Fabrication of Discrete Materials by Interface-Selective Sol-Gel Polymerization

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Self-hydrolyzing inorganic precursors underwent interface selective sol-gel polymerization at different interfaces between water and templates. This interface sol-gel polymerization was applied to fabricating discrete materials by encapsulating various materials with silica, titania, iron oxide and alumina.

Sol-gel reaction in aqueous solutions is one of the most useful methods to coat small complex templates with inorganic materials and has been applied to fabricating discrete inorganic and hybrid materials that were replica of the templates. Selective gel formation at the interface between templates and water is highly desired to obtain discrete materials and there have been two distinctive approaches to accomplish interface selective sol-gel reactions; confining inorganic precursors to interfaces[1,2] and guiding sol-gel reaction by attractive electrostatic interactions between templates and gel-forming species.[3–10] Confining silica precursors to interfaces was partially successful as only large spherical silica materials were obtained[1] or only monolithic silica materials were obtained.[2] Attractive interactions were introduced in fabricating discrete silica materials mainly by carrying out reactions at pH's higher than the isoelectric point (ISP) of silica using positively charged templates such as tobacco mosaic virus,[3] positively charged gel fibers,[4,5] vesicles of positively charged lipids,[6,7] polystyrene latex particles, filamentous crystals[9] and collagen fiber.[10] Monolithic materials were obtained when non-positively charged materials such as microemulsions,[11–13] non-positively charged gel fibers,[5,10] bacterial superstructures,[14] and arrays of living yeast cells[15] were used as templates. These previous works showed that only organic materials that meet certain requirements could be used as templates to fabricate discrete materials. We are describing results showing that restrictions on choosing templates could be largely relieved when amphiphilic self-hydrolyzing tetrakis[2-(2-methoxyethoxy)ethoxy]silane (TMEES) and tetrakis(2-methoxyethoxy)silane (TMES) were used as silica precursors. Also, other amphiphilic precursors of titania, alumina, and iron(III) oxide gave similar results. We are describing mainly about fabricating silica materials in this report.

^{29}Si NMR spectra of a 30 wt% TMEES solution in water taken at different times (Figure 1) showed that TMEES started to hydrolyze as soon as it was dissolved in water. Hydrolysis of TMEES completed in approximately 30 minutes and tetrahydroxysilane (THD) and hexahydroxydisiloxane (HHDS) were main components in the mixture at this time. Aqueous solution of TMEES and TMES in concentration up to 30 wt% did not gel within a few days. However, spherical toluene drops coated with silica were observed in shaking mixtures of toluene, water and TMEES (or TMES) within 30 minutes. Considering that THD and HHDS were main components in aqueous solutions of TMEES in 30 minutes, the formation of silica at water-toluene interface by polymerization of THD and HHDS was most likely.

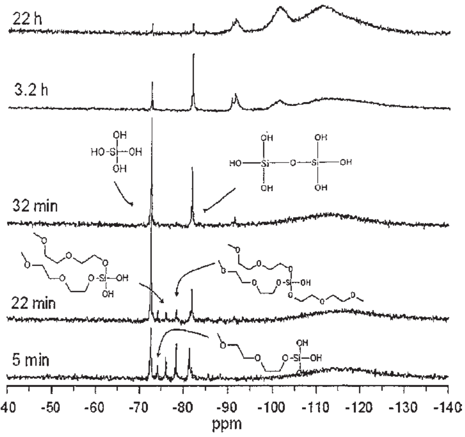

Figure 1. ^{29}Si NMR spectra of an aqueous solution of 30 wt% TMEES.

In similar experiments carried out mixing toluene with aqueous solutions of TMEES and TMES annealed at room temperature for 30 minutes and TEOS agitated with water for 6 hours instead of TMEES and TMES, silica formed immediately at toluene-water interface. All these pre hydrolyzed mixtures were expected to contain significant amounts of THD and HHDS. When aqueous mixtures of these precursors were left for longer than 18 h, interface-selective silica formation did not occur. The fact that none of commercially available silica sols (Ludox CL, Ludox TMA, and Ludox AM-3) induced interface selective silica formation under the same conditions also supported the above explanation. There was not noticeable difference when CTAB or TWEEN were used to prepare stabilized toluene drops dispersed in water and we are currently using CTAB or TWEEN to prepare smaller oil drops.

The fast gel formation in the presence of toluene might be ascribed to the high concentration of THD and HHDS at the interface caused by interface active nature of these molecules. That is, the original precursors (TMEES and TMES) were soluble in both water and toluene but the precursors became less soluble in toluene as they were hydrolyzed. Consequently, the hydrolyzed precursors took the nature of surfactants and concentrated at water-toluene interface to polymerize. This interface selective silica formation using TMEES took place in aqueous systems with pHs between 3 and 10 at room temperature. As interface selectivity was inherent nature of gel forming species in this study, non-positively charged materials were expected to be useful as templates in this method. This was proved by the fact that vesicles of zwitterionic DOPC, DOPE, negatively charged 1,2-dioleoyl-*sn*-glycero-3-[phospho-rac-(1-glycerol) sodium salt] (DOPG) and positively charged DOTAP were commonly coated with silica when they were exposed to TMEES in neutral aqueous system. Formation of silica on vesicles of DOPG suggested that other materials with phosphate ions such as nucleic acids might be useful as templates in this method. Figure 2 shows a giant DOPC vesicle coated with silica while it was held by a micropipette with a diameter of approximately 20 μm. The content of the vesicle could be sucked into the micropipette and the shrunken vesicle-silica hybrid sphere could be reblown. Vesicles without silica skin cannot be manipulated like shown in Figure 2. Figure 2 also shows that silica skin formed on the vesicle was flexible. Lipid tubules of zwitterionic 23 : 2 diyne PC were also coated with silica within 4 h by this method. The surface of silica tubules obtained after calcining silica coated tubules seemed to be smoother than those reported in a previous work.[16]

