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A Self-Templated Approach to TiO_2 Microcapsules

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ABSTRACT

A self-templated approach has been developed for the synthesis of TiO_2 microcapsules with tunable size and wall thickness by heating sol–gel derived TiO_2 microspheres with poly(acrylic acid) (PAA) in a diethylene glycol (DEG) solution. PAA plays a crucial role in the formation of microcapsules by crosslinking the surface TiO_2 nanoparticles and preventing them from dissolution by DEG. Hollow microcapsules form when DEG molecules penetrate the outer layer and remove the core materials by forming soluble titanium glycolate.

Interest in colloidal microcapsules has been mainly stimulated by their use in important applications, for example, as drug carriers, coating materials, photonic devices, and nanoscale reaction vessels.[1−5] While polymeric capsules can be prepared directly by emulsion polymerization,[6] ceramic microcapsules are conventionally produced through templating processes[7−10] except recently demonstrated surfactant/emulsion based routes or processes involving sonochemical or solvothermal reactions.[11−17] Colloidal microspheres of silica or polystyrene are commonly used as sacrificial templates, which are selectively removed after shell formation, leaving behind hollow capsules of the coating material.[18] One research challenge in fabrication of ceramic microcapsules therefore has been the development of generalizable approaches for coating various materials on the templates, for example, through the well-known sol−gel process. A notable method was recently developed by Caruso and Möhwald et al. using a layer-by-layer self-assembly technique to coat the templates with alternating layers of oppositely charged polyelectrolytes.[1,19−21] One advantage of this approach is that a great number of inorganic materials, in the form of nanoparticles, can be incorporated into the coating to form organic−inorganic composite microcapsules.

Although templating methods have proved to be very useful for preparing microcapsules, direct synthesis approaches are still preferred in practical applications due to significantly reduced production cost and the ease of scaling up. To this end, we report here a self-templated process for direct preparation of hollow TiO_2 microcapsules from their solid counterparts without the involvement of additional sacrificial templates. TiO_2 colloidal microspheres are first prepared using well-developed sol−gel methods, more specifically, by hydrolyzing titanium precursors such as titanium(IV) isopropoxide or titanium(IV) ethoxide with water in an alcohol solution.[22−24] Such microspheres are formed through the coagulation of amorphous TiO_2 nanoparticles.[25] After separation from the original solution, the microspheres are transferred into a diethylene glycol (DEG) solution containing a small amount of surfactant−poly(acrylic acid) (PAA). Keeping the system at a temperature of ~200 °C for an appropriate time finally leads to the formation of TiO_2 microcapsules.[26] We found that use of other polyols such as ethylene glycol (EG) instead of DEG also produces similar results. The microcapsules can be conveniently separated from the reaction solution by centrifugation and subsequently cleaned with anhydrous ethanol and finally dispersed in polar solvent such as water and alcohols.

The hollowing process involves the initial crosslinking of surface TiO_2 nanoparticles by PAA and the subsequent dissolution of core TiO_2 in DEG. It has been previously reported that ethylene glycol dissolves TiO_2 powders at high temperatures with bases such as triethylenetetramine or alkali metal hydroxide acting as catalysts.[27−29] We noticed that TiO_2 microspheres freshly synthesized using the sol−gel process can be dissolved in pure DEG or EG by heating them at elevated temperature without the addition of any catalyst. In the absence of PAA, however, the microspheres simply shrink and finally dissolve into the molecular glycolate which is soluble in the glycol solution. The formation of glycolate upon heating can be simply verified by adding water to the supernatant of the reaction solution; a white precipitate forms instantly as the result of hydrolysis of the titanium glycolate.

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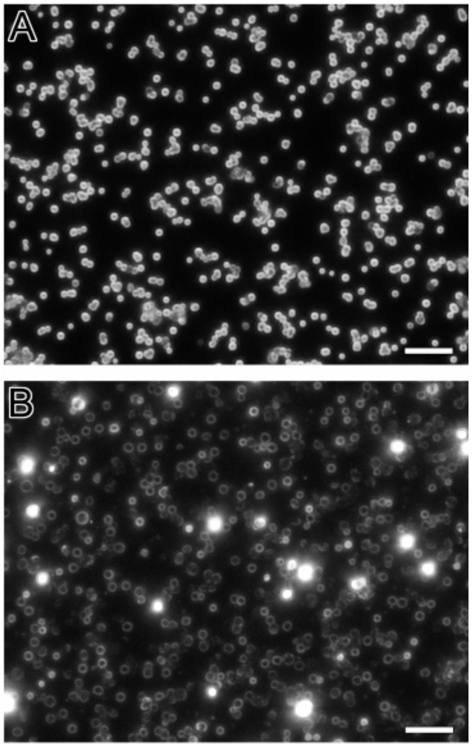

Figure 1. Dark-field optical microscopy images of (A) the primary TiO_2 microspheres and (B) the corresponding microcapsules. The particles were dispersed in DEG and then deposited as a thin liquid film on a silicon substrate to reduce their movement during imaging. All scale bars are 10 μm.

Interestingly, heating TiO_2 microspheres in the presence of PAA slows the dissolution and produces microcapsules during the process. As will be discussed in detail later, the function of PAA is believed to consist of binding to the surface TiO_2 nanoparticles during the initial stage of heating, crosslinking them into a stable shell and slowing their dissolution in DEG. The core material of the TiO_2 microspheres, however, can be dissolved at high temperatures because, unlike PAA chains, DEG molecules can penetrate the porous surface layer of TiO_2 microspheres. The combined effect of the surface crosslinking and protection by PAA and core dissolution by DEG results in the formation of TiO_2 microcapsules with controllable wall thickness.

The hollowing process was supported by experimental observations and microscopic measurements. The optical density of the solution gradually decreases during the heating process because titanium glycolate is soluble in the solvent, and it has no absorbance in the visible region. As a result, the originally white turbid solution becomes almost transparent at the later stage of heating as the solid microspheres transform into hollow capsules with thin walls, while the number density of particles were kept identical, as estimated through optical microscopy observations. Figure 1 shows dark-field optical images of the primary titania microspheres and the corresponding microcapsules redispersed in DEG after cleaning. Similar to the primary spheres, the microcapsules disperse well in polar solvents such as DEG and water and still maintain the spherical shape. The scattering power of the microcapsules as observed in the dark field, however, is much weaker than that of primary microspheres, which is consistent with the fact that the microcapsules contain much less materials than the solid particles. Comparison of the two optical images shows sharp contrast between the dark center and bright periphery of each microcapsule, but not for the parent solid particles, supporting a hollow morphology for the microcapsules.

We have systematically monitored the shape evolution of the TiO_2 colloidal particles from solid spheres to microcapsules during heating in the mixture of DEG and PAA. The results are shown in the scanning electron microscopy (SEM) images of Figure 2. After heating for ~30 min, some of the particles become slightly deflated, as shown in Figure 2B, although most of them retain the original spherical shape. Further heating of the system allows the formation of hollow capsules with much thinner walls so that every particle deflates and collapses onto the substrate upon drying, as can be observed in Figure 2C. A few isolated microcapsules are highlighted in the insets of Figure 2C, from which one can notice that their walls are quite soft so that they collapse upon drying. Also, it is commonly observed that TiO_2 colloids may aggregate into merged dimers or trimers during the sol−gel preparation. Their corresponding microcapsules still maintain the original shape, as depicted in the example of a trimer shown at the bottom right corner of Figure 2C. Continuous heating leads to microcapsules with thinner walls, as can be seen by comparing the images in Figure 2B−D. An extremely thin wall of a few nanometers forms before the microcapsules are completely dissolved. It is worth noting that the microcapsules are in the collapsed form only when they are dried on the solid substrates. We observed that they maintain spherical form in solvents such as water, alcohol, or DEG, as demonstrated by optical microscopy in Figure 1.

