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Formation of Yolk/SiO_2 Shell Structures Using Surfactant Mixtures as Template

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Over the past years, hollow colloidal particles have stimulated great interest due to their potential applications in controlled delivery systems, catalysis, and as vessels for confined reaction.[1] Templating against various types of colloid particles is probably the most effective and general method for the generation of hollow colloidal particles from materials as diverse as inorganic ceramics, organic polymers, and their hybrids after the subsequent removal of the core by either thermal decomposition or chemical dissolution.[1−4] An important aspect about hollow colloidal particles is that their interior functionalization could be achieved by encapsulating guest species, which would endow them with diverse properties. The incorporation of nanoparticles (NPs) as movable cores into these hollow colloidal particles (yolk/shell structures) has been explored by several groups;[5] meanwhile, novel properties could also be introduced to the hollow colloidal particles. Notably, Kamata et al. reported that incorporation of movable Au NPs as cores into polymeric hollow spheres could provide an optical probe for monitoring the diffusion of chemical reagent into and out of the shell.[5a] Somorjai et al. demonstrated that the Pt cores in the Pt@CoO yolk/shell structure could act as catalysts for ethylene hydrogenation.[6]

Commonly, yolk/shell structures are prepared based on a template-assisted approach, in which the core particle is coated with double shells with different materials and then the inner shell is selectively removed using a solvent or calcination.[5a,7] However, this method often needs surface functionalization of the NPs to grow the double shells around the cores. There are also some reports on the preparation of yolk/shell structures from core/shell NPs through reaction with the shell via the Kirkendall effect[6,8a] and other processes[8b] or selective etching of the core particle to decrease its size.[9] However, these methods still need the preparation of core/shell NPs, and the synthetic procedures are multistep and complex. Moreover, a preshell/postcore method has been demonstrated for the preparation of the yolk/shell structure,[10] but it is hard to control the core size and small NPs are often found around the shells.

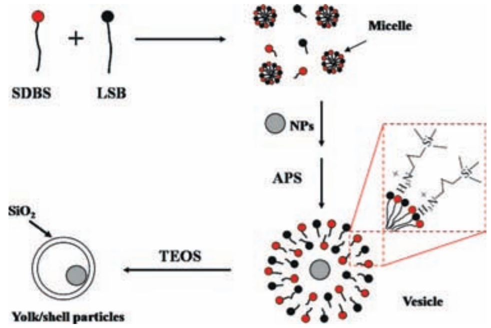

Figure 1. Schematic procedure used to generate yolk/SiO_2 shell particles containing movable NP cores.

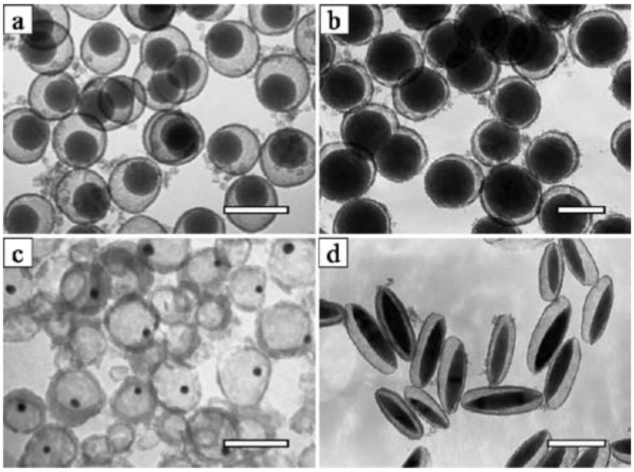

Figure 2. TEM images of yolk/shell structures encapsulated different kinds of NP cores: (a) 90 nm SiO_2 NPs, (b) 220 nm SiO_2 NPs, (c) 10 nm Au NPs, and (d) spindle-like Fe_2O_3 particles. Scale bars: (a, b, d) 200 nm; (c) 100 nm.

In this paper, we develop a simple and general method for the fabrication of yolk/shell structures through a one-step encapsulation of particles by SiO_2 shells in aqueous mixtures of surfactants. Various yolk/shell structures with different particle cores, such as SiO_2@SiO_2, Au@SiO_2, and Fe_2O_3@SiO_2, have been successfully prepared. The synthetic procedure for the yolk/SiO_2 shell structures includes three main steps, as shown in Figure 1. The first step involved the dispersion of the NPs, typically SiO_2 and Au, into an aqueous mixture of lauryl sulfonate betaine (LSB), a zwitterionic surfactant, and sodium dodecyl benzenesulfonate (SDBS), an anionic surfactant, with a 1:1 mol ratio. In the next step, 3-aminopropyltriethoxysilane (APS) was added to induce the formation of vesicles with movable NP cores. Meanwhile, some of the protonated APS that was used as a costructure-directing agent[11] was attached to the surfaces of the vesicles through electrostatic attraction. Finally, SiO_2 shells were produced through a sol−gel process by hydrolysis of the APS and tetraethyl orthosilicate (TEOS).

