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LETTER

Silica nanoparticles-walled microcapsules

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Colloidosomes are microcapsules with shells consisting of coagulated or partially fused colloid particles [1]. Since Dinsmore and collaborators [2] proposed the first concept of colloidosomes, many types of colloidosome structures have been proposed and discussed, and the research related to colloidosomes had become an attractive subject of many research groups. For example, Paunov et al. [3] reported the fabrication of ''hairy'' colloidosomes with shells of polymeric microrods. Wang et al. [4] produced the magnetic colloidosomes using a nanoparticle interfacial self-assembly method. Using the principles of colloidosomes, Binks and collaborators [5] investigated the temperature-induced inversion of nanoparticle-stabilized emulsions. Due to its novel microstructures, colloidosomes are expected to have potential applications in many areas of science and technologies [6]. It has been recognized that the colloidosome membranes offer a great potential in controlling the release rate of entrapped species. Their major advantage is that the membrane pores size can be varied by varying the size of the particles and by controlling their degree of fusion. The fabrication of colloidosomes not only provides a way to construct novel microstructures with nanosized building-blocks, but also gives a new way to generate microcapsules with controllable permeability. Currently, the fabrication processes of colloidosomes are mainly based on the assembly of nanoparticles at the oil–water interfaces. In those processes, solid fine particles are first prepared and then these solid particles are assembled at the oil–water interface to produce the colloidosome structures. In this letter, we demonstrate the direct fabrication of silica colloidosome via a simple sol–gel process. The resultant silica colloidosomes are hollow, silica nanoparticles-walled microcapsules.

Microcapsules are novel structures which are designed for the protection, transmission and controlled releasing of active ingredients such drugs, proteins, vitamins, flavors, gas bubbles, or even living cells. Versatile core materials are encapsulated for several reasons, such as improvement of long-time efficiency, stabilization against environmental degradation, easy handling through solidification of liquid core, and maintenance of non-toxicity of degradation products [7]. In a microcapsule system, the controlling behavior of the microcapsule is greatly determined by the structure and properties of the shell material used. Currently, the commonly used wall materials are urea formaldehyde and melamine formaldehyde (MF) resins. With the expanding applications of microcapsules, in some case, these microcapsules will be used in more rigorous conditions, e.g., at high temperatures. The commonly used wall materials cited above cannot meet these challenges. In addition, how to well construct the microstructures of the walls is still a challenge to researchers. Herein, we demonstrate the fabrication of a new type of silica nanoparticles-walled microcapsule.

The schematic microstructure of the silica nanoparticles-walled microcapsule is shown in Fig. 1. This silica nanoparticles-walled microcapsule can be well constructed by using a two-step sol–gel process shown in Fig. 2.

The principle for the formation of uniform silica nanoparticles is based on a two-step sol-gel process which is found in a literature method [8]. Using this two-step sol–gel method, uniform silica nanoparticles can be prepared. In this two-step sol–gel method, silica precursors were firstly hydrolyzed in aqueous media under the catalysis of diluted acid, and then ammonia was introduced for the

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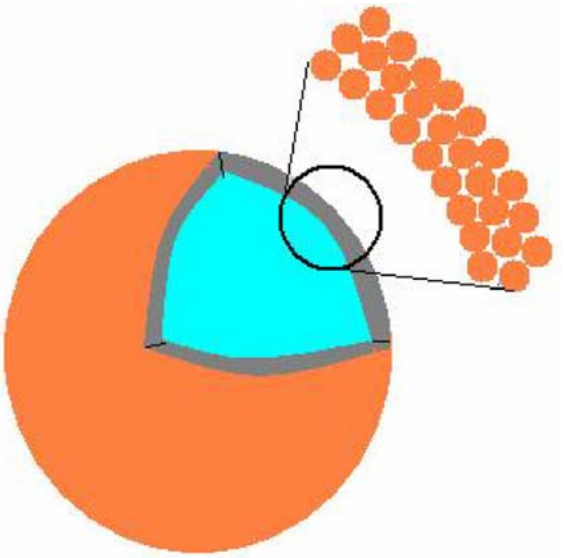

