Monodisperse Organosilica Microcapsules with Functional Groups by Self-catalysis

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On the basis of the self-catalytic sol–gel reaction of methyl trimethoxysilane (MTMS) and 3-aminopropyl trimethoxysilane (ATMS) at oil/water interface, monodisperse organosilica microcapsules with functional groups were prepared in one step at room temperature, without any surfactant or mediating reagent.

Silica-based microcapsules are gaining extensive attention because of their applications in wide areas, such as controlled storage and release, adsorption, and catalysis. To prepare silica-based microcapsules, several methods have been developed, e.g., surfactant-assisted supermolecular assembly,[1] emulsion templating,[2] reverse microemulsion,[3] water/oil/water interfacial reaction,[4] polymer aggregate templating,[5] hydrothermal synthesis,[6] and ultrasound-mediated morphosynthesis.[7] However, batch production of loaded microcapsules prefers a more facile one-step way. In situ encapsulation of oil droplet within silica, without any surfactant or mediating reagent, has not been reported. Here, we prepared organosilica microcapsules at room temperature, based on self-catalyzed sol–gel reaction at interface.

Chemically inert and volatile repellent *N*,*N*-diethyl-*m*-toluamide (DEET, Aldrich) was selected as a model oil to be encapsulated. A typical synthesis procedure is described as follows: a mixture of 1.0 mL of methyl trimethoxysilane (MTMS, Aldrich) and 1.0 mL of DEET was dropped into the mixture of 50 mL of de-ionized water and 0.5 mL of 3-aminopropyl trimethoxysilane (ATMS, Aldrich), and stirred for 6 h at room temperature, by a magnetic stirrer at 1000 r/min. A white dispersion was finally obtained. The as-prepared dispersion was cast onto silica wafer and copper grid, respectively, and observed by a field emission scanning electron microscope (FE-SEM, JEOL JSM-6335F) and a transmission electron microscope (TEM, Philips CM-20, 120 kV). The sediment after centrifugation was air-dried for 24 h and analyzed using an IR spectrometer (Perkin-Elmer System 2000, in KBr tablet) and a thermogravimetric (TG) analyzer (NETZSCH STA 449C, in air atmosphere and heating rate of 10 °C/min).

When MTMS or ATMS alone was added into water, there is not gelling even after 24 h stirring. When both of MTMS and ATMS existed, the gelling reaction quickly occurred and the solution changed into white dispersion. Similar catalytic effect was reported by Ottenbrite et al.[8] They analyzed the composition of the gelled solid spheres and confirmed that ATMS was involved in the solid gel spheres. Therefore, the sol–gel reaction between MTMS and ATMS was recognized as a self-catalytic procedure. In this study, a highly positive ζ-potential, +29 (±4) mV, was obtained for the synthesized capsules (Brookheaven Zeta Plus Analyzer), confirming the distribution of ATMS amine groups at the outer face. These amine groups effectively avoided the aggregation of capsules by charge repulsion and provided active sites for further functional decoration and chemical immobilization. This feature makes the capsules superior to those reported in the previous emulsion templeating method.[2]

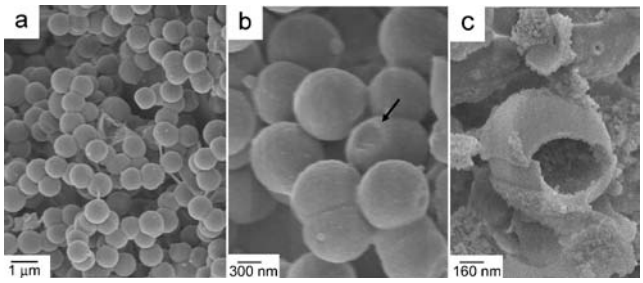

Figure 1. SEM images of monodisperse organosilica microcapsules (see text for the detail of a, b, and c).

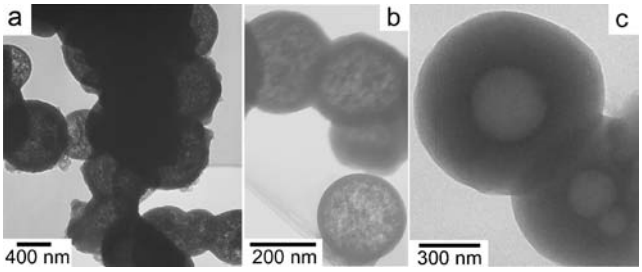

Figure 2. TEM images of organosilica microcapsules containing DEET (see text for the detail of a, b, and c).

Figure 1 shows the SEM images of obtained organosilica capsules. Monodisperse spheres are about 900 nm in diameter. In contrast to this result, polydisperse spheres were reported in the previous water/oil/water interfacial reaction method.[4] In a highly magnified image (Figure 1b), a broken capsule with hollow cavity was clearly seen, as pointed by an arrow. By careful observation, there were some granule heaves at the capsule surfaces. Figure 1c shows a crashed capsule, having a relatively smooth outer surface and an inner face with many granules. Nearby were some pieces from other crashed capsules, which also had granule surface morphology.

