to those fixed at the moment of capsule formation.

Here, a simple preparation method for polymer–silica double layered capsules is described (Fig. 1). These are fabricated through interfacial polymerization and successive formation of an internal silica layer from pre-included precursors. This silica inner shell performs the role of an internal framework to provide stability to the flexible polymer capsules, which are deformable in polymer-swellable solutions. Therefore, core material exchange and complete removal of core substances, free from irreversible shape deformation, can be achieved. The hollow capsules with a polymer–silica double shell, which have selective permeability depending on the swelling tendency in solution, are stable towards various manipulations: drying, isolation, core substance exchange, dispersion in various solvents and reactions inside capsules, to provide important characteristics for practical applications.

Melamine–formaldehyde (MF) microcapsules which were formed from condensation at an octadecane droplet–water interface, according to general procedures,[8,9] were investigated for the permeability of the shell and for core substance release. Under the conditions where MF capsules were dispersed in various solvents, it was found that the spherical shape of the MF capsule was deformed to a hemispherical shape, along with release of octadecane, when MF capsules were dispersed in swellable organic solvents such as chloroform and toluene. There was no deformation and no core release upon dispersion in aliphatic alcohols, hexane or water. Deformation of the MF capsule was not reversible, so hemispherical particles could not be returned to a spherical structure once the octadecane was dissolved out and the capsule structure had collapsed to a hemisphere. The size of the capsule did not affect the degree of

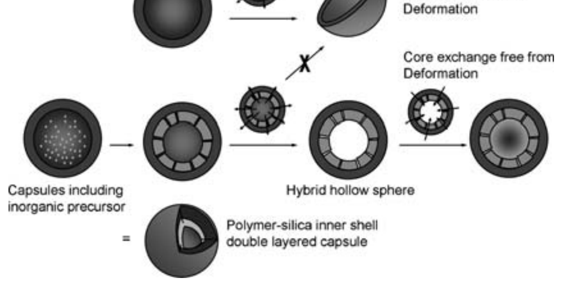

Fig. 1 Schematic illustration of the formation of a hollow sphere with a silica inner shell and core substance exchange.

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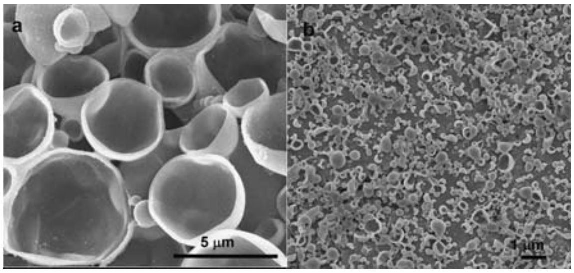

Fig. 2 SEM images of hemispherical shape of MF capsules: (a) deformed shell of MF capsules with octadecane core; (b) deformed shell of MF capsules with TEOS and octadecane core.

deformation, as shown in Fig. 2a. All MF capsules with diameters ranging from 5 μm to 300 nm with 40–60 nm wall thickness were deformed to hemispheres.

To obtain capsules with properties that would allow core removal and exchange, while avoiding deformation of the structure, a silica inner layer was introduced as a framework against deformation of the outer polymer shell. An interfacial polycondensation method enabled the inorganic precursor, which was dissolved in the organic phase, to be included in the core of the capsules. In this work, tetraethyl orthosilicate (TEOS) was successfully included in MF capsules as a core substance, as a mixture with octadecane. The average capsule diameter, as measured by dynamic light scattering, was 360 nm and was distributed across a range of sizes from 100 to 500 nm. These capsules, obtained from polycondensation of melaminetrimethylol on droplets of a TEOS–octadecane mixture (1 : 4 weight ratio), showed a decreased size compared with that of capsules containing only an octadecane core, whose size was 4.3 μm average diameter and mainly ranged from 3 to 6 μm. This decrease in capsule size was supposedly caused by the changed stability of oil droplets resulting from adding TEOS in octadecane core under the same emulsification conditions.

