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# Surfactant-assisted synthesis of helical silica

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#### Abstract

Amorphous helical silica was synthesized at room temperature from tetraethoxysilane (TEOS) under the presence of cetyltrimethylammonium bromide (CTAB) in acidic conditions. The formation conditions of the silica helices were studied carefully. It was found that the reaction time and temperature, molar ratio of TEOS and CTAB and types of acids are crucial to the formation of helices. © 2006 Elsevier B.V. All rights reserved.

Keywords: Silica; Helix; Surfactant; CTAB

# 1. Introduction

In the past few years, numerous studies have been carried out on the synthesis and characterization of various quasi one-dimensional (1D) materials [1]. Recently, nanohelix has attracted much attention in nanoscience because of its unique structure and specific property [2]. Although helical structure is common in nature, e.g. double helices in DNA, it is still a hard work to obtain inorganic materials with helical morphology. Many efforts have been made to get helical nanostructures of inorganic materials by using chemical vapor deposition and template methods. Some inorganic materials with helical structure have been synthesized including carbon nanotube [3], oxides [2,4–6], metals [7] and other materials [8]. Among all of the inorganic helical nanostructures, silica is one of the most intensively studied objects [5,6]. The helical silica was normally obtained by templated methods [5] or via sol-gel pathways [6]. Helical silica has been used in enantioselective synthesis of organic compounds [9]. 1D silica can also be used in chromatography and luminescence [10], and it is becoming

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more and more important in many fields. Along with the fast increasing of application studies, more reliable and economic preparation strategies of helical silica are needed. In this paper, we reported a very convenient method for the fabrication of silica helices in solution.

## 2. Experimental

The Silica helix was synthesized by a cetyltrimethylammonium bromide (CTAB)-assisted solution approach in acidic conditions. The procedure involves the formation of a mixed solution of HNO3 and surfactant CTAB and the subsequent growth of silica helix by the hydrolyzation of the tetraethylorthosilicate (TEOS) in the above solution. A typical synthesis is as follows: A mixture of H<sub>2</sub>O/CTAB/ HNO<sub>3</sub> (H<sub>2</sub>O: 20 ml, CTAB:  $1.25 \times 10^{-3}$  mol dm<sup>-3</sup>, HNO<sub>3</sub>:  $2 \text{ mol dm}^{-3}$ ) was stirred in a 50 mL beaker at room temperature for 20 min, after which TEOS was added. The solution was then kept under quiescent conditions for 2 h. The molar ratio of H<sub>2</sub>O:HNO<sub>3</sub>:CTAB:TEOS was varied in the range of 100:3.6:0.18-0.0045:0.45. The resultant materials were filtered, washed with distilled water and ethanol several times and air-dried. Ultrasonic and stirring were also used in some experiments in order to

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study the effect of solution state. Ultrasonic irradiation was accomplished with two types of sonicator, one is B5-E Ultrasonic Cleaner ( $55 \pm 6\%$  kHz, 21 W cm<sup>-2</sup>, Bransonic, USA), and the other is JY92-2D Sonifier with a high-intensity ultrasonic probe (10 mm diameter, Ti horn, 20 kHz, 0–1000 W cm<sup>-2</sup>, Xinzhi Co., China). The morphology and size of the products were studied by transmission electron microscopy (TEM) with a JEOL 200CX microscope operating at 120 kV.

The as-prepared products were further treated by calcination at 560 °C in air for 6 h or through a solvothermal process using ethanol as solvent at 150 °C for 63 h.

### 3. Results and discussion

Fig. 1A shows a typical TEM image of as-prepared silica helices at room temperature under quiescent condition. The helices are 50–80 nm in diameter and several to tens of micrometers in length. As shown in Fig. 1B–G, except single helices, double helix and hollow helix can also be obtained in the products. The pitch distance and helical angle of different helices are diverse. The EDX spectrum reveals that the helices consist of silicon and oxygen. Selected-area electron diffraction (SAED) patterns indicate that the products were of amorphous structure.

In order to investigate the formation mechanism of helix, several experiments were carried out to determine the factors that are important for the formation of helical silica.

Adjusting the growth time can modify the quantity and diameter of helices. Along with the increase of reaction time, the quantity of helices increased at first, at the mean time, the diameter of the helices became larger (Fig. 2). However, when the reaction time exceeded 8 h, the diameter of helix became smaller and smaller and the quantity became less and less. At last, the helix disappeared. This indicates that the silica helices are unstable and this kinetically metastable state is transformed into a more thermodynamically stable phase during aging.

The concentration of CTAB is one of the important factors for the formation of helices. Silica helices were obtained at CTAB/TEOS molar ratios of 1/2.5-1/100, and no helices were produced if the ratios went beyond the range. The optimal molar ratios are 1/40-1/50 ( $C_{\text{CTAB}} = 6.25 \times 10^{-3}-5.00 \times 10^{-3} \text{ mol dm}^{-3}$ ).



Fig. 1. