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Preparation of frustule-like 1,2-ethylene-silica nanospheres through a chiral amphiphile/organic solvent dual-templating approach

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ABSTRACT

Hollow silica nanospheres with mesopores in the walls have been widely studied because of their potential applications in catalysis and drug release. Hollow organosilica nanospheres also attracted much attention because of their tunable wall backbones and wider applications. Herein, frustule-like 1,2-ethylene-silicas were obtained using a chiral amphiphile, $CHCl_3$, and a dual-templating approach. The morphologies and pore architectures of the 1,2-ethylene-silicas are tunable by changing the amount of $CHCl_3$ in the reaction mixture. With the addition of $CHCl_3$ in the reaction mixtures, hollow 1,2-ethylene-silica nanospheres with opened mesopores in the walls were feasible. Moreover, 1,2-ethylene-silicas with mesopores on the surfaces and coiled pore channels within the walls were obtained using the chiral amphiphile in a single-templating approach. These 1,2-ethylene-silicas were characterized using field-emission scanning electron microscopy, transmission electron microscopy, X-ray diffraction and N_2 sorptions.

1. Introduction

Hollow silica nanospheres with mesopores in the walls, especially frustule-like nanostructures, have been widely studied due to their potential applications in catalysis and drug release [1–4]. Generally, these hollow silica nanospheres with vertical, horizontal, random, and three-dimensional pore channels in the shells were prepared through dual-templating approaches [5–21]. Recently, it was reported that hollow silica nanospheres with vertical pore channels could be prepared through a single-templating approach [22]. The structural transition of the chiral amphiphile/silica oligomer assemblies in the reaction mixture played an important role in the formation of this hierarchical structure. However, the reports on hollow organosilica nanospheres that can be widely functionalized are few [23–29].

Shinkai's group did the pioneering work of controlling the morphologies of silicas using chiral amphiphiles [30–36]. Templated by the organic self-assemblies of these chiral amphiphiles, silicas with a variety of morphologies and pore architectures were obtained. However, it is still hard to control the morphologies and pore architectures of organosilicas through this traditional sol–gel transcription approach [36]. When the sol–gel transcriptions were carried out in water or mixtures of water and alcohols, a cooperation mechanism was found [37–41]. The interactions of chiral amphiphile and silica oligomer control the morphologies and pore architectures of the silicas and the morphologies and pore architectures of organosilicas can be simply controlled [42–47]. For the aromatic ring-bridged bis(silsesquioxanes), the circular dichroism spectra indicated that the aromatic rings stacked chirally within the walls [45]. Since the hollow silica nanospheres with mesopores in the walls can be prepared using chiral amphiphiles, hollow organosilica nanospheres can be prepared [48]. Herein, frustule-like 1,2-ethylene-silicas were obtained using a chiral amphiphile and $CHCl_3$ using a dual-templating approach. Moreover, 1,2-ethylene-silicas with mesopores on the surfaces and coiled pore channels within the walls were obtained using a chiral amphiphile and a single-templating approach.

2. Experimental

2.1. Materials

1,2-Bis(triethoxylsilyl)ethane (BTESE) was purchased from Gelest, Inc. The synthesis and characterization of L-18Val6NEt$_3$Br were published elsewhere (Fig. 1) [22].

2.2. Synthesis

Preparation of mesoporous 1,2-ethylene-silica nanotubes using L-18Val6NEt$_3$Br, **S0.** Amphiphile L-18Val6NEt$_3$Br (100 mg,

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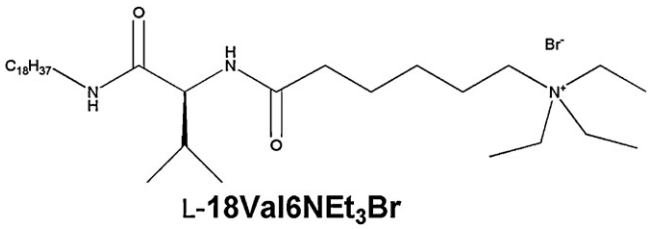

Fig. 1. Molecular structure of the low-molecular-weight amphiphile.

0.16 mmol) was dissolved in a solution of 50.0 mL deionized water and 0.35 mL NaOH (2.0 M) at 80 °C. Then, 0.50 mL of BTESE (1.35 mmol) was dropped into the mixture at a stirring rate of 1500 rpm. The reaction mixture was kept at 80 °C for 2 h. The template was removed by extracting it with a mixture of HCl (36 wt%) and methanol for 48 h.

Preparation of mesoporous 1,2-ethylene-silicas using L*-18Val6-NEt$_3$Br and CHCl$_3$,* **S05** *and* **S20**. The typical synthetic procedure was as follows. Amphiphile L-18Val6NEt$_3$Br (100 mg, 0.16 mmol) was dissolved in a solution of 50.0 mL deionized water and 0.35 mL NaOH (2.0 M) at 55 °C. Five minutes later, a desired volume of $CHCl_3$ was added into the solution at a stirring rate of 1500 rpm. The desired volume of $CHCl_3$ was 0.5 and 2.0 mL for samples **S05** and **S20**, respectively. Then, 0.50 mL of BTESE (1.35 mmol) was dropped into the mixture. The reaction mixture was kept at 55 °C for 2 h. The template was removed by extracting it with a mixture of HCl (36 wt%) and methanol for 48 h.

2.3. Characterization

Transmission electron microscopy (TEM) images were obtained using a FEI TecnaiG220. Field emission scanning electron microscopy (FESEM) images were taken on a Hitachi 4800. Small-angle X-ray diffraction (SAXRD) patterns were taken on an X' Pert-Pro MPD X-ray diffractometer. Specific surface area and pore-size distribution were determined by the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods using N_2 adsorption isotherm measured by a ASAP 2020M+C instrument.

3. Results and discussion

Low-molecular-weight amphiphiles (LMWAs) attracted attention because of their applications in cosmetics and medicines [49,50]. They can self-assemble into a variety of nanostructures through H-bondings, ionic interactions, hydrophobic associations and π–π stackings. Amphiphile L-18Val6NEt$_3$Br can produce physical gels in tetrahydrofuran, 1,4-dioxane, benzene, nitrobenzene, acetonitrile, and tetrachlorocarbon [22]. However, it exhibits high solubility in chloroform. Fig. 2 shows the FESEM images of the samples **S0**, **S05,** and **S20** obtained by adding 0.0, 0.5, and 2.0 mL of $CHCl_3$, respectively, in the reaction mixtures. For **S0**, nanotubes with mesopores on the wall surfaces were identified (Fig. 2a). These mesopores did not arrange in a high degree of order. The diameters of the nanotubes and the mesopores on the surfaces were about 40 and 4.0 nm, respectively. For **S05**, a mixture of nanotubes and hollow spheres with opened mesopores

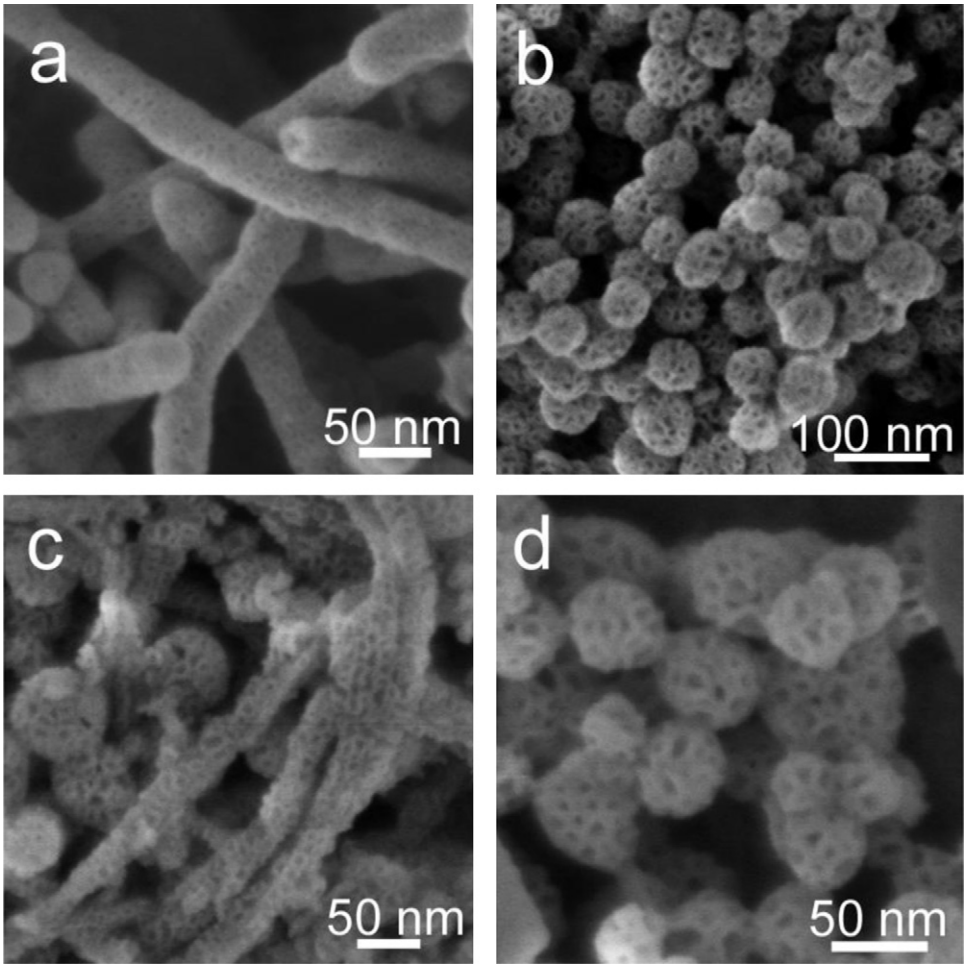

Fig. 2. FESEM images of the 1,2-ethylene-silicas, (a) **S0**; (b) and (c) **S05**; (d) **S20**.