The composition and structure of the microcapsules were characterized using the thermogravimetric analysis (TGA) and X-ray diffraction (XRD). Figure 3A shows the TGA curve recorded by heating the dry powder of the microcapsules in a nitrogen flow. The initial mass loss of ~3.4% at low temperatures corresponds to desorption of physically adsorbed water molecules. The major weight loss of ~27.8% spans from ~200 to 450 °C and involves the removal of chemically bonded glycol and PAA molecules on the particle surfaces and the subsequent decomposition of all organic species.[30] Careful examination of the TGA curve within this range indicates that there might be two separated processes. The first one occurs between ~293 and 338 °C, corresponding to the decomposition transition of the surface-bonded glycol ligand. It has been reported that pure titanium ethylene glycolate has a sharp transition at a temperature around ~340 °C.[28,31,32] The lower decomposition temperature and the gradual transition profile in the present work might indicate that these ligands are surface bounded. The second transition from ~338 to 430 °C is believed to be associated with the decomposition of PAA molecules that link the surface TiO_2 nanoparticles together.[30] The overall weight loss after heating to 600 °C is significantly lower than the value for pure titanium glycolate, suggesting that the majority of the

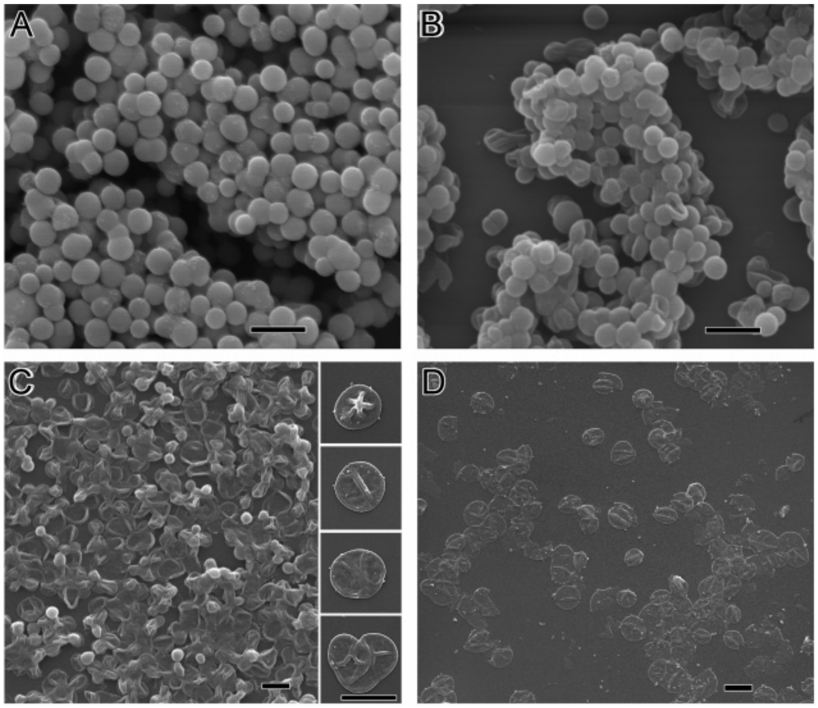

Figure 2. SEM images showing the shape evolution of TiO_2 colloids from solid microspheres to microcapsules after heating with PAA at 200 °C in DEG for (A) 0 min, (B) 30 min, (C) 40 min, and (D) 45 min. All scale bars are 2 μm.

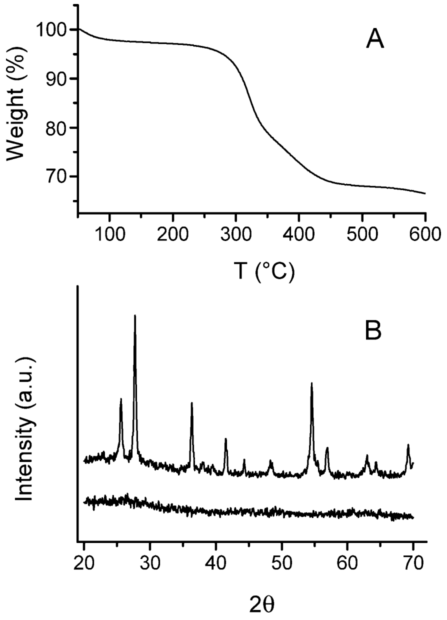

Figure 3. (A) TGA curve of TiO_2 microcapsules recorded in N_2 atmosphere; (B) XRD patterns of as-synthesized TiO_2 microcapsules (bottom) and TiO_2 microcapsules annealed at 500 °C in N_2 atmosphere for 2 h (top).