Figure 2 presents the TEM images of organosilica capsules. In Figure 2a, although the capsules were partly covered by some impurities, their dark shells and light cores were clearly observed. In average, the capsules were 900 nm in diameter and around 70 nm in shell thickness. Notably, many dark spots distributed over the light core area. This uneven transparency confirmed the heterostructure in capsule walls. This result was in accordance with the previous SEM results. Therefore, it was reasonable to propose that the shell was an assembly from individual granules at the interfaces. And possibly, there were micropores in the walls. The assembly procedure should be controlled

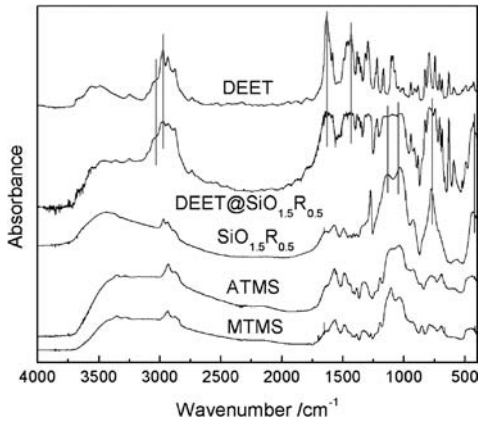

Figure 3. FTIR spectra of MTMS, ATMS, DEET, gel spheres from MTMS and ATMS ($SiO_{1.5}R_{0.5}$), and the synthesized capsules (DEET@$SiO_{1.5}R_{0.5}$).

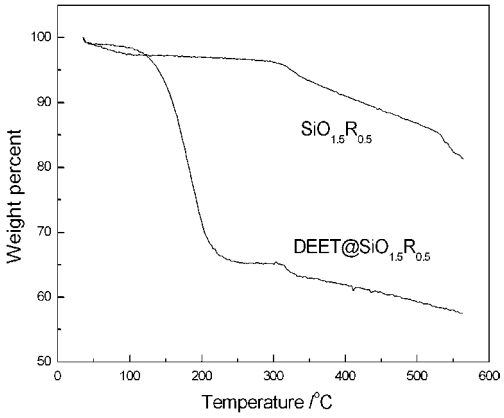

Figure 4. TG curves of organosilica solid spheres ($SiO_{1.5}R_{0.5}$) and corresponding microcapsules (DEET@$SiO_{1.5}R_{0.5}$).

by the MTMS diffusion from oil droplet to the interface, since the hydrolysis and gelling reactions between MTMS and ATMS were at a higher rate.[8] Further research will be done to reveal the reaction procedure in detail.

Notably, the capsule diameter and shell thickness can be conveniently tuned via adjusting the reagent ratios and concentrations, depending on what mechanical strength and load capacity are desired. Several images of capsules from different recipe were presented in Figure 2. Figure 2b shows the capsules about 300 nm diameter and 30 nm thickness. They were synthesized according to the following recipe: a mixture of 1.0 mL of MTMS and 1.0 mL of DEET was dropped into a mixture of 1.0 mL of ATMS and 200 mL of water. Figure 2c shows the capsules about 900 nm diameter and 260 nm thickness. Their recipe was following: a mixture of 1.0 mL of MTMS and 0.4 mL of DEET was dropped into a mixture of 0.5 mL of ATMS and 50 mL of water. The capsule in Figure 2c did not show the granule heterostructure, because of the large thickness.

IR spectra of original reagents and synthesized products are showed in Figure 3. Both MTMS and ATMS quickly hydrolyzed during IR measurement, and the produced –OH groups made the identification of $-NH_2$ groups very difficult. The spectra of MTMS and ATMS were almost the same, except for the range from 1000 to 1100 cm^{-1}. The peaks in this range were attributed to Si–O–C and Si–O–H bonds. After they gelled into solid spheres ($SiO_{1.5}R_{0.5}$, absence of DEET), the characteristic peaks of Si–O–Si bond appeared at 430 and 774 cm^{-1}. When DEET was introduced into the synthesis system, the obtained capsules (DEET@$SiO_{1.5}R_{0.5}$) gave diagnostic peaks of both DEET and gel from MTMS and ATMS. The 3030 and 2978 cm^{-1} peaks were assigned to aromatic and aliphatic C–H bonds; the 1631 and 1433 cm^{-1} peaks were assigned to DEET C=O and phenyl groups, respectively. These results confirmed the presence of DEET in the capsules.

Figure 4 presents the TG curves of pure organosilica spheres $SiO_{1.5}R_{0.5}$ and organosilica capsules DEET@$SiO_{1.5}R_{0.5}$ from the recipe described in the experimental part. The weight of solid spheres was kept constant between 100 and 250 °C; while the capsules lost 33 wt % in the same temperature range. This weight loss was attributed to the evaporation of DEET from the capsules. By assuming the organosilica density as 2.0 g/cm^3, this DEET content agreed well with the shell scale (about 1/6 of the capsule radius). The capsulate efficiency against the total DEET was calculated as 55% from the product weight and the DEET content in capsules. This low value may be due to the part solubility of DEET in water and the DEET loss during sample drying.

In summary, organosilica microcapsules with functional groups were prepared simply by an interfacial sol–gel reaction, without any surfactant or special mediating reagents. Self-catalytic reaction between MTMS and ATMS was employed, and monodisperse microcapsules were produced in high yield. The repellent DEET was encapsulated in an efficiency of 55%, and occupied 33% of the capsule weight. These capsules can also be used to encapsulate other kinds of oils: the convenient route of one step at room temperature. The capsulate oils may be released through the micropores in capsule walls or by mechanical crash of the walls.

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