Tunable Cavity of Titania Spheres

Templated Synthesis of Inorganic Hollow Spheres with a Tunable Cavity Size onto Core–Shell Gel Particles**

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Inorganic coated polymer (core–shell) capsules and hollow spheres have increasingly attracted interest because of their potential applications in catalysis, controlled delivery, artificial cells, light fillers, low dielectric constant materials, acoustic insulation, and photonic crystals.[1] These particles have been synthesized by using monodisperse particles and their arrays as templates. There are two main approaches: the first is to form capsules by the controlled reaction of inorganic materials with polymer particles;[2] the second is to coat nanoparticles onto polymer particles by deposition. This is usually combined with a layer-by-layer (LBL) technique to obtain multilayered capsules.[3] The multilayer can be composed of a variety of materials, such as polymers, and inorganic materials.[4] The layer thickness is controlled either through the concentration of the coating materials or through the LBL cycling time. However, obtaining the desired layer thickness by this process is time consuming.

Titania/polymer is one of the model systems for the study of encapsulation and hollow sphere preparation. Although coating onto polymer particles by a controlled sol–gel process is simple, the coated layer is heterogeneous with coagulation.[5] Hollow titania shells can be formed by spray drying the exfoliated titanate/nanosheet suspension followed by heating,[6] but the size distribution of the hollow spheres is broad. Furthermore, the titania shell is very thin, about 1–2 % of the hollow sphere diameter, thus resulting in fragile spheres. Alternatively, LBL adsorption of polyelectrolytes and nanoparticles around individual polymer particles has been developed in the preparation of monodisperse titania-coated-polymer capsules and hollow spheres. The shell thickness is controlled through the cycling time.[7] Xia and coworkers have reported a preferential particle surface coating by a sol–gel process of titania onto a polymer particles array confined between two substrates.[8] In this reaction, the experimental conditions must be strictly adhered to.

All previous experiments that relate to the synthesis of capsules have focused on two geometrical parameters: shell thickness; and cavity size, because these factors determine the mechanical and adsorption properties of the spheres. Hollow spheres with a tunable cavity size can be very useful, not only in practical application but also in the study of physical phenomena, such as optical resonance in a cavity. Until now, to our knowledge, all the methods used to produce hollow spheres have been based on the outward growth of inorganic materials from the surface of the sphere. Therefore, the core size and the cavity size of the hollow spheres were not tunable. It is difficult to create a smaller cavity for a given polymer particle template because these template particles are rigid and cannot be diffused inwardly by a precursor.

Herein, we describe a new approach to generate inorganic coated polymer capsules and hollow spheres with tunable interior-cavity sizes. The key is to use core–shell gel particles as templates that allow an inward diffusion and growth of the precursor inorganic materials inside the gel particle. The hollow spheres can have either a smooth or a porous surface, depending on whether an electric field is applied. The desired cavity size of the hollow spheres and the thickness of the inorganic shell are determined only by a one step sol–gel process.

The core–shell gel template particles were synthesized by an inward sulfonation of polystyrene particles with concentrated sulfuric acid. Sulfuric acid and sulfone groups were simultaneously derived in the gel shell, which was confirmed by differential scanning calorimetry (DSC) and FTIR.[9] The monodispersity of the core–shell gel particles was ensured by synchronous sulfonation. At maximum conversion, the polystyrene core disappeared. This method used for the preparation of core–shell gel particles is simple, and therefore advantageous over traditional emulsion polymerization methods.

It was reported that titania forms preferentially in sulfonated polystyrene-gel shells containing protons.[10] The titania–gel S2 capsules became larger (284 nm in diameter) than the polystyrene particle (275 nm in diameter). After the polystyrene cores were dissolved, the hollow spheres (Figure 1 a) were the same size as the capsules. The thickness of the gel–titania was uniform, about 45 nm, and the cavity diameter was 194 nm. After the capsules were calcined at 450 °C for 2 h, the diameter of the cavity was not affected. However, the shell thickness was reduced to about 18 nm (Figure 1 b and 1 c). The shell also became coarser as the anatase phase was formed during calcination of the amorphous titania, as verified by wide-angle X-ray diffraction (WAXD). The hollow spheres are fragile and easily fragmentized into bowllike pieces (Figure 1 c). When the sample S4 is used as a template, the inorganic shells of the hollow spheres are thicker and the cavities are smaller than those prepared by using the S2 gel as the template. These S4-prepared spheres are more mechanically stable than the corresponding S2-prepared spheres with a well-retained spherical shape (Figure 1 d). The titania–S6 composite particles have a larger diameter of about 424 nm (Figure 1 e). Solid titania spheres