titanium in the microcapsules is still in the dioxide form. Figure 3B shows the XRD patterns taken from a sample of microcapsules before and after annealing at 500 °C for 2 h in an inert atmosphere of N_2. Similar to primary TiO_2 microspheres, the microcapsules show no distinguishable diffraction peaks, suggesting an amorphous structure. After annealing at 500 °C, the sample was converted to the crystalline form of TiO_2−anatase. Further heating of the sample above 600 °C induces a phase transition from the anatase to the rutile structure, and the corresponding XRD pattern indicates the presence of both phases.

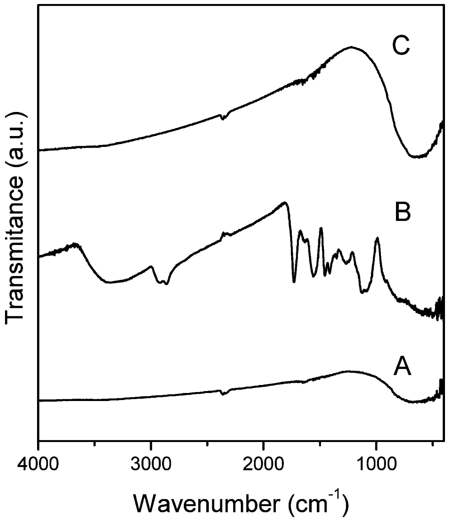

Figure 4. FT-IR spectra of (A) primary colloidal TiO_2 microspheres; (B) as-synthesized TiO_2 microcapsules (C) annealed TiO_2 microcapsules.

Fourier transform infrared spectroscopy (FTIR) was performed to further characterize the composition and structure of the microcapsules. Figure 4 shows the spectra taken from dry powders of primary TiO_2 microspheres, microcapsules, and microcapsules that have been annealed at 500 °C. All of the samples show a relatively intense broad band in the vicinity of 400−800 cm^{-1} due to the Ti−O vibration.[30] The microcapsules exhibit more complex absorption features than both the primary microspheres and the annealed samples. The broad band centered at ~3400 cm^{-1} can be attributed to stretching vibration of hydroxyl groups.

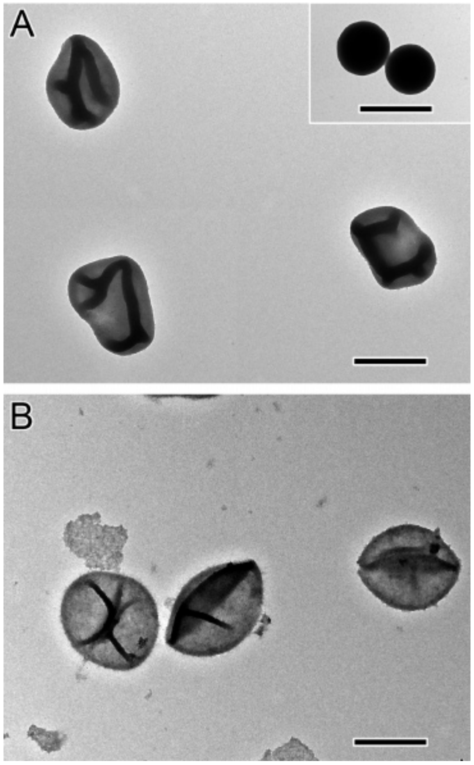

Figure 5. TEM images of TiO_2 microcapsules heated at 200 °C for (A) 40 min, (B) 45 min. The inset in (A) shows the primary TiO_2 microspheres. All scale bars are 1 μm.