Fig. 1 Schematic showing the structure of the silica nanoparticles-walled microcapsule

condensation of the sol and as a result, uniform silica nanoparticles were formed. Herein, the principle of this two-step sol–gel method was extended to an oil–water interface. In our method, silica precursors were firstly hydrolyzed in diluted nitric acid solutions, and then oil-phase material (core material) containing ammonia-precursors (e.g., triethylamine) was introduced to the silica sol solution. Under vigorous stirring, the oil phase materials were dispersed in the silica aqueous sol solution as fine oil drops. With the diffusing and hydrolyzing of the ammonia-precursor to ammonia at the oil–water interface, silica nanoparticles formed at the oil–water interface under the catalysis of ammonia. As a result, these fine oil drops will be surrounded and encapsulated by the silica nanoparticles. With the progressing of the condensation reaction, the formed silica nanoparticles will assemble closely layer by layer and thus forming the final shells of the microcapsules. In this in situ process, these silica nanoparticles can be coagulated together, as a result, silica nanoparticles were fused together closely. In a typical procedure, the fabrication process can be accomplished as follows:

(1) Hundred milliliters diluted nitric acid aqueous solution (0.05 ml concentrated HNO_3 was added to 100 ml water) was heated to 60 °C. Two milliliters methyl-trimethoxysilane (MTMS) was introduced to the solution and kept stirring for 2 min to prepare the silica sol (Fig. 2, step 1). (2) About 0.25 g triethylamine (TEA) were dissolved in 5 ml hexane (to stabilize TEA in hexane, 0.05 g Span-80 was also introduced into the hexane solution) and then the hexane solution was introduced to the silica sol solution under vigorous stirring. After the vigorous stirring, hexane was suspended in the silica sol solution as oil drops (Fig. 2, step 2). (3) With the diffusing and hydrolyzing of TEA to NH_3 at the oil–water interface, silica nanoparticles will form at the oil–water interface, and thus forming the shell of the microcapsule. The final silica microcapsule products were collected by centrifugation and washed with ethanol and water sequentially. The morphology of the silica nanoparticles walled-microcapsules were characterized using an optical microscope (Nikon Optiphot-pol) and a field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6335F).

Figure 3a shows an optical microscope image of the microcapsule. The optical microscope image was recorded by a typical transmission light method. This image shows that these silica microparticles are spherical and likely to be hollow due to a clear outline of the sphere. The SEM image in Fig. 3b illustrates the good spherical shape of the silica microcapsule. Figure 3c shows the SEM image of a broken microcapsule. The wall and the cavity of the microcapsule can be seen clearly. It also indicates that the thickness of the walls is less than 1 μm. From the pictures shown in Fig. 3 we can conclude that well constructed spherical microcapsules have been prepared.

Figure 4 shows the SEM image of a collapsed microcapsule and the corresponding enlarged section of its wall. Figure 4a reveals that the thickness of the wall is about 0.5–1 μm and the diameter of the microcapsule is about 70 μm. Figure 4b presents an enlarged section of the wall selected from the microcapsule in Fig. 4a, indicating that the walls are composed of close-packed layers of nanoparticles. The apertures between these silica nanoparticles provide ideal channels for the delivery and release of active core ingredients.

In summary, silica nanoparticles-walled capsules have been produced using a novel sol–gel process, in which silica nanoparticles were formed at the oil–water interface and thus forming the walls of the microcapsules. This

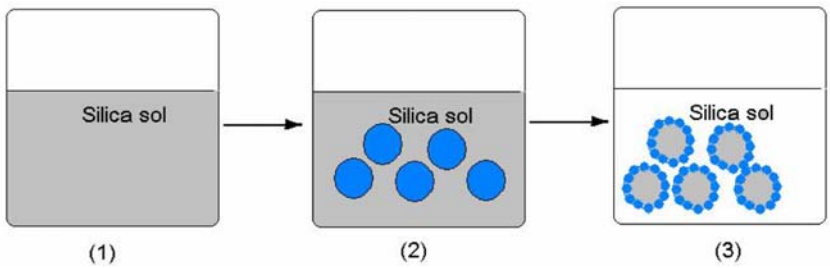

Fig. 2 The process for the fabrication of the silica nanoparticles-walled microcapsules

