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Synthesis of hollow mesoporous silica spheres and carambola-like silica materials with a novel resin sphere as template

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ABSTRACT

Hollow mesoporous silica spheres with wormlike mesoporous were synthesized by a dual-templating method using resorcinol/formaldehyde resin spheres as hard templates and cationic surfactant (CTAB) as soft template. The average particles diameters were adjusted by changing molar ratio of TEOS/CTAB. Carambola-like silica materials with hollow structure can be obtained using one-pot method.

1. Introduction

Hollow silica spheres with mesoporous shell have raised increasing interest for combining the characteristic of both macroporous and mesoporous structures. Hence, such porous structures can act as a micro reactor, and be used for controlled release of drug delivery, adsorption and catalyst [1–3]. Among many synthesis methods [4–7], a dual-templating method [8] has been widely applied and researched for the synthesis of hollow mesoporous silica spheres (HMSs). Surfactant (CTAB, block copolymer) and some organic/inorganic polymers as soft/hard-template can produce the mesoporous and hollow interior during the hydrolysis and condensation of the silica precursor. Le et al. [9] fabricated HMSs using nanosized calcium-carbonate particles as solid template and CTAB as soft template. But transmission electron microscopy (TEM) shows that there exists obvious aggregation among the particles. Blas et al. [10] prepared monodisperse, no aggregated hollow silica nanoparticles with a homogeneous ordered mesoporous shell by a dual-templating method, which employed polystyrene latexes with anionic or cationic surface charges and CTAB acted as the solid/soft templates. Qi et al. [11] reported a facile and scalable process to synthesize smooth, uniform and monodisperse HMSs using concentrated polystyrene latex as template.

However, most of the preparation processes need to modify the hydrophobic, chemically inert surfaces of these templates, augmenting the preparation complexity. More polymerized agents and additives are introduced to increase the preparation cost and environment pollution, especially polystyrene latex. Therefore, it is still necessary to develop a facile, low-cost template for preparing HMSs. Recently, Liu et al. [12] fabricated resorcinol/formaldehyde (RF) resin spheres with uniform and controlled particles size with the extension of the Stöber method. We believe RF resin spheres can be a novel template for fabricating hollow inorganic materials. Herein, in the present work, we reported the synthesis of HMSs by the dual-templating method (RF resin spheres as sacrificial template, CTAB as soft template). The shell thickness can be tuned by changing the molar ratio of TEOS/CTAB. Simultaneously, we proposed a formation mechanism of HMSs, and corresponding characterizations showed that RF resin spheres become a novel template to replace other templates, such as polystyrene latexes. In addition, carambola-like silica materials were obtained by one-pot method.

2. Experimental

Synthesis of HMSs. 0.2 g of RF resin spheres was added to a solution containing 10 ml of ethanol, 5 ml of deionized water, 0.1 ml of ammonia aqueous solution (25 wt%) and 0.1 g of CTAB under vigorous stirring at room temperature. The mixture stirred for 20 min before adding TEOS. The molar ratio of TEOS/CTAB were 1.7, 3.4, 5.0, 6.7 and 8.4. The mixture was kept at room temperature for 3 h, and subsequently heated for 24 h at 100 °C under a static condition. The solid products were collected by centrifugation and washed with deionized water. The templates were removed by calcining in air at 550 °C for 3 h. The resulting samples were labeled as HMSs-*x*, where *x* represented the TEOS/CTAB molar ratio.

Synthesis of carambola-like silica materials. 0.1 ml ammonia aqueous solution was mixed with a solution containing 8 ml ethanol and 20 ml deionized water, and then stirred for more than 1 h. Subsequently, 0.1 g CTAB was added and continually stirred for 30 min. Then 0.2 g