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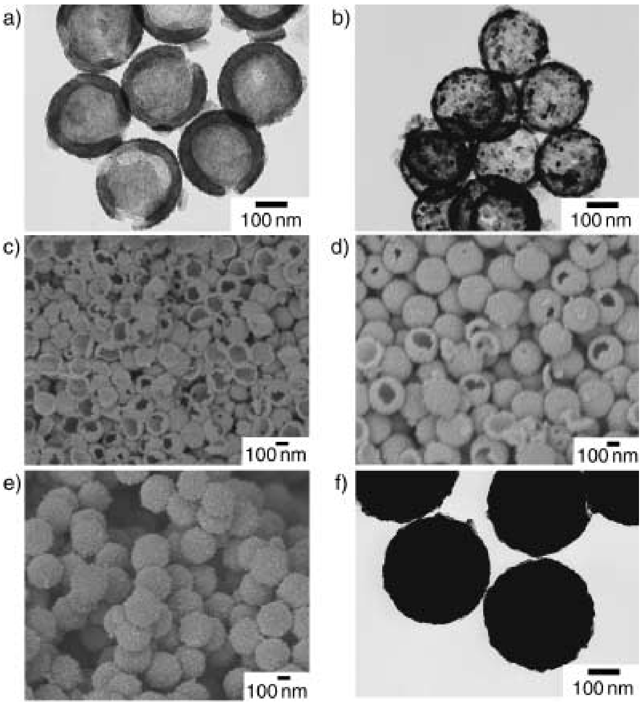

Figure 1. Morphologies of the representative titania coated polystyrene capsules and the structured titania spheres. a) Transmission electron microscopy (TEM) image of hollow titania spheres prepared after the dissolution of the polystyrene cores from the titania/S2 capsules. b) TEM image and c) Scanning electron microscopy (SEM) image of the hollow titania spheres after calcination of the polystyrene cores from titania/S4 capsules at 450 °C for 2 h. d) SEM image of the hollow titania spheres after the calcination of polystyrene cores from titania/S4 capsules at 450 °C for 2 h. e) SEM image and f) TEM image of the titania spheres prepared after the titania/S6 composite spheres were calcined at 450 °C for 2 h.

(i.e., without a cavity) were prepared after calcination (Figure 1 f). The thickness of the titania shell and the core (cavity) size of the capsules were controlled in the whole particle radius range, which is consistent with the TGA results that show an increase in the titania/polymer weight ratio. This series of experiments demonstrate that by varying the sulfonation time, we can obtain monodisperse core–shell gel particles with tunable gel thickness and controllable core size.

We now focus on the surface morphology of the hollow spheres. When the capsules were prepared by a sol–gel process in a direct electric field of 1×10^4 V m^{-1}, the capsules with pillared surfaces were obtained as shown in Figure 2 a. This porous surface morphology differs from the smooth surface prepared without an electric field as shown in Figure 1. After removing the polystyrene core by calcination at 450 °C for 2 h, the pillared surface was retained (Figure 2 b). The mesopores, with sizes ranging from 10 to 20 nm on the pillared surface of the capsules, appear interconnected before and after calcination (Figure 2 c and 2 d). The BET measurements show that the specific surface area of hollow spheres with pillared surfaces is about 101 m^{2}g^{-1}, which is larger than those of the non-pillared spheres formed without electric field (74 m^{2}g^{-1}). A combination of mesoporous surfaces with a tunable cavity makes the hollow spheres particularly suitable for applications in catalysis and adsorption.

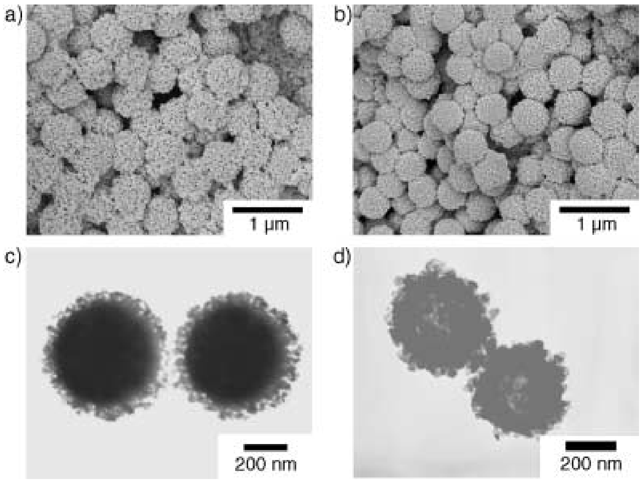

Figure 2. Morphologies of the surface pillared capsules and hollow titania spheres. a) SEM image and b) TEM image of the titania/S2 capsules. c) SEM image and d) TEM image of the hollow titania spheres after calcination.