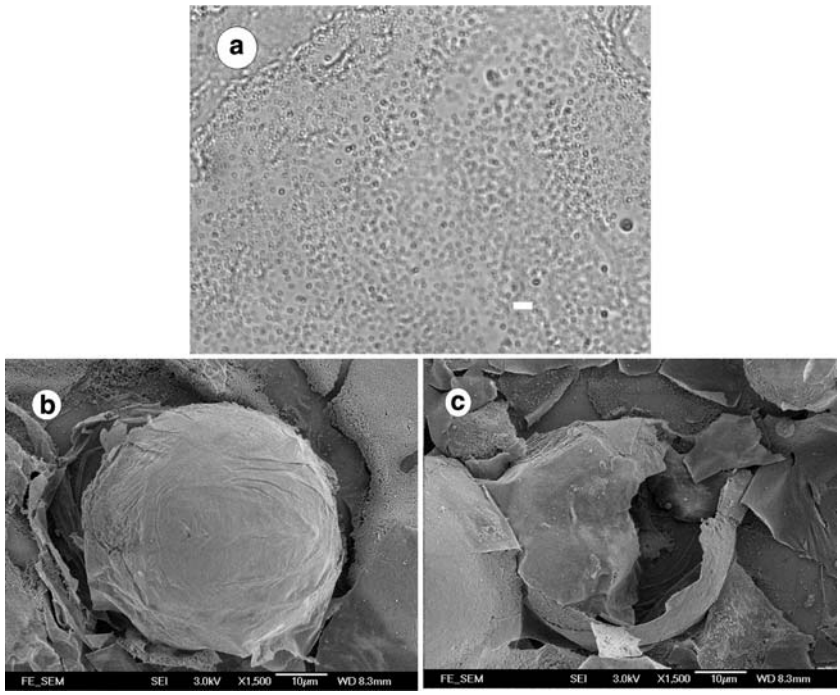

Fig. 3 The optical microscope image (**a**, bar = 100 μm) and SEM images (**b**, **c**, bar = 10 μm) of the silica nanoparticles-walled microcapsules

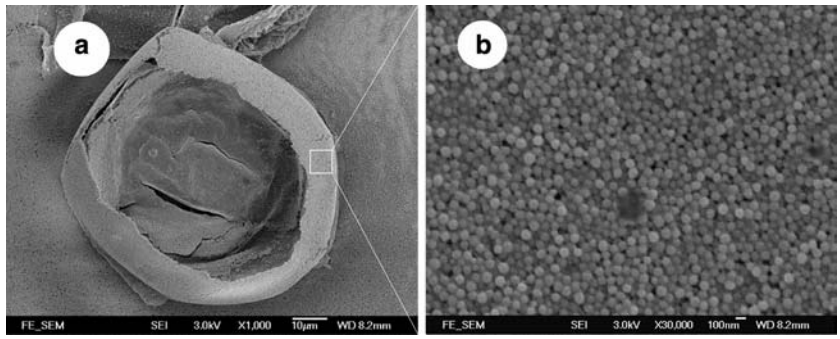

Fig. 4 The SEM images (**a**, bar = 10 μm **b**, bar = 100 nm) of the silica microcapsules

process can be extended to any oil–water system to produce silica particles-walled microcapsules. These nanoparticles-walled microcapsules can successfully meet many of the key requirements for the encapsulation.

References

1. Paunov VN, Noble PF, Cayre OJ, Alargova RG, Velev Orlin. D (2005) Mater Res Soc Symp Proc 845(AA5 18):1
2. Dinsmore AD, Hsu MF, Nikolaides MG, Marquez M, Bausch AR, Weitz DA (2002) Science 298:1006
3. Noble PF, Cayre OJ, Alargova RG, Velev OD, Paunov VN (2004) J Am Chem Soc 126:8092
4. Duan HW, Wang DY, Sobal NS, Giersig M, Kurth DG, Mohwald H (2005) Nano Lett 5:949
5. Binks BP, Murakami R, Armes SP, Fujii S (2005) Angew Chem-Int Edit 44:4795
6. Cao AM, Hu JS, Liang HP, Wan LJ (2005) Angew Chem-Int Edit 44:4391
7. Sukhorukov G, Fery A, Mohwald H (2005) Prog Polym Sci 30:885
8. Hah HJ, Kim JS, Jeon BJ, Koo SM, Lee YE (2003) Chem Commun 14:712