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Formation of monodisperse silica microparticles with various shapes and surface morphologies using double emulsion templates

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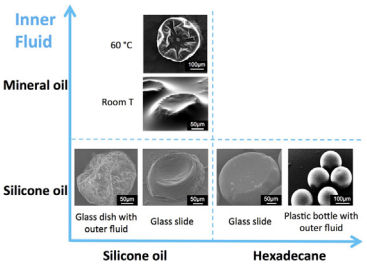
HIGHLIGHTS

- We present a simple method to generate various types of silica microparticles.
- Silica microparticles are monodisperse and the porosity can be controlled.
- We find that their types can be tuned by varying just a few key parameters.
- The types include smooth and crumbled microshells, microdisks, and microspheres.

GRAPHICAL ABSTRACT



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ABSTRACT

We report a simple method to generate monodisperse mesoporous silica particles from double emulsion templates generated by glass capillary microfluidic devices. Silica precursors in the middle phase of double emulsion templates are polymerized and self assembled to mesoporous structures of triblock copolymer templates. We find that various types of silica microparticles, including smooth and crumbled microshells, microdisks, and microspheres, can be generated by varying polymerization temperature and the outer fluid. This method provides a convenient strategy to generate silica mesoporous microparticles with a variety of shapes and surface morphologies by tuning a few key parameters.

1. Introduction

Surfactant-templated ordered mesoporous silica materials have many applications such as delivery of DNA [1] and drugs [2,3] into animal cells and plant cells [4], catalysts for selective organic transformations [5], and electronics with integral organic functionality [6]. Uniform monodisperse mesoporous silica spheres have attracted particular interest due to potential applications in sensors [7], encapsulation and biomolecule delivery [8]. Synthesis of mesoporous silica materials via lyotropic liquid crystal templates was discovered several years ago, by utilizing the self-assembly structure of amphiphiles as a template [9,10].

Since Stöber's first synthesize of monodisperse non-porous silica nanoparticles using hydrolysis and condensation of tetraalkoxysilane in alcoholic solution in 1968 [11], many groups have tried to modify Stöber's method to synthesize monodisperse mesoporous silica particles that have very high surface area. Andersson et al. [12] designed an emulsion and solvent evaporation (ESE) method by combining emulsification with the evaporation-induced self-assembly (EISA) method [13,14]. Using this method, they synthesized well-ordered 2D hexagonal spherical mesoporous silica particles. Because they used inhomogeneous vigorous stirring to prepare emulsions, the resulting droplets

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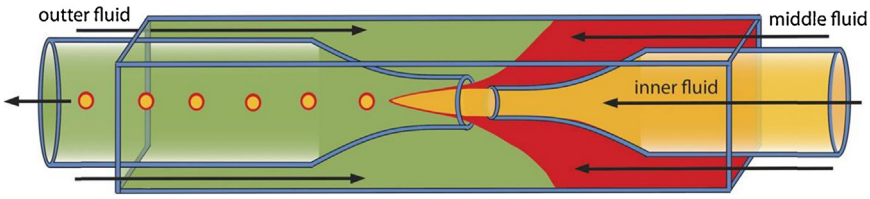

Fig. 1. Schematic illustration of a 3-capillary microfluidic device for the formation of double emulsions.

Table 1
Combinations of inner and outer fluids.

	Surfactant for inner fluid	Inner fluid	Surfactant for outer fluid	Outer fluid
A	3% Span 80	Mineral oil	3% Dow 749	90% light silicone oil and 10% heavy silicone oil
B	3% Dow 749	Light silicone oil	3% Dow 749	90% light silicone oil and 10% heavy silicone oil
C	3% Dow 749	Light silicone oil	4% ABIL–EM90	90% hexadecane and 10% heavy silicone oil
D	3% Dow 749	Light silicone oil	4% ABIL–EM90	hexadecane

and final particles have a broad size distribution. A modified synthesis method was reported that can generate sub-micrometer scale monodisperse super-microporous silica spheres whose sizes can be controlled by varying the synthesis temperature, the solvent mixture ratio and the source chemicals of silica [15]. Lee et al. have reported the formation of monodisperse mesoporous microspheres combining the microfluidic generation of uniform droplets with diffusion induced self-assembly in microchannels [16]. Recently, a one-step microfluidic method was reported to synthesize hollow silica microshells [17]. This work used interfacial polymerization of silica precursors on water-in-oil droplets generated by a microfluidic device. Specifically, they use cationic surfactant cetyltrimethylammonium bromide (CTAB) dissolved in a 1:1 water/ethanol phase. Silica precursors in the oil phase then diffuse onto the water/oil interface and polymerize there. The hollow silica microspheres are more desirable for the use of encapsulation because of their high capacity.

Another convenient common method to generate a shell structure is using double emulsion templates [18]. Double emulsions are emulsions with smaller droplets of a third fluid within the larger drops. Although emulsions are not in an equilibrium state, if an emulsion's interface is stabilized by a suitable surfactant the droplets can maintain their integrity for a long time [19]. Because of the intermediate fluid, the innermost fluid can be separated from the continuous phase. This feature makes double emulsions highly desirable in many areas, such as controlled release [20,21], separation, and encapsulation [21,22].

Traditionally, emulsions are produced by vigorously shaking two immiscible liquids with a small amount of surfactant. The shaking generates enormous shear force that breaks up a fluid in another fluid, resulting emulsion droplets. However, this method results in droplets with a wide size distribution. In addition, the resulting emulsions cannot be finely controlled so it is hard to study the properties of individual droplets.

Similarly, double emulsions can be produced in two steps: first, the inner droplets are emulsified in the middle phase, and then the first emulsion dispersed in another phase [23,24]. Each step results in an emulsion with a high polydisperse distribution. Therefore, these double emulsions are poorly controlled in both size and structure, which limits their application. By using flow focusing, coaxial T-shape microchannels, monodisperse double emulsions can be achieved [25,26]. But it requires a two-step droplet breakup and re-emulsified into continuous phase.

The 3-capillary microfluidic devices can generate uniform double emulsions in a single step [27–29]. This microfluidic device can control not only the outer and inner drop sizes precisely, but also the number of droplets encapsulated in each large drop. This device

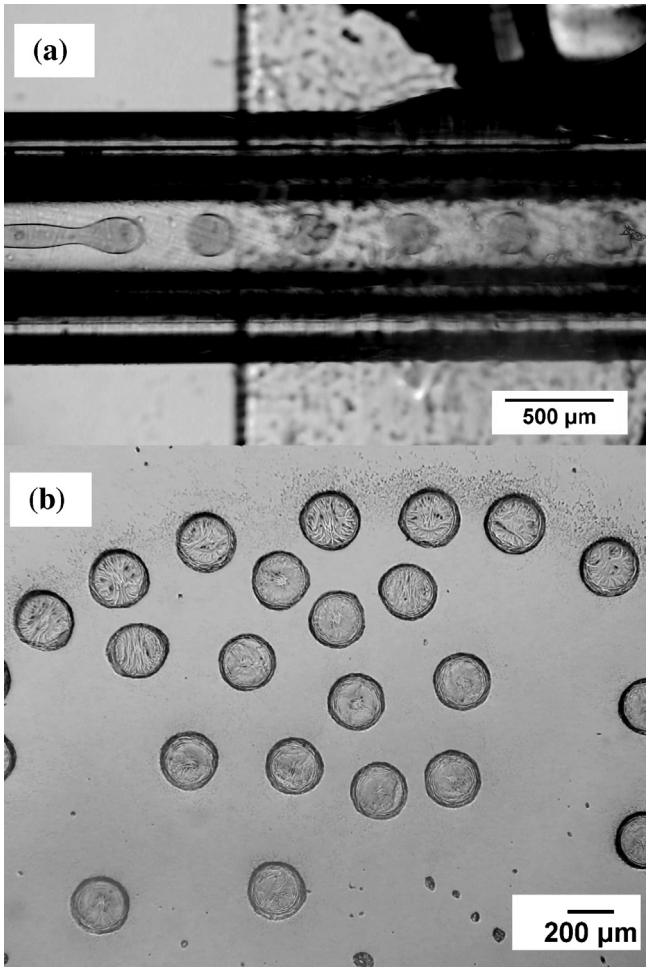

Fig. 2. (a) Optical microscope image of fluids passing through the exit orifice and breaking up into double emulsion droplets. (b) Optical microscope image of silica microshells obtained by polymerizing double emulsions of Composition A (Table 1) at room temperature on a glass slide.

is constructed with three glass capillaries, two cylindrical ones, and a square one, as shown in Fig. 1. The innermost fluid flows through the injection tube, the middle fluid is pumped through the middle part between the outside of the cylindrical tube and the inside of the square tube, and the outer fluid is pumped from the opposite direction of the other side of the square capillary coaxial region. When the drag force overcomes the interfacial tension due to the