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Synthesis of Monodisperse Hollow Silver Spheres Using Phase-Transformable Emulsions as Templates

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The strategy to fabricate monodisperse hollow spheres in size and shape is of burgeoning interest because the resulting hollow nano- and microspheres are of great technological importance for their potential applications in catalysis, photonic crystal, chromatography, protection of biologically active agents, fillers (or pigments, coatings), waste removal, and large bimolecular-release systems.[1,2]

There are a variety of chemical and physicochemical methods, including heterophase polymerization/combined with a sol−gel process,[3] emulsion/interfacial polymerization strategies,[4] spray-drying method,[5] self-assembly techniques,[6] and surface living polymerization process,[7] employed to prepare hollow spheres comprising polymeric or ceramic materials. One of them is the templating method, which is particularly interesting and frequently used to fabricate hollow spheres with homogeneous, dense layers. The templates used in synthesis can be divided broadly into two classes.[8] The first class of these templates is called soft templates, which are normally organic (small molecules or oligomers)-based, such as natural organic compounds,[9] ionic liquids,[10] and monomers or solvents.[11] For example, Shelnutt and co-workers[11b] obtained dendritic Pt nanoshells using lipoporphyrin-stabilized nanodroplets of an organic solvent in water as templates. Bon and co-workers[11c] used TiO_2-stabilized monomer/solvent (including the initiator) emulsions as templates, which were then polymerized overnight at 51 °C to fabricate organic−inorganic hybrid hollow spheres. Generally, the soft-template method is relatively convenient to generate hollow spheres, but evident difficulties are also associated with this synthesis, such as susceptibility to reaction surroundings (e.g., stirring rate, ionic strength, pH, and solvent), polydisperse hollow particles in size and shape, especially for synthesis of metal hollow spheres.[11b,12] The second class is called hard templates (including Cu_2O,[13] SiO_2,[14] C,[15] and polymeric beads[16]). For example, Xia et al.[17] successfully synthesized hollow platinum spheres with spherical colloids of amorphous selenium as templates. However, although the hard-template approach can produce monodipserse and size-tunable hollow spheres, the synthetic templates should be prepared first via complicated chemical routes. More unfortunately, removal of the core particles by selective dissolution in an appropriate solvent (mostly for inorganic templates) or by calcination at elevated temperature in air (mostly for polymeric beads) is indispensable in the hard-template approaches in order to obtain hollow spheres. Recently, we developed a "one-step" method to successfully synthesize monodisperse hollow silica and titania spheres.[18] In this method, the positively or negatively charged polystyrene particles were used as templates, when the SiO_2, TiO_2, or ZnO shells from their precursors (tetraethoxysilane, tetra-n-butyl titanate, zinc acetate dihydrate, respectively) were coated on the core particles via electrostatic interaction, the core particles were "dissolved" subsequently even synchronously in the same media during coating process to directly obtain hollow SiO_2, TiO_2, or ZnO spheres. This approach neither needed additional dissolution nor calcination process to remove the polystyrene cores.

In this communication, we report for the first time the preparation of monodisperse and size-tunable hollow Ag spheres with phase-transformable emulsions composed of natural beeswax as templates. Our method has several important advantages over other techniques. First of all, since beeswax is a hard and tough solid substance consisted of multiple small molecules such as alkanes and esters,[19] this

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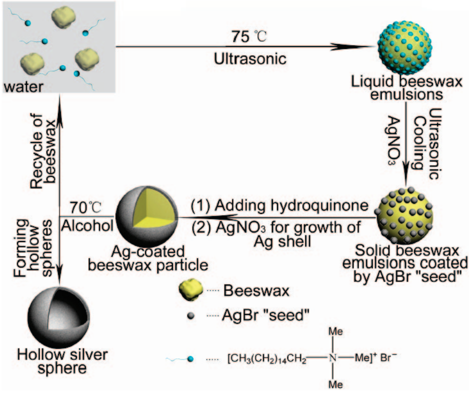

Figure 1. Schematic of the formation of hollow silver spheres using phase-transformable emulsion as template.

approach combines both the monodisperse and size-controllable virtue from hard-templates and the easily removable merit from soft-templates. Second, because the template is from natural beeswax and can be recycled, the whole process is environmentally friendly. Third, because natural beeswax has a relatively low phase-transformable temperature from solid to liquid ($T_m = 62-67$ °C), the cores can be easily removed under much more benign conditions than traditional hard templates, namely, lower temperature by aid of small amount of "ordinary" solvents like ethanol. The detailed experimental is described in the Supporting Information.

A brief procedure for fabrication of hollow Ag spheres with phase-transformable emulsions of natural beeswax as templates is depicted in Figure 1. First, a mixture of beeswax and hexadecyltrimethylammonium bromide (CTAB) aqueous solution containing KBr was heated to 75 °C to produce molten-state beeswax, followed by an ultrasonic process to obtain monodisperse, stable emulsion droplets of beeswax (the emulsion droplets of beeswax were changing from liquid to solid as the temperature decreased). The mean diameter of the emulsion droplets is 160.5 nm and the polydispersity index is 1.046 calculated from around 100 emulsion droplets in TEM images.[20a] During the ultrasonic process, a small amount of $AgNO_3$ solution (molar ratio of 0.8−1 for Ag^+ to Br^-) was added to form negatively charged AgBr "seeds", which were adsorbed onto the positively charged surfaces of droplets through electrostatic attraction. The AgBr seeds were then reduced to Ag nanoparticles bound to the solidified beeswax particles. Because the Ag nanoparticles on the beeswax cores can act as the catalyst and significantly accelerate the reduction process while the reduction of AgBr in continuous phase is very slow,[21] more Ag particles were deposited on the surfaces of beeswax particles when more $AgNO_3$ was added and reduced.[21] This led to monodisperse and dense Ag-coated beeswax spheres. When the resultant dispersion was heated at 70 °C by the aid of a small amount of ethanol, the beeswax cores were easily transferred from inside to outside because beeswax was transformed from solid to liquid again, leaving ahead well-defined hollow Ag spheres.

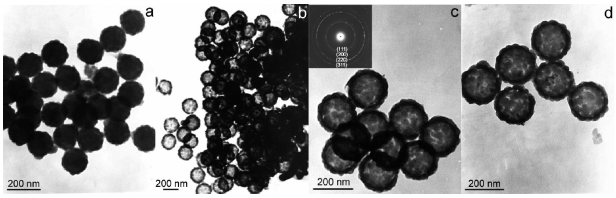

Figure 2. Typical TEM images of emulsion of beeswax and hollow Ag spheres. (a) AgBr "seed"-coated beeswax spheres; (b) hollow silver spheres from 30 mL of $AgNO_3$ solution; (c) higher-magnification image of (b) and inserted SAED pattern; (d) hollow Ag spheres from 40 mL of $AgNO_3$ solution.

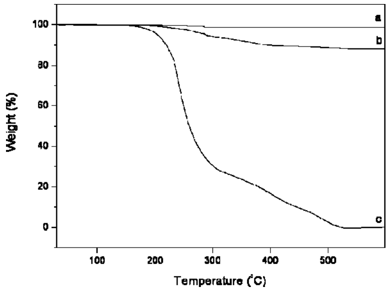

Figure 3. TGA of three different samples: (a) hollow silver spheres; (b) silver-coated beeswax sphere; (c) pure beeswax.

Figure 2 presents the typical TEM images of the AgBr seeds-coated beeswax particles and the final spheres. As one can see, a stable and uniform emulsion droplets of beeswax with a mean size of 160 nm can be obtained in this approach (Figure 2a). When 30 mL of $AgNO_3$ solution was added, the mean size of the spheres was increased to 200 nm (images b and c in Figure 2), a strong contrast between the dark ring and the pale center was an evidence of the hollow nature of spheres. The selected area electron diffraction (SAED) pattern recorded on a hollow sphere, as displayed in the inset of Figure 2c, has clear diffraction rings that correspond to the face-centered cubic (fcc) structure of Ag nanoparticle on hollow sphere surface,[22] and the hollow sphere is polycrytalline in nature. When the amount of $AgNO_3$ solution was increased to 40 mL, the mean size of hollow silver spheres was increased to 210 nm (Figure 2d). This means that the size of hollow silver spheres can be tunable through modulating the amount of $AgNO_3$ solution. No free AgBr seeds or Ag nanoparticles are found in these pictures, indicating that AgBr seeds or Ag nanoparticles were exclusively deposited onto the surfaces of beeswax particles. The "island" surface morphology of hollow silver spheres implies that a multilayer-by-layer growth mode operated in optimum formula has transferred into Skranski-Krastanov one after deposit reached certain critical thinkness.[23]

All of the diffraction peaks of the XRD pattern of as-synthesized products (see the Supporting Information, Figure S1) can be indexed to fcc silver, which is in good agreement with the value in the literature (JCPDS card No. 04−0783). No diffraction peak characteristic of AgBr is observed in the prepared sample, which indicates that the amount of AgBr in the sample is essentially negligible. The crystalline size of the hollow Ag spheres is estimated to be around 8 nm by Scherrer's formula. TGA curves (see Figure 3), reveals there is around 11.3% of weight loss for Ag-coated beeswax

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spheres and complete loss for pure beeswax up to 600 °C but almost no weight loss for hollow Ag spheres. This further attests completely hollow structure of Ag spheres. From the TGA curve of Ag-coated beeswax spheres, we can also calculate the wall thickness of silver shell is ~20 nm based on the known core size (160 nm in diameter) and densities of silver (10.5 g/cm^3) and beeswax (0.96 g/cm^3).[20b] These results further confirm that this approach can fabricate a dense silver coverage on the beeswax beads, and then completely hollow Ag spheres.

