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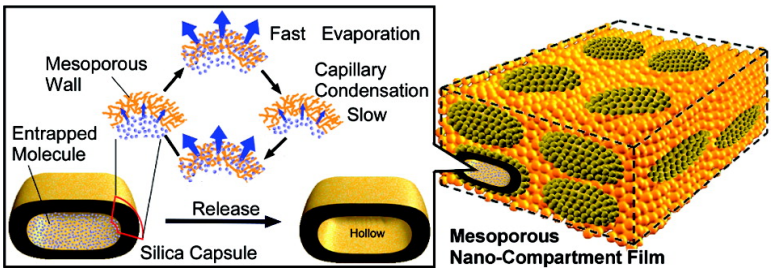

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Stimuli-Free Auto-Modulated Material Release from Mesoporous Nanocompartment Films

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Preparation of surface coatings or thin films from nanostructured materials with controlled release functions is of paramount importance for development of biomedical and cosmetic applications such as skin protection, transdermal therapy, and tissue regeneration.[1] The most desirable features of nanomaterials for these purposes include thin film morphologies containing robust microcontainers with well-defined channels or valves. These requirements have been investigated separately as seen in microcontainer fabrication,[2] controlled release through mesopores,[3] and thin film assembly of capsule structures,[4] but all the features have not been fully integrated. For the successful combination of the three aforementioned requirements, we here report layer-by-layer (LbL) assembly of robust mesoporous silica capsular containers (Figure 1). Surprisingly, the thus-formed "mesoporous nanocompartment film" exhibits auto-modulated release behavior of encapsulated materials such as water, fragrance, and UV-absorber. This new finding could be of great use for energy-less and clean *stimuli-free* controlled material release.

The silica capsules used in this work were synthesized from zeolite crystals according to our previous reports.[5] They have homogeneous dimensions (1000 × 700 × 300 nm^3) and are of hollow morphology with a nearly monodisperse pseudohexagonal prismatic shape. Capsule walls are mesoporous and 35 nm thick (Figure 2a) with a uniform pore size distribution centered at 2.2 nm diameter, a specific surface area of 726 $m^2\ g^{-1}$, and a specific pore volume of 0.83 $cm^3\ g^{-1}$. Preliminary experiments on direct LbL assembly between anionic silica capsules and cationic poly(diallyldimethylammonium chloride) (PDDA) resulted unfortunately in uneven film morphology (Figure 2b) probably because of aggregation of the silica capsules upon mixing with the counter polyelectrolyte. More detrimentally, these films were easily detached from the surface upon exposure to an aqueous phase during water washing and subsequent PDDA adsorption precluding their use in practical applications where contact with such an aqueous phase would be required. In order to overcome this difficulty, silica nanoparticles with average diameters of either 20 or 50 nm (silica-20 or silica-50) were added as coadsorbents at a weight ratio of 10:1 to the silica capsules in the LbL assembly. Increase of film mass upon LbL multilayer fabrication was confirmed by using quartz crystal microbalance (QCM) measurements (Figure S1).[6] Regular frequency shifts after complete drying, indicating constant film growth, were observed at each adsorption step of silica particle/capsule mixture and PDDA. As shown in scanning electron microscopic (SEM) images (Figure 2c), the silica capsule morphology was maintained with silica-50 particles coated on the surface. A cross-sectional view of the nanocompartment film further illustrates that the silica capsules (with silica-20 on the surface) are embedded within the smooth film (Figure 2d). Analysis of these images provides a coverage ratio of about 3:1 for the silica particle and the silica capsule in both cases (silica-20 and silica-50), corresponding to silica particle/capsule weight ratios of about 10:1 and 20:1 for silica-20/capsule and silica-50/capsule, respectively.

Subsequently, mesoporous nanocompartment films prepared by using 10 LbL cycles were subjected to water entrapment and evaporation experiments through immersion of the films in water for 3 h followed by QCM frequency monitoring in air. Interestingly, a stepped mode of water release (frequency increase) was observed

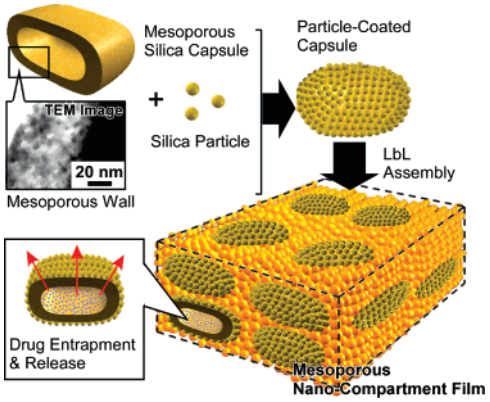

Figure 1. Schematic illustration of the formation of silica particle/capsule nanocompartment film.