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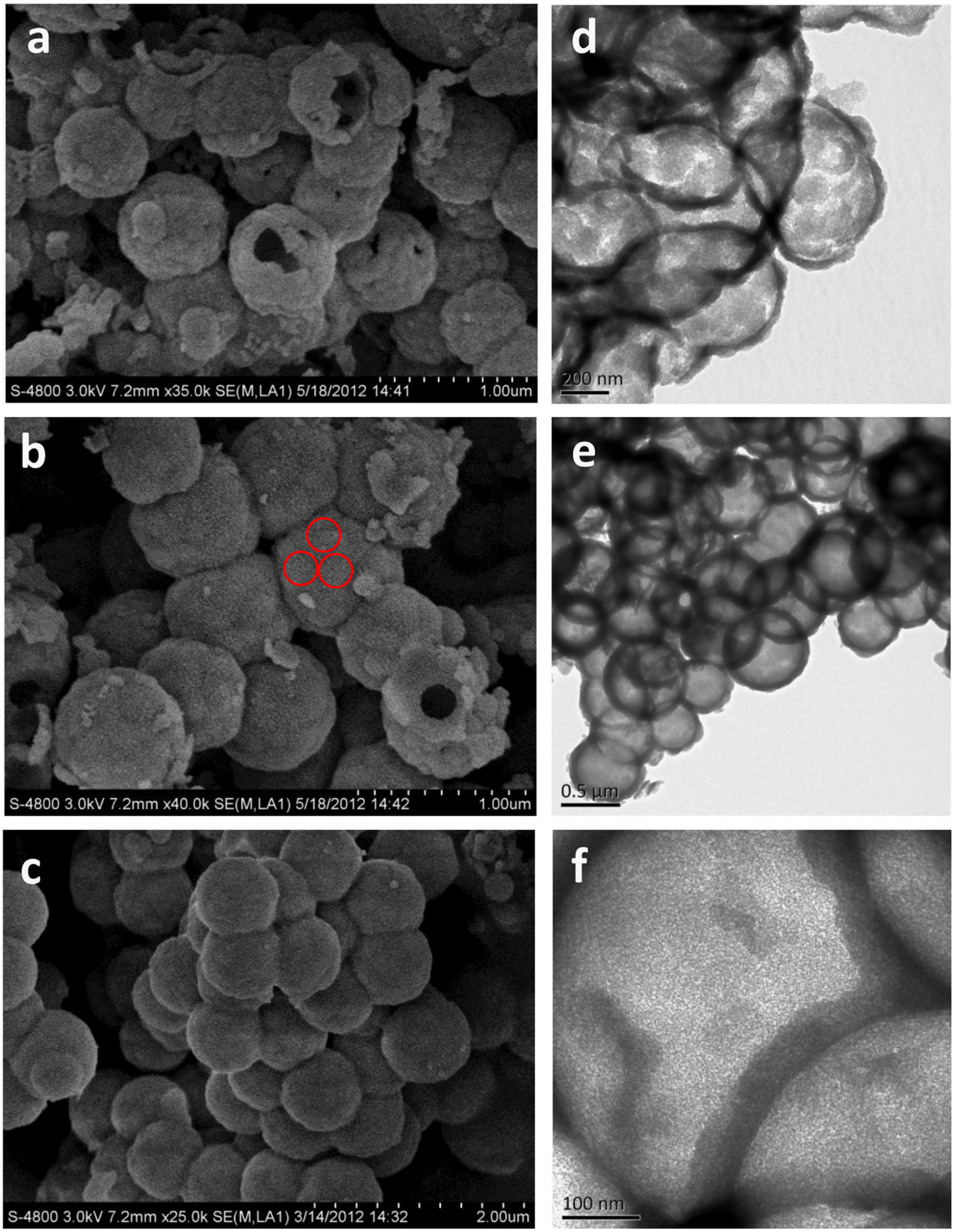

Fig. 1. SEM images of HMSs prepared at different molar ratios of TEOS/CTAB: (a) HMSs-5.0; (b) HMSs-6.7; (c) HMSs-8.4; TEM images of HMSs-3.4 (d), and HMSs-6.7 with different magnifications (e, f). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

resorcinol and formaldehyde solution (0.28 ml) was added under stirring for 30 min. The solution was stirred for 20 h at 30 °C. After addition of TEOS (TEOS/CTAB molar ratio of 3.4) for another 4 h, the solution was subsequently heated for 24 h at 100 °C under a static condition. The next step is consistent with the preparation process of HMSs.

Characterization. The products were characterized by powder X-ray diffraction (XRD) pattern, using a Rigaku D/MAX-2500 XRD system with Cu Kα radiation. Scanning electron microscopy (SEM) was performed on a HITACHI S-4800-I scanning electron microscope. TEM were obtained on a JEOL JEM-2010 electron microscope. N_2 isotherm measurements were performed on a Micromeritics TriStar 3020 at 100 °C under a static condition.

3. Results and discussion

In the initial experiment, we employed the direct coating method to introduce the silica source onto the surface of resin spheres without adding CTAB. Nevertheless, the crater-like silica materials were