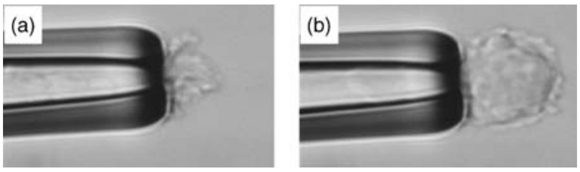

Figure 2. A vesicle of DOPC coated with silica held by a micropipette; (a) content was sucked into the pipette and (b) re-blown.

Oil drops coated with silica collapsed when they were exposed to air. Self-standing hollow spheres in the air were obtained when 5–10 wt% polystyrene (PS) solutions in toluene were used to prepare oil drops. Figure 3(a) shows a TEM image of a silica-PS hollow sphere that had a diameter of approximately 70 nm and a wall approximately 7 nm thick. The thickness of the wall was much higher than the maximum thickness calculated assuming that the total volume of wall was equal to the volume of polystyrene and TMEES. The thicker wall might have formed as the sphere shrank during the evaporation of toluene in the air. Figures 3(b) and 3(c) show SEM images of silica-PS hollow spheres and calcined silica spheres. Hollow silica-PS hybrid spheres with diameters smaller than 100 nm could be easily prepared in this method using microemulsions prepared using surfactants such as CTAB or TWEEN.

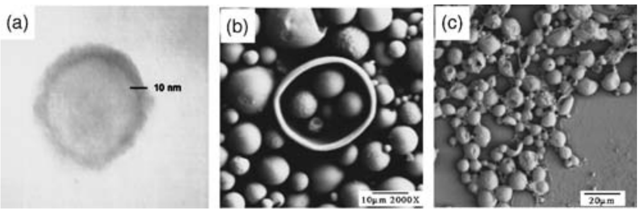

Figure 3. (a) A TEM image of a hollow PS-silica hybrid sphere (left), (b) an SEM image of hollow PS-silica hybrid spheres and (c) an SEM image of silica materials obtained by calcining hollow silica-PS hybrid spheres.

Assuming that small molecules from precursors of other metal oxides would react similarly, we examined aluminum (III) tris(2-(2-methoxethoxy)ethoxide) (TMEAL), titanium (IV) bis((ammonium lactato)-dihydroxide) (TBAL), and iron (III) acetylacetonate (IAA). Even though we do not have specific experimental data yet, adding these precursors to oil-water mixtures proved that all these precursors formed discrete materials (Figure 4) just like TMEES did. Therefore, we expect that small molecules (monomeric and dimeric) formed from different precursors are interface active and interface-selective polymerization can be accomplished if such small molecules can be provided in systems where interfaces are present.

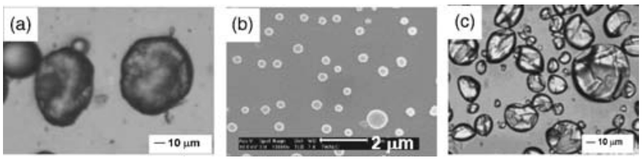

Figure 4. (a) Deformed iron(III) oxide spheres containing toluene, (b) hollow alumina spheres obtained by calcining PS-alumina hollow spheres, and (c) deformed titania spheres containing toluene. Deformation took place as toluene evaporated.

Reaction conditions for interface selective gel formation of TMES, TMEES, TMEAL, and TBAL included neutral pH at room temperature that was the mildest reaction conditions one could establish. Gram negative Escherichia coli and gram positive Bacillus therungenies were coated alive with these metal oxides by simply adding appropriate precursors to these microorganisms dispersed in distilled water. Cell counting experiment showed that most of the cells survived the coating. Figure 5 shows alumina materials obtained by calcining E. coli that were treated with TMEAL for different period of times.

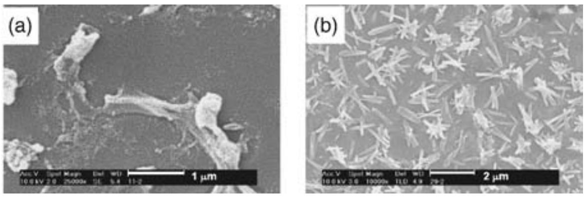

Figure 5. Alumina materials obtained by calcining E. coli coated with alumina by treating with TMEAL (a) for 5 minutes and (b) for 24 h (right).

The method described in this report might be very useful for encapsulating different materials that were not possible to be encapsulated that would be useful for different applications.

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