Figure 2 displays transmission electron microscopy (TEM) images of different kinds of synthesized yolk/shell structures. Yolk/shell structures using SiO_2 particles with average diameters of ~90 nm as core particles are presented in Figure 2a. The yield of the product is very high, and almost each particle is encapsulated by a thin shell with a thickness of ~10 nm (Supporting Information, Figure S1). The shell is composed of amorphous SiO_2, which is confirmed by the EDX and SAED (Figure S2). As can be seen from the image, the product is spherical and nearly monodisperse. In comparison to the cores in the product with initial SiO_2 particles, the sizes are almost unchanged and each shell encapsulates only one SiO_2 particle, which usually is not located in the center of the shell. It is therefore deduced that the encapsulated SiO_2 particle is

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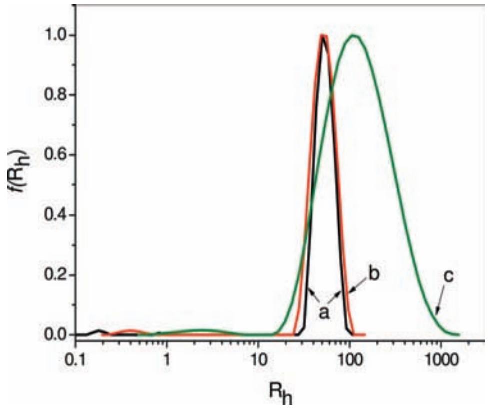

Figure 3. DLS plots of the samples with dispersion of 90 nm SiO_2 NPs: (a) aqueous solution, (b) surfactant mixtures solution ($C_{tot} = 10$ mM with mol ratio of LSB/SDBS = 1:1), (c) adding 10 mM *n*-butylamine into the solution (b). The concentration of the SiO_2 NPs is ~0.5 mg/mL.

free to move within each shell. Interestingly, when the diameters of the core SiO_2 particles changed from 90 to 220 nm, the yolk/shell structure also can be produced (Figure 2b). It is likely that the shell can accommodate particles with different sizes through adjusting its shell size. Furthermore, this unique method using the surfactant mixtures as a template can be extended to the synthesis of other encapsulated particles. Figure 2c illustrates the Au@SiO_2 yolk/shell structure through using colloidal Au NPs as core particles. In addition to embedding spherical particles in the SiO_2 shell, this method can also encapsulate particles with different shapes. Figure 2d shows the resulting yolk/shell structure with spindle-like Fe_2O_3 as core particles. The SiO_2 shell keeps the spindle-like morphology with a rather uniform thickness.

To investigate the formation mechanism of the yolk/shell structure, dynamic light scattering (DLS) was used to monitor the changes of apparent hydrodynamic radius (R_h) of the solution in the whole process. After dispersing 90 nm SiO_2 NPs in the surfactant mixtures, the R_h value is ~53 nm, which is almost the same as that of the SiO_2 NPs in aqueous solution (Figure 3a,b). This result implies that no vesicle is produced in this process. Due to the facile hydrolysis and condensation of the APS, it is difficult to measure the DLS data. Herein, we used *n*-butylamine to replace the APS to probe the role of the costructure-directing agent, APS, in the formation of the yolk/shell structure. Figure 3c shows that the R_h value obviously increases from 53 to 120 nm after *n*-butylamine is added into the solution containing SiO_2 NPs, LSB, and SDBS. It is clear that the costructure-directing agent induces the formation of vesicles with SiO_2 NPs encapsulated in their voids, which is partly supported by the experimental result of Zhai et al. that an LSB and SDBS mixture solution with different mole ratios induce the formation of vesicles in a sufficiently concentrated NaCl solution.[12] In our experiment, we propose that, with their alkyloxysilane group inserting into the surfactants assembly, the NH_2 groups of the APS decrease the electrostatic repulsion of the negatively charged groups of the surfactants, which induces the formation of vesicles with NPs in their voids through lowering the headgroup area of the surfactants.

After the formation of vesicle encapsulated NPs, a portion of the NH_2 groups of the APS is protonated and interacts with the surface of the vesicles through electrostatic attraction. Through fast hydrolysis and condensation of the APS and TEOS, a silica shell gradually forms on the surface of the vesicles, which is shown in TEM images of the product at different reaction times (Figure S3). Compared with the as-prepared sample, just a few particles with very thin shells can be observed around their surface after 10 and 20 min (Figure S3a and S3b). Interestingly, most of the particles have been encapsulated by the formed shells through prolonging the reaction time to 30 min (Figure 3c). After 1 h, the morphology of the product is almost the same as that of the as-prepared structure, although its shell is much thinner and loosely stacked (Figure S3d). Throughout the experiment, the structure of the vesicles does not collapse during the sol−gel process of silica sources, which result in the silica shell completely replicating the vesicle's structure. This may be attributed to the synergetic effect existing in the surfactant mixtures when they can interact attractively with each other or meet various conditions.[13] During the sol−gel process, small silica NPs are produced and stick to the vesicle's surface through electrostatic attraction, while the synergetic effect in the surfactant assembly (vesicle) strengthens the bilayer membrane and prevents it from collapse or phase separation.

In conclusion, we have demonstrated a general and simple method for the synthesis of yolk/SiO_2 shell structures by using surfactant mixtures as a template. By dispersing different kinds of NPs in the surfactant mixtures, yolk/SiO_2 shell structures encapsulating the movable particle cores could be produced. The formation mechanism of these novel structures is also addressed in terms of the vesicle formation induced by the APS and the synergetic effect between the surfactants.

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Supporting Information Available: Detailed experimental procedure and other results. This material is available free of charge via the Internet at http://pubs.acs.org.

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