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Preparation of solid, hollow, hole-shell and asymmetric silica microspheres by microfluidic-assisted solvent extraction process

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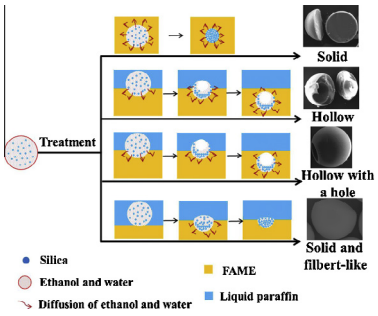
HIGHLIGHTS

- Monodisperse silica microspheres were prepared by solvent extraction process.
- Microfluidic technique was used to prepare silica sol droplets.
- Solid, hollow, hole-shell and asymmetric silica microspheres could be prepared.
- The cavity size and hole size could be adjusted.

GRAPHICAL ABSTRACT

Silica microspheres with solid, hollow, hollow with a hole and filbert-like solid structures are prepared based on interfacial solvent extraction of a silica sol droplet formed in a simple microfluidic device.



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ABSTRACT

Present work demonstrated the facile preparation of silica microspheres with various structures (solid, hollow, hollow with a hole and filbert-like solid). These were prepared by first forming monodisperse silica sol droplets in a simple microfluidic device, followed by extracting the solvent from the droplets in an extractant or at the interface between the extractant and liquid paraffin at different conditions. The effect of different extractants and extracting temperature was investigated. The products were characterized by optical microscope and scanning electron microscope. Extraction in fatty acid methyl ester (FAME) at room temperature led to formation of solid silica microspheres, while extraction at the interface between FAME and liquid paraffin at 60 °C resulted in formation of hollow silica microspheres. Use of mixture of castor oil (CO) and dimethyl carbonate (DMC) as extractant resulted in formation of hollow silica microspheres with a hole on the surface, whereas increase in the DMC content in extracting medium led to formation of filbert-like silica solid microspheres. Change in size of cavity and hole was studied by changing the extracting temperature. The formation process and mechanism of these silica microspheres are proposed based on the diffusion rate. The relationship between the size of the microspheres and the state of the droplet at the interface is correlated.

1. Introduction

Inorganic microspheres have attracted much attention due to their wide applications in many areas, such as catalyst supports, adsorbents, sensors, drug carriers, and photoelectric materials [1–5]. According to their internal structure, they can be cataloged as solid and hollow ones. The inorganic solid microspheres can be synthesized by the Stöber method [6], spray drying [7], hydrothermal synthesis [8], emulsion polymerization [9] and so on. The resulting products always exhibit good sphericity.

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However, asymmetrical filbert-like inorganic solid microspheres have not been reported yet.

On the other hand, inorganic hollow microspheres have recently been paid much more attentions than their solid counterparts because of their lower density, larger specific surface area and higher capacity. They are most commonly prepared by the template methods [10–12], although other template-free methods, such as Ostwald ripening process [13], self-assembly [14], emulsion polymerization [15], and chemical selective etching [16], are also reported. These methods are either dependent on the uniform sacrificial templates, or careful controlling of synthesis conditions, or use of multisteps. Recently, the microfluidic technology has shown remarkable capabilities for preparing monodisperse particles [17–21], inorganic TiO_2, carbon, SiO_2 hollow microspheres based on interfacial polymerization [22–25], chitosan and chitosan/silica hybrid microspheres [26,27], Fe_3O_4@ZIF-8 magnetic core–shell microspheres [28], however, it is still a challenge to easily tune the internal structure of the microspheres between hollow and solid.

Another type of the inorganic hollow microspheres, i.e., the one with a hole in the surface of the microsphere, is recently developed. This type of microspheres exhibits "lock–key" effect and are more useful for loading objects such as cells and confining a microreaction [29]. Up to now, SiO_2 and TiO_2 are the mainly inorganic components which exhibit this structure, although it has been seen on some organic components, including poly(o-methoxyaniline) [30], polystyrene (PS) [31–33], poly (methyl methacrylate) (PMMA) [32], poly-(L-lactide) (PLLA) [32], poly(acrylamide-ethylene glycol dimethacrylate) (AA-EGDMA) [34], polymethylsilsesquioxane (PMSQ) [35], polyurethane (PU) [36], PS/polydivinylbenzene (PDVB) [37], poly(ethoxylated trimethylolpropane triacrylate) (PETPTA) [29], and poly(N-isopropylacrylamide) [38]. Mainly, particle or emulsion-template methods are used to prepare these organic hollow microspheres with a hole in the shell [37]. Similarly, the SiO_2 hollow microspheres with a hole in the shell can be also prepared by the emulsion-template methods [39–42]. On the other hand, the TiO_2 hollow microspheres with a hole are prepared by hydrothermal synthesis [43]. However, these methods are difficult to control the hole size and the particle size distribution of the microspheres is quite broad. Furthermore, preparation of inorganic microspheres with desirable cavity and spherical morphology is still a challenge.