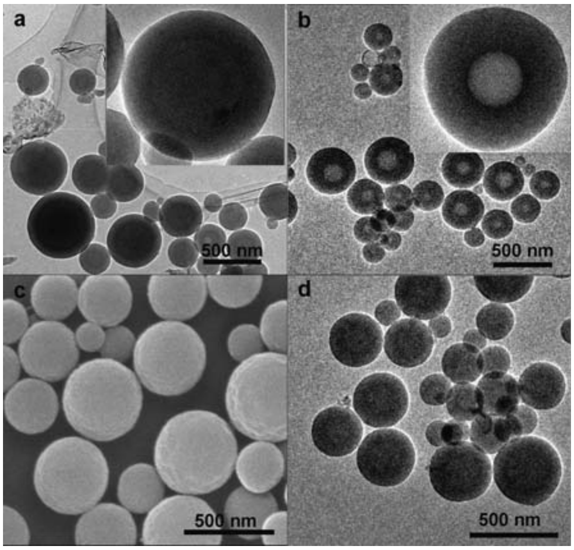

Fig. 3 TEM and SEM images of hybrid capsules with silica inner shells: (a) hybrid capsules with an initial octadecane core; (b), (c) hollow hybrid capsules after dissolution of the octadecane core; (d) hybrid capsules with a polystyrene core.

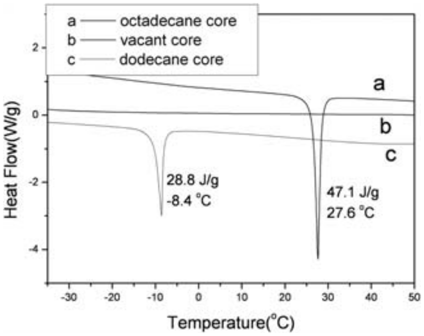

Fig. 4 DSC thermograms of microcapsules with various core substances: octadecane, vacant core and dodecane.

The MF capsules containing TEOS were still unstable to deformation before aging to form the silica inner layer: dispersion in chloroform as a core substance extraction condition transformed MF capsules to the hemispherical shape (Fig. 2b). The dispersion of capsules with TEOS–octadecane cores in diluted aq. NH_3 solution turned TEOS into a silica layer, which was located at the inner surface of the polymer outer shell. TEM images of MF capsules with silica inner shells showed a newly formed layer, which was observed as a darkened layer. This inner shell was clearly observed in hollow capsules, where the octadecane core was eliminated, emptying the core (Fig. 3b). There was also no deformation of these hybrid capsules in various organic solvents, such as chloroform, toluene and tetrahydrofuran, which had caused shape deformation of the MF capsules. The octadecane core material was still able to be dissolved out during dispersion in chloroform, to afford hollow capsules without any structural change from a spherical shape, as seen in Fig. 3c. In the TEM images, a relatively bright core as an empty space was observed in capsules compared to the core in octadecane filled capsules (Fig. 3b). The content of octadecane in the hybrid spheres was measured by differential scanning calorimetry (DSC; Fig. 4), which clearly showed heat flow from endothermic melting of the core substances. Thus, 19 wt% of octadecane content was calculated from the measured ΔH_m, 47.1 J g^{-1} (ΔH^0_m of pure octadecane is 243 J g^{-1}). After dispersion in chloroform, the content of octadecane decreased, disappearing within 60 min, and the thermogram showed no further heat flow at the melting temperature range. The silica layer was estimated as 22–25 wt% content through elemental and thermogravimetric analyses. Based on the properties of the hybrid capsules with vacant inner spaces, which have structural stability and permeability in the selected solvent, testing of core substance exchange was conducted through injection of dodecane as a new core substance. To inject dodecane into the capsule core, the melamine–formaldehyde shell needed to be re-swelled to have permeability, so chloroform as the swellable solvent was mixed with dodecane and the hollow capsules were dispersed in the chloroform–dodecane mixture. During dispersion of vacant capsules in the chloroform–dodecane solution, dodecane would pass through the swelled polymer/silica inner shell, along with chloroform. The DSC thermogram showed only dodecane remaining and chloroform was not detected, which should have been evaporated during vacuum drying. In this manner, the core

