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Controlling the pitch length of helical mesoporous silica (HMS)

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ABSTRACT

The effects of synthesis conditions including the co-structure directing agent (CSDA)/amphiphile molar ratio, reaction temperature, and pH value on the pitch length of the helical mesoporous silicas (HMSs) have been comprehensively investigated. It has been found that the external diameter of the HMS rod increased with increasing CSDA/amphiphile molar ratio, reaction temperature, and pH value, while the pitch length increased linearly with increasing diameter of the HMS rod in a settled condition. The driving force for the formation of HMS has been considered to be the 2d-hexagonally-ordered propeller-like micelles with moment M_0 which can be related to the pitch length (p) and diameter (d) of the micelle ($M_0 \propto \frac{d}{p}$). The shorter pitch length of the micelle would give rise to a strong moment for the hexagonally-stacked rods in the same micelle diameter, and vice versa with a longer pitch length. It was shown that the moment of the propeller-like micelle was not significantly changed by varying the TMAPS/SDS molar ratio or the pH value, but obviously affected by the reaction temperature.

1. Introduction

It is well known that various helical architectures can be formed by the self-assemblies of small molecules in nature [1–16]. General, the supramolecular chirality can be generated through the use of chiral molecules or a combination of chiral and achiral molecules. However, the spontaneous formation of chiral supramolecular assemblies from achiral molecules indicates that the supramolecular chirality is not simply generated from the molecular chirality [17–23]. Understanding the expression of molecular information at the macroscopic level in the construction of helical structures is of fundamental importance.

In these decades, chiral nanoporous inorganic materials have attracted considerable attention due to their potential applications in the fields of nano-fabrication, chiral selectivity, chiral recognition, and chiral catalysis [24,25]. Using the sol–gel transcription method [26], helical organogel structures have been successfully transferred to helical inorganic architectures such as the single-stranded helix [27], double helix [28], multiple helix [29], and inner helix [30]. Recently, we have achieved the first synthesis of chiral mesoporous silica through the self-assembling of chiral amphiphiles based upon a co-structure directing agent (CSDA) method [31–34]. Transmission electron microscopy (TEM) combined with image simulations confirmed that such material, with a twisted hexagonal rod-like morphology, possesses hexagonally-ordered channels that wind around the central axis of the rods [31–33]. The enantiomeric excess can be precisely controlled by the reaction temperature and the steric chemistry of the templating amphiphiles [35]. Helical propeller-like packing of the chiral amphiphiles is considered to be the motivity for the formation of the chiral mesoporous silica [35].

On the other hand, helical mesoporous silicas (HMSs) were successfully synthesized by using both cationic and anionic achiral amphiphiles as the template [36–39]. Tang et al. attributed the origin of the helical mesostructure to particle morphology transformation that would reduce the surface free energy [37]. Trewyn et al. reported the synthesis of HMS using room-temperature ionic liquid (RTIL) as the template, and proposed that the tight packing of the planar structure of the imidazolium groups of the RTIL would result in twisted micelles [38]. Wang et al. attributed the forming of helical mesostructures to the topological defects existing in a silicate liquid crystal seed that can initiate and direct the growth of HMS [39]. Nevertheless, the detailed mechanisms and controlling factors that enable the formation of such helical macroscopic structures, and the relationship between the molecular interactions and meso and macroscopic structure are not fully understood as yet, and hence a comprehensive understanding of the factors governing the formation of these helical structure is of great importance not only in mimicking nature but also in preprogramming molecules to give specific architecture and defined functionality [40–45].

Herein, we present detailed studies of HMS through controlling the synthetic parameters by an easy and effective method. HMSs have been synthesized by using anionic achiral amphiphile SDS as the directing agent, *N*-trimethoxysilylpropyl-*N*,*N*,*N*-trimethylammonium chloride (TMAPS) as the CSDA and tetraethyl orthosilicate (TEOS) as the silica source. The effects of synthetic parameters, such

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as the TMAPS/SDS molar ratio, temperature, and pH value upon the morphology and mesostructure of the HMSs have been carefully examined by using scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and N_2 adsorption–desorption. The present study provides not only a more controlled synthesis of HMS but also highlights a number of important features to further the study of the helicity expression in the supramolecular assemblies.

2. Experimental section

2.1. Chemicals

SDS (TCI), TMAPS, (Azmax), tetraethyl orthosilicate (TEOS, TCI) were purchased and used as received.

2.2. Synthesis

HMSs were synthesized under various conditions using SDS as the structure directing agent, TMAPS as CSDA, and TEOS as a silica source. The molar composition of the reaction mixture was: 1SDS/xTMAPS/yNaOH/7TEOS/1680H_2O, where x and y was varied in the range of 0.34–0.54 and 0–0.018, respectively. Typical synthesis was performed as follows: 0.30 g SDS and 0.17 mg NaOH were dissolved in 30 g deionized water to form a clear solution under stirring, then 1.4 g TEOS and 0.38 g TMAPS were added into the clear solution at room-temperature while the mixture was being vigorously stirred. The mixture was stirred for 0–30 min and then allowed to react at 0–50 °C under static conditions for 20 h and followed by aging for 24 h at 90 °C. The product was collected by centrifugal separation, washed with deionized water and dried at 80 °C overnight. Amphiphile was removed by exhaustive solid–liquid extraction overnight using HCl (1 M) in ethanol or calcination in air at 550 °C for 6 h.

2.3. Characterization

Powder XRD patterns were recorded on a Rigaku X-ray diffractometer D/MAX-2200/PC using Cu K_α radiation (40 kV, 20 mA) at the rate of 1.0°/min over 2θ range of 1.5–6.0°. The microscopic features of all samples were observed with SEM (JEOLJSM-7401F). To observe genuine external surface, the samples were observed without any metal coating. HRTEM images were taken from thin edges of particles supported on a porous carbon grid, using JEOL JEM-2100F electron microscope having 0.14 nm instrumental resolution equipment operated at 200 kV. The sample was suspended in ethanol using ultrasound after which a droplet of the suspension was dried on this grid. The nitrogen adsorption/desorption isotherms were measured at 77 K with a Quantachrome Nova 4200E porosimeter. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method and the pore size was obtained from the maxima of the pore size distribution curve calculated by the Barrett-Joyner-Halenda (BJH) method using the adsorption branch of the isotherm. The pH values were measured by Delta 320 pH digital meter and adjusted by using sodium hydroxide solution.

3. Results

3.1. Effect of TMAPS/SDS molar ratio on the pitch length of HMS

In our previous work, it was found that the mesoporous materials were hardly formed without CSDA (3-aminopropyltrimethoxysilane (APS) or TMAPS) in the anionic amphiphile templating system [34]. While the alteration of the state of the amphiphiles has been an effective strategy for controlling the mesophase structure based upon the charge matching between the amphiphiles and CSDA [46]. In order to investigate the effects of TMAPS on the morphology and mesostructure of the HMS products, the TMAPS/SDS molar ratio was adjusted over a range from 0.34 to 0.54; while the synthesis molar composition was: 1SDS/xTMAPS/0.0042NaOH/7TEOS/1680H_2O. The mixture was stirred with 600 rpm for 10 min at 25 °C and then allowed to react under static conditions for 6 h, and further maintained (statically) at 90 °C for 24 h.

As shown by the SEM images (Fig. 1), all of these materials were composed of rods with a twisted hexagonal rod-like morphology. It can be seen that the higher molar ratio of TMAPS/SDS gave rise to the thicker rods with smaller aspect ratio. The XRD patterns (Fig. 2) of the calcined samples synthesized with TMAPS/SDS molar ratio range of 0.38–0.46 show three well-resolved peaks in the range of $2\theta = 1.5$–$6.0°$ indexed to 10, 11 and 20 diffractions, which are characteristic two-dimensional (2d)-hexagonal *p*6*mm* mesophase. When the TMAPS/SDS molar ratio was decreased to 0.34, only one broad peak appeared in its XRD pattern, which can be assigned to the main peaks of the characteristic *p*6*mm* mesophase. Schmidt [47] has reported recently that only the (10) reflection visible in XRD pattern still have the possibility to have a high degree of ordering for the material with pore radii of 2.5–3.25 nm. Considering the material synthesized at the molar ratio of TMAS/SDS 0.34 has the pore size of 1.7 nm (Table S1). Therefore the broad peak indicates that the HMS possessed the less uniform and disordered pores. The XRD patterns of the samples prepared at TMAPS/SDS

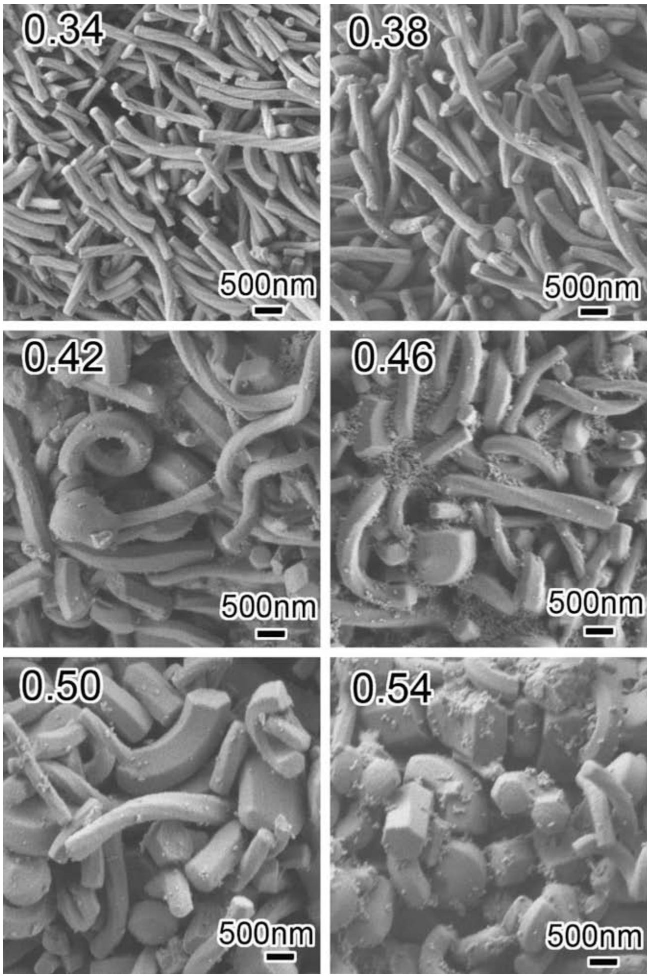

Fig. 1. SEM images of the calcined HMSs with TMAPS/SDS molar ratios of 0.34 (a), 0.38 (b), 0.42 (c), 0.46 (d), 0.50 (e) and 0.54 (f).