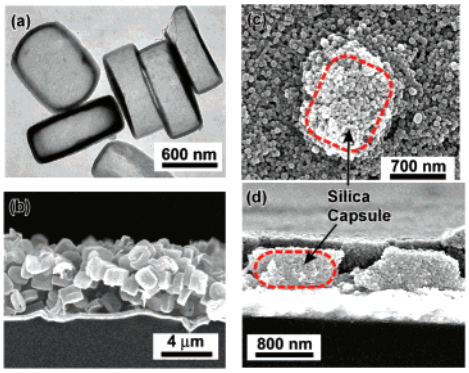

Figure 2. Images of different silica capsules and their films: (a) TEM images of the silica capsules; (b) SEM images of the film assembled by LbL method using silica capsule and PDDA; (c) top SEM view of silica-50/capsule nanocompartment film; (d) cross-sectional SEM view of silica-20/capsule nanocompartment film.

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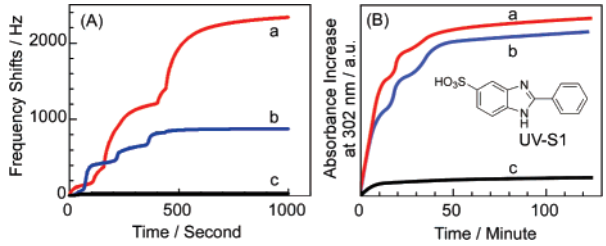

Figure 3. (A) QCM frequency shifts upon water release and (B) absorbance changes at 302 nm upon UV-S1 release: (a) the silica-20/capsule nanocompartment film; (b) the silica-50/capsule nanocompartment film; (c) the silica-20 film. These films were prepared using 10 LbL cycles.

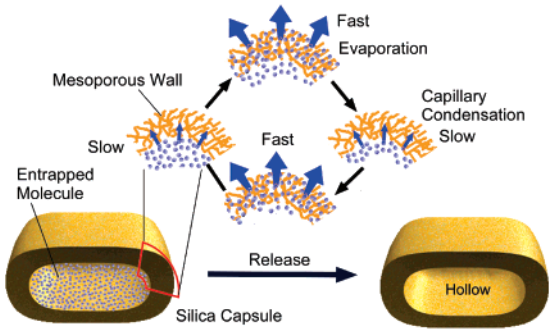

Figure 4. Proposed mechanism for the evaporation of water molecules from silica capsules. Interior encapsulated water molecules are evaporated into the mesoporous wall of the silica capsules and then are evaporated out to air phase.

for both the nanocompartment films ((a) and (b) in Figure 3A for silica-20/capsule and silica-50/capsule, respectively). In sharp contrast, films composed of silica-20 particles alone showed virtually no variation in the QCM frequency shift (Figure 3A(c)), indicating a lack of water trapping ability for the nanoparticles themselves. On the basis of the frequency shifts, the silica-20/capsule and silica-50/capsule nanocompartment films have an average encapsulated proportion of water of about 65 and 45%, corresponding to the hollow volume of the silica capsule (interior void and wall pores).

Over the course of our experiments, it was found that the initial amount of encapsulated water contained within the nanocompartment film strongly influences the stepping process of evaporation (Figure S2)[6] but does not depend on the thickness of films themselves (Figure S3).[6] A three-step shift in QCM frequency corresponds to an encapsulated water content of 50−75%, while there are only one or two steps for encapsulated proportions less than 50% (Table S1).[6] Since the silica capsule interior has a volume 4 times that of its mesoporous wall, the stepwise water release originates in the non-equilibrated rates between evaporation of water from the mesopore channels to the exterior and the capillary penetration of water from container interior to the mesopore channels (Figure 4). Therefore, the multiplicity of steps in the QCM frequency shift is essentially determined by the ratio between the quantity of entrapped material and the pore volume (see Table S1), and timing of the steps may be controlled by balancing capillary penetration and rate of evaporation. The stepwise material release was reproducible and could be observed even for repeated use of the nanocompartment film (Figure S4)[6] and was similarly observed for other substances such as fragrances (e.g., limonene) (Figure S5).[6] Recently, a similar three-stage infiltration of aqueous solution was reported in a nanoporous silica gel system containing multiple promoter molecules,[7] where the three-stage plateau infiltration was caused by pressure-induced encapsulation into different size pores.

This unusual mechanism for material evaporation from the nanocompartment films stimulated us to make application of the silica/capsule films for controlled release of the therapeutically important UV-absorber (UV-S1) in the aqueous phase (Figure 3B). As suggested by absorbance changes in both of the mesoporous nanocompartment films, step-like auto-modulated release of UV-S1 was again confirmed ((a) and (b)), while films containing silica-20 alone encapsulated a much smaller quantity of UV-S1 and lacked sustained release capability (c).

In conclusion, we have prepared mesoporous nanocompartment films composed of silica particles and hollow silica capsules using a simple LbL technique. In contrast to previous examples, the nanocompartment films exhibit *stimuli-free* auto-modulated material release, due to the special morphology of silica capsules. These films are also promising materials for drug delivery and could well lead to improvements in therapeutic efficacy.

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Supporting Information Available: Experimental details and QCM data on LbL assembly. This material is available free of charge via the Internet at http://pubs.acs.org.

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