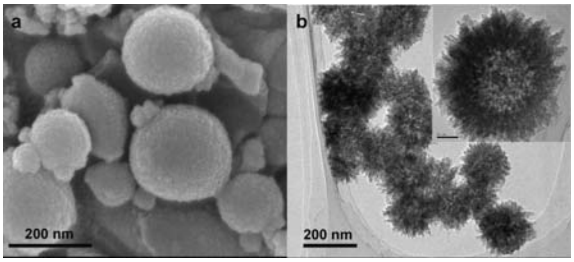

Fig. 5 (a) SEM and (b) TEM images of silica inner shells after peeling off the MF layer.

was filled with dodecane to 13 wt%, which was calculated from the measured endothermic heat flow, 28.8 J g^{-1} (ΔH^0_m of pure dodecane is 216 J g^{-1}.). The solvent-selective swelling effect of the MF layer is also important in the case of injection of chemicals into the core. The dispersion of hybrid hollow spheres in water mixed with butanol showed no injection of butanol into the core. When the core filling experiment was carried out in dodecane without mixing with chloroform, there was no injection of dodecane into the core. These results indicate that the MF shell only becomes permeable upon dispersion in a swellable solvent such as chloroform. As observed in MF spheres without an internal silica layer, chloroform makes the MF layer swell and deformable to a hemispherical shape, which occurs not in the drying process but in solution where the core is still filled with solution. Based on these results, the permeability of the MF layer in chloroform is caused by loosened chain packing and enlarged pores in the MF layer resulting in its flexibility, but the spherical shape is maintained in the case of hybrid spheres due to the internal silica framework.

In a similar manner as seen for core substance exchange, styrene as a chemically reactive molecule was also injected into hybrid hollow capsules. In this study, styrene carried out the dual roles of wall swelling solvent and the incoming core substance. The hybrid hollow capsules were dispersed in styrene containing azobisisobutyronitrile (AIBN). After filling the cores with styrene, capsules were dispersed in water and heated to promote polymerization. The TEM image of capsules with darkened core areas, compared to those with empty cores, clearly indicates filling with polystyrene (Fig. 3d). DSC analysis for the capsules with polystyrene cores showed a T_g of polystyrene of 96 °C, the usual polystyrene T_g.

For the direct observation of the silica inner shell, elimination of the outer melamine–formaldehyde shell was performed by exposure to UV-ozone and successive dispersion in 3 M aq. HCl. The resulting bare inner shells observed by SEM had rough surface morphology that seemed to be an aggregated layer of silica particles (Fig. 5a and b). The bare inner shells with empty cores were fragile and easily shattered into 5–10 nm sized silica particles during ultrasonication in solution. This indicated that the silica inner shell was formed by loosely interconnected particles underneath the polymer layer. The magnified TEM image of the silica shell shows a shell structure composed of 5–10 nm sized aggregated particles. In the silica wall layer, the directions of interconnected particles stand toward the center and are vertical to the surface. This structure of the wall layer seems to possess cracks or channels between elongated agglomerates, which may afford the permeability seen in these capsules.

In summary, submicrometer sized polymer–silica hybrid capsules were fabricated, in which the internal silica layer was formed from pre-included precursors in the capsules. The silica inner shell has the role of a framework, preventing irreversible deformation of the hollow capsules. Based on structural stability and the solvent-selective permeability, the core can be removed and exchanged. Styrene monomer as an incoming substance was also successfully included and polymerized inside capsules, demonstrating functionality for applications as micro-/nano-containers and reactors.

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