To observe the morphology and structure of hollow Ag spheres more clearly, the hollow spheres were ultrasonically treated to hopefully obtain some broken spheres and then viewed by SEM. It can be seen that the resultant hollow Ag spheres are monodisperse and well-defined (images a and b in Figure 4), the higher magnification SEM images of the broken spheres (images c and d in Figure 4) indeed show a vivid hollow structure. The mean wall thickness of hollow Ag spheres prepared from 30 mL of $AgNO_3$ solution is 20 nm, which is coincident with TGA result. When the amount of $AgNO_3$ solution was increased from 30 to 40 mL, the mean wall thickness was increased from 20 to 25 nm, indicating that we can also control the wall thickness of hollow Ag spheres through adjusting the amount of $AgNO_3$ solution. Porosity measurement shows that the obtained hollow Ag spheres have a mean pore diameter of 3.8 nm on their shells, which is large enough for the transference of liquid cores (small molecules, 70 °C) through silver wall. Moreover, no fractured, deformed, or collapsed hollow Ag spheres are found, indicating natural beeswax is a good template for preparation of well-defined hollow spheres.

The stabilization of emulsion droplets of beeswax during phase-transformation from liquid to solid during ultrasonic process is a big challenge. Based on the solid−liquid transition of paraffin/water emulsions studied by Golemanov et al.[24] When two solid particles collide with each other, the point contacts between them do not lead to sufficiently strong adhesion force so that the particles can be easily separated after contact; thus, no coalescence can occur. When two liquid drops collide with each other, a plane-parallel film is formed between them. The emulsion film that intervenes between the colliding drops is stabilized by steric or electrostatic repulsive forces if appropriate surfactants are used, and thus the drop−drop coalescence is again difficult. However, if semisolid drops collide, just as the emulsion droplets of beeswax in this study is changing from liquid to solid (the temperature was decreasing after the water bath at 75 °C was removed), some beeswax crystals formed on the drop surface protruding from the solidifying drop surface into the interior aqueous phase can tear the film between the drops. This "pin" effect of the solid surfaces could facilitate the coalescence of liquid drops. To suppress the so-called "pin" effect, more surfactant and/or solid particles with 10−20 nm are needed, which can create a more or less steric protective sheath around the drops. In this study, if too much surfactant is used, some micelles are formed and adsorbing AgBr seeds. These AgBr seeds are subjected to subsequent reduction and growth in the bulk of the aqueous phase rather than on the surfaces of the emulsion droplets. But if the concentration of CTAB is controlled slightly above critical micelle concentration without intervention of AgBr seeds, the emulsion droplets of beeswax do not have enough resistance to coalescence. Because no free AgBr seeds and Ag nanoparticles are observed by electron micrographs in this system, and the emulsion of beeswax is very stable, we would believe that AgBr seeds adsorbed on the surfaces of emulsion droplets may act as Pickering emulsifier, just as nanosilica.[25] Moreover, the absorption of AgBr seeds on the surfaces of emulsion droplets does not prohibit reversible changes in droplet size because there is no barrier against the lateral diffusion of droplets at the oil−water interface; these droplets can suck or release beeswax molecules under an ultrasonic wave until the monodisperse emulsion is formed.

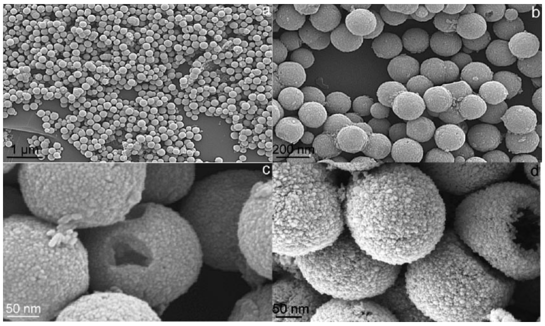

Figure 4. Typical SEM images of hollow Ag spheres: (a) large-scale monodisperse hollow Ag spheres; (b) hollow spheres from 30 mL of $AgNO_3$ solution; (c) higher-magnification image of (b); (d) hollow spheres from 40 mL of $AgNO_3$ solution.

In summary, we have demonstrated a novel and facile method for fabrication of hollow Ag spheres using the phase-transformable emulsions composed of natural beeswax as templates. Because beeswax is a solid and tough aggregate of multiple small molecules and has a relatively low phase-transformable temperature from solid to liquid and vice versa, this approach can produce monodisperse and size-tunable hollow Ag spheres like hard-template methods, and the cores are easily removed like soft-template methods. Moreover, the natural beeswax template can be recycled, so the whole process is environmentally friendly. We believe that the above method can be applied to the synthesis of other noble metal hollow spheres (e.g., Au, Pt, Pd). The prepared samples may find potential applications in chemical and biological sensors, photonic crystals, catalytic reactions, and surface-enhanced Raman scattering-based analytical devices.

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Supporting Information Available: Experimental details and XRD of hollow spheres (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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