The size of the titania pillars and their separations are tens of nanometers, which greatly differs from the reported micrometer pillars on common polymers.[11] This fact is related to the decrease of the initial growing wavelength of the pillars with interfacial tension.[11] The hollow titania spheres prepared by dissolution can be dispersed stably in both polar (e.g., water, ethanol, THF) and nonpolar (e.g., toluene) solvents. This suggests that the interior surface of the hollow sphere is amphiphilic, which may result from the polystyrene coils tethered to the sulfonated polystyrene–titania composite. This is reasonable assuming that the sulfonation frontier can traverse a polystyrene chain coil. Rutile was prepared after calcination of the titania spheres at 900 °C. At an intermediate temperature for example 600 °C, anatase and rutile coexist.

Ordered arrays were formed by drying the capsule dispersion in an ethanol/water mixture. The arrays became robust after aging owing to a further titania gelation. After the removal of the polystyrene cores, either by dissolution or by calcination, the ordered structure was retained.

In conclusion, we have demonstrated a new approach to create titania–polymer capsules and hollow titania spheres by using sulfonated polystyrene core–shell gel particles as templates. The thickness of the titania shell and the cavity size are controlled in the entire particle radius range. Applying an electric field can produce capsules and hollow spheres with pillared surfaces. After the removal of the cores by dissolution, the hollow titania particles are amphiphilic. This approach could be applied to the preparation of other capsules and hollow spheres of varied compositions, for example, silica and polyaniline.

Experimental Section

Sulfonated-polystyrene core–shell gel-template particles: Monodisperse polystyrene particles with a diameter ranging from 100–500 nm were prepared by seed-emulsion polymerization.[9] The freeze-dried polystyrene particles were immersed in large quantity of concentrated sulfuric acid and stirred at 40 °C and for the appropriate time, thereby controlling the thickness of the sulfonated-polystyrene-gel shell. After the product was separated by centrifugation ($4500\,\mathrm{r\,min^{-1}}$), then washed with ethanol, sulfonated-polystyrene core–shell gel particles were obtained. The template gel particles S1, S2, S3, S4, S5, S6 were prepared by a sulfonation of an example polystyrene particle of 275 nm in diameter for 1, 2, 4, 8, 12, 24 h.

Titania–gel capsules: The gel particles were immersed in a large amount of a tetrabutyl titanate (TBT)/alcohol (1:1 vol/vol) mixture for 8 h to allow a saturated adsorption of TBT on the shell. The TBT swollen gel particles were separated by centrifugation, and 0.1 g of this product were dispersed into ethanol/water (1:1 vol/vol; 10 mL) and stirred at ambient temperature for 2 h to allow the sol–gel process to occur.

Surface pillared capsules: Monodisperse polystyrene particles, about 400 nm in diameter, were sulfonated at 40 °C for 4 h, which yielded the core–shell gel particles, S0. These core–shell particles, were immersed in a TBT/alcohol (1:1 vol/vol) mixture for 8 h, and separated by centrifuge, and 0.1 g of the TBT swollen gel particles were dispersed into ethanol (5 mL). An electric field was applied to the particles for 15 min; the apparatus was composed of two vertical platinum plated electrodes approximately 4 cm apart. The electric field was maintained at about $10^4\,\mathrm{v\,m^{-1}}$, ethanol/water (1:1 vol/vol; 2 mL) was introduced into the system during the reaction time, and surface pillared capsules were obtained.

Hollow titania spheres: The polystyrene cores were removed from the capsules either by dissolution with *N,N*-dimethylfomamide or by calcination at 450 °C for 2 h.

Characterization: Very dilute suspensions of the samples in ethanol were dropped onto carbon-coated grids, and the solvent was rapidly evaporated; a JEOL 100CX transmission electron microscope was used to observe the particle morphology at an acceleration voltage 75 kV. The samples were coated with Pt (ca. 3 nm) by vacuum sputtering for SEM observation. A JEOL 6700F field emission scanning electron microscope was used at a voltage of 3 kV. Wide-angle X-ray powder scattering (Rigaku D/max-2500) was used to characterize the crystalline type of titania. Thermogravimetric analysis on a Perkin-Elmer TGA 7 was used to determine the inorganic content of the capsules. Nitrogen adsorption was performed on a Micromeritics OMNISORP 100CX porosimeter.

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