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Preparation of helical mesoporous ethylene–silica nanofibers using CTAB and (*S*)-2-methyl-1-butanol

Sibing Wang, Baozong Li, Lifeng Bi, Ming Zhang, Yuanli Chen, Yi Li, Yonggang Yang *

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China

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ABSTRACT

The morphology and pore architecture of mesoporous ethylene–silicas were controlled using cetyltrimethylammonium bromide (CTAB) as the template and (*S*)-2-methyl-1-butanol (MB) as a co-structure-directing agent. X-ray diffraction, nitrogen sorption, field emission scanning electron microscopy and transmission electron microscopy techniques have been used to characterize the ethylene–silicas. When the MB/CTAB molar ratio is 20, mesoporous nanoparticles with lamellar mesopores on their surfaces were identified. Helical nanofibers were obtained at the MB/CTAB molar ratios of 0.5–10. Although MB could not drive the formation of single-handed helical nanofibers, with increasing the MB/CTAB molar ratio, the diameter and the helical pitch of the mesoporous ethylene–silica nanofibers decreased and the pore size increased.

1. Introduction

With the developing of supramolecular templating approaches, materials based on siloxane networks with structural order and containing different organic functional groups have been reported [1–3]. Because of incorporating of various organic bridging groups into silica framework and their uniform distribution inside walls of ordered mesopores, periodic mesoporous organosilicas (PMOs), exhibit a distinct advantage over mesoporous silicas. Their functional groups bridge between the two silica atoms, which can enhance molecular accessibility in absorbance and catalysis applications, and sensing devices, and thus gain the opportunities for further modification [3].

Using surfactants or copolymers as supramolecular templates is a widely studied topic to control the morphology and pore architecture of the PMOs. Helical structures should be the most exciting ones, because they can be used as supports of catalysts, chiral sensors, and the stationary phase of chiral HPLC. Recently, helical mesoporous silica materials have been successfully obtained using achiral cationic surfactants [4–8]. However, the reports for the preparation of the helical PMO nanofibers are rare [9–11]. Moreover, the helical pitches were not controlled. Herein, the helical mesoporous ethylene–silica nanofibers were prepared using cetyltrimethylammonium bromide (CTAB) as the template and (*S*)-2-methyl-1-butanol (MB) as a co-structure-directing agent. The helical pitch of the nanofiber is controllable by changing the MB/CTAB molar ratio.

2. Experimental

2.1. Synthesis

CTAB and MB were purchased from Sinopharm Chemical Reagent Co., Ltd. Bis(triethoxysilyl)ethane (BTESE) was purchased from Gelest, Inc.. A typical synthetic procedure for the helical mesoporous ethylene–silica nanofibers is shown as follows: A mixture of 25 wt.% aqueous ammonia solution (25 mL) and CTAB (2.74×10^{-4} mol) was stirred in a 50 ml beaker at 40 °C for a few minutes until it become clear solution. A mixture of MB (2.74×10^{-4} mol) and BTESE (15×10^{-4} mol) was added at the stirring rate of 1000 rpm. The mixture was stirred at 40 °C for 3 h, followed by aging at 100 °C for 24 h. The resultant white precipitate was filtered and dried to yield the as-prepared mesoporous ethylene–silica. CTAB was removed by extracting with a mixture of 80 mL of methanol and 10 mL of 36 wt.% aqueous HCl solution for 24 h.

2.2. Characterization

The transmission electron microscopy (TEM) images were obtained using a FEI TecnaiG220. The field emission scanning electron microscopy (FESEM) images were taken on a Hitachi S-4700. Specific surface area and pore-size distribution were determined by the Brunauer-Emmett-Teller (BET) and the Barrett-Joyner-Halenda (BJH) methods using N_2 adsorption isotherm measured by a Micrometeritics ASAP 2020 M + C instrument. The small angle X-ray diffraction (SAXRD) patterns were recorded on an X′ Pert-Pro MPD X-ray diffractometer.

* Corresponding author. Tel./fax: +86 512 65882052.
E-mail address: ygyang@suda.edu.cn (Y. Yang).

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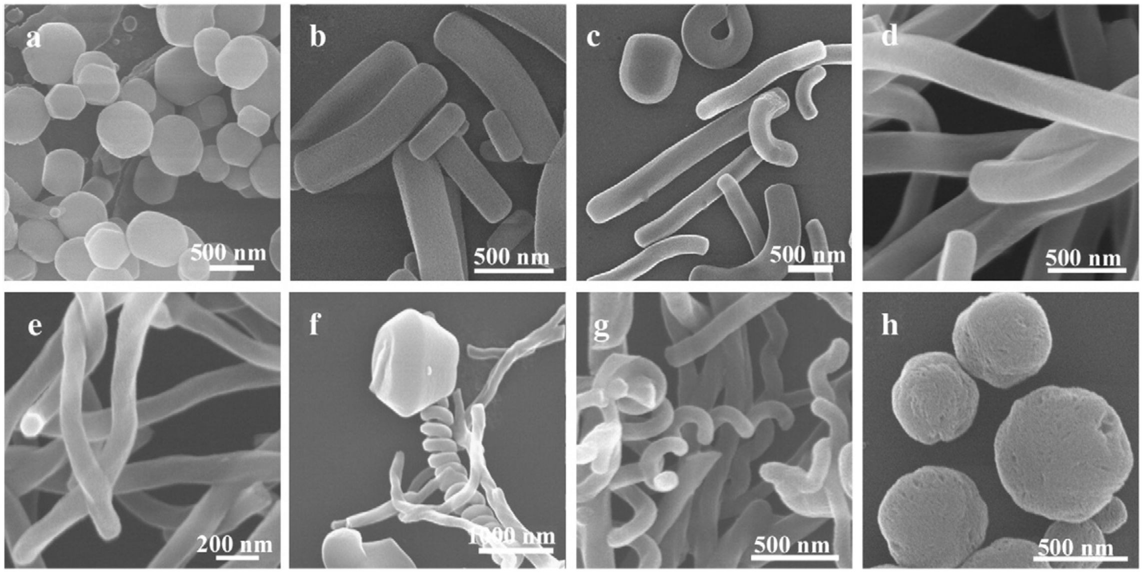