Some characteristic bands such as the C−H stretching vibrations at 2921 and 2863 cm^{-1} and the C−C−O stretching vibrations at 1086 and 1042 cm^{-1} indicate the existence of glycol molecules.[31] The multiple bands between 1200 and 1600 cm^{-1} can be assigned to various vibrational modes of PAA, and the intense band at 1730 cm^{-1} is attributable to the carboxylic acid groups. The weak band at 1635 cm^{-1} indicates the presence of intramolecular hydrogen bonding between TiO_2 and PAA molecules.[33] The bands at lower wave number range are mostly related to titanium. The bands at 1127, 1053 cm^{-1} can be assigned to C−O−Ti, characteristic of diethylene glycol linked to titanium. The broad band below 800 cm^{-1} again confirms the presence of Ti−O−Ti bonds, which lead to the conclusion that the shells are composed of TiO_2.[30,34]

The changes in morphology, size, and wall thickness can be more clearly observed using transmission electron microscope (TEM). Parts A and B of Figure 5 show typical TEM images of microcapsules heated for ~40 and ~45 min, respectively. The primary TiO_2 microspheres are shown in the inset of Figure 5A for comparison. One can immediately notice that a dramatic size increase occurred during the transition from solid primary microspheres (~750 nm) to hollow microcapsules (~1.5 μm). The overall size of the microcapsules further increases and the wall thickness decreases upon additional reaction, as can be seen by comparing parts A and B of Figure 5. Careful inspection of the SEM images in Figure 2 also reveals the similar trend of size increase during the hollowing process, which cannot be simply attributed to the collapsed form of the microcapsules.

By combining the results of TGA, XRD, and FTIR and other experimental observations, we can conclude that the microcapsules are mainly composed of TiO_2 nanoparticles with PAA and glycol attached to the surfaces. We propose the following process for the formation of microcapsules: Sol−gel derived TiO_2 microspheres are composed of amorphous TiO_2 nanoparticles and they are porous in nature. Upon heating to high temperatures, the PAA molecules first bind to those TiO_2 nanoparticles located on the microspheres' surfaces. With its multiple carboxylate groups on a single polymer chain, PAA acts as a crosslinker to connect adjacent nanoparticles into a stable shell and protects them against rapid dissolution by DEG. With its bulky size, PAA only infiltrates a limited amount into the solid microsphere due to porosity near the surface of the sphere. Further dissolution of TiO_2 preferentially occurs inside the microspheres after DEG penetrates the outer layer and reacts with the core materials which have no protection from PAA. Thus, the removal of core materials by forming soluble titanium glycolate leaves hollow microcapsules behind. The shell of the microcapsules becomes thinner upon continuous heating at high temperatures and eventually disappears as all the TiO_2 transforms into glycolate. Because the polymer chains are stretchable, the separation between adjacent surface nanoparticles may increase after the removal of cores. This explains why the size of microcapsules becomes significantly larger in comparison to the primary microspheres. Also, because the linking PAA chains are flexible, the microcapsules are not able to support themselves when they are dried on a solid substrate.

In summary, we have developed a self-templated approach for the synthesis of TiO_2 microcapsules with tunable size and wall thickness. This process produces microcapsules directly from the sol−gel derived TiO_2 microspheres, eliminating the need for costly sacrificial templates and time-consuming shell-coating/core-removing steps associated with conventional procedures. PAA is believed to play a crucial role in the formation of microcapsules by crosslinking the surface nanoparticles together, while DEG simply dissolves the titania core. The well-developed sol−gel process allows the convenient tuning of the size of the primary TiO_2 microspheres from ~300 nm to above 1 μm by controlling the reaction conditions of hydrolysis, for example, by changing the ionic strength of the solution or by adding surfactants such as hydroxypropyl cellulose (HPC).[22−24,35] Hollow microcapsules with various sizes can thus be produced from these TiO_2 microspheres. We believe the current procedure might be extended to produce microcapsules from other materials because a number of oxides such as silica, ceria, zirconia, and barium titanate have been found to be dissolvable in hot glycol solution in a mechanism similar to that of titania.[36−38] Also, it is expected that the size of the capsules can be reduced to tens of nanometers by starting with nanometer-scale primary TiO_2 particles, thus opening the door to various applications such as nanoscale reactors in catalysis.[39]

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