Herein, we report a versatile method to fabricate silica microspheres with solid, hollow, hollow with a hole and the filbert-like solid structures in a simple microfluidic device. The synthesis process is based on solvent extraction in a silica sol microdroplet that is suspended on the interface between the extractant and the non-extractant. Although the droplet solvent extraction method has been applied to prepare solid microspheres, such as TiO_2 [44], SiO_2 [45], ordered mesoporous silica microspheres [46–48] and hollow colloidal crystals microspheres [49], it is conducted by immersing the droplet containing the precursor totally in the extractant, leading to equal solvent extraction in every direction. To the best of our knowledge, this is the first report on preparation of materials based on interfacial extraction of droplets between extractant and non-extractant. The different extracting rates of the two parts of the microdroplets result in the formation of hollow structure, which can be further tuned to hollow structures with a hole in the shell. When the extracting rate is fast enough, filbert-like microspheres can be obtained. Thus, by changing the operating mode and the composition of the extractant, silica microspheres with several kinds of internal structure and morphology can be produced. These microspheres may be potentially used as catalyst supports, microreactor, or capturers for cells [29].

2. Materials and methods

2.1. Materials

Tetraethoxysilane (TEOS), Span 80, and liquid paraffin were all purchased from Sinopharm Chemical Reagent Co., Ltd. Absolute ethanol and methylene blue were acquired from Wuxi Yasheng Chemical Co., Ltd. (Wuxi, China) and Shanghai SSS Reagent Co., Ltd. (Shanghai, China), respectively. Fatty acid methyl esters (FAMEs) were prepared in lab by transesterification of cottonseed oil with methanol in a microreactor with the assistance of catalyst KOH [50]. Castor oil was bought from Wuxi Zhanwang Chemical Co., Ltd. (Wuxi, China).

2.2. The microfluidic device

A microneedle and a PTFE tube were vertically arranged and sandwiched between two PMMA plates. The needle with 110 μm i.d. and 2 cm length was used for transferring the dispersed phase, and the PTFE tube with 500 μm i.d. and 4 cm length was used for collecting the microdroplets. The continuous-phase was introduced from an inlet of the PMMA plate perpendicular to the needle (Fig. 1). The solvent-assisted thermal press technique was used to bond the two PMMA plates. Prior to use, the bonded microchip was cleaned by distilled water.

2.3. Preparation of the silica sol solution

The silica sol solution was prepared by hydrolyzing 5.2 g of TEOS in a mixture of 14 g of ethanol and 2.7 g of 0.07 M hydrochloric acid under magnetic stirring at room temperature for 2 h. The silica content in the solution was ca. 6.8 wt%. In some cases, 0.1 mg of methylene blue was added into the silica sol solution to facilitate the observation.

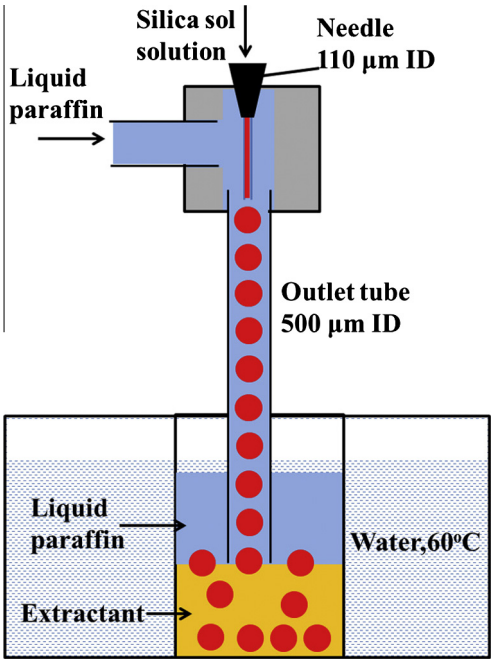

Fig. 1. Schematic illustration of the microfluidic device and the preparation process.