Fig. 1. FESEM images of the mesoporous ethylene–silicas. (a) S0; (b) S05; (c) S1; (d) S2; (e) S4; (f and g) S10; and (h) S20.

3. Results and discussion

The ethylene–silicas prepared at the MB/CTAB molar ratios of 0, 0.5, 1.0, 2.0, 4.0, 10, and 20 were named **S0**, **S05**, **S1**, **S2**, **S4**, **S10**, and **S20**, respectively. Fig. 1 shows the FESEM images of the ethylene–silicas. Before taking FESEM images, the samples were covered by platinum. Although helical mesoporous silicas and ethenylene–silicas can be prepared in 25 wt.% aqueous ammonia solution [4,11], only short hexagonal ethylene–silica nanorods, 200–500 nm diameter and 200–500 nm length, were obtained. Therefore, the morphology of the mesoporous solid is also sensitive to the precursor. It was shown previously that hybrid silica/surfactant micelles were formed during the sol–gel process [11]. The interactions of the bridged organic groups and the alkyl chains of the surfactants might play an important role in controlling the morphologies of the PMOs. The formation of these nanorods should follow a cooperation mechanism.

Alcohols are able to decrease the critical micelle concentrations of CTAB in aqueous [12]. The increase of the molarity of alcohol induces the formation of rod-like and worm-like micelles from sphere micelle. Hence, it is reasonable to obtain one-dimensional solid by adding MB. Although the helical ethylene–silica nanofibers were obtained in a broad range of MB/CTAB molar ratios, from 0.5 to 10, counted from the FESEM images, the number of left-handed helical nanofibers was almost equal to that of right-handed helical ones (Fig. 1b–g). The interactions between MB and CTAB are too weak to transfer the chirality of MB to the mixed micelles of CTAB and MB. The increase of entropy and the reduction of surface free energy are proposed to drive the formation of helix [4,5]. It was found recently that the increase of the interactions between chiral dopant and CTAB can enhance the tendency to form one-handed helical nanostructures [13]. For **S05**–**S10**, helical nanofibers combined with toroids (less than 10%) were identified in the FESEM images. With increasing the MB/CTAB molar

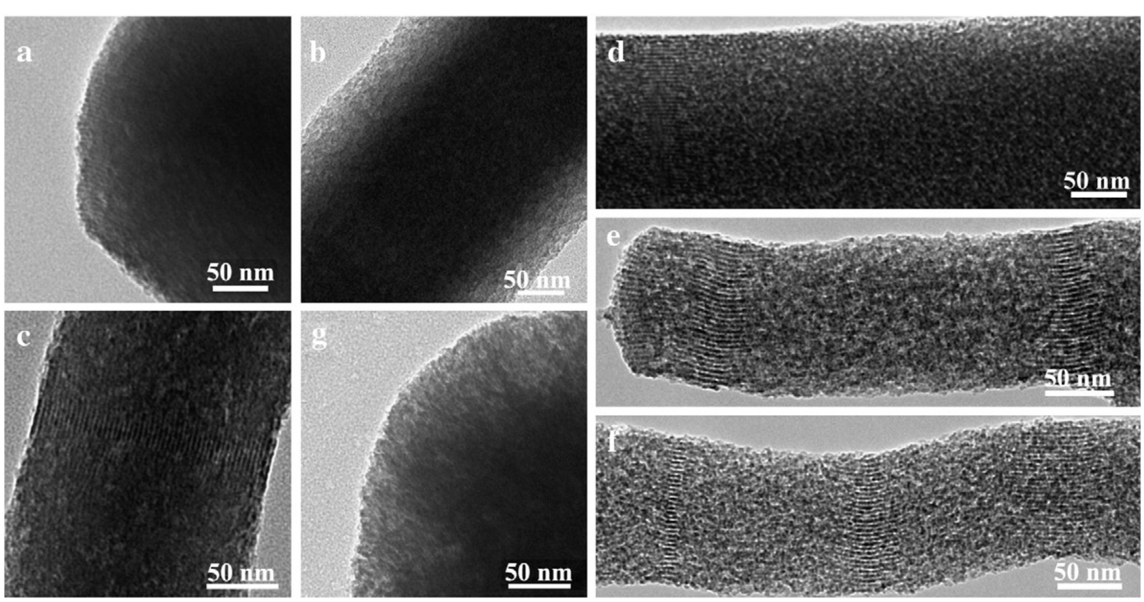

Fig. 2. TEM images of the mesoporous ethylene–silicas. (a) S0; (b) S05; (c) S1; (d) S2; (e) S4; (f) S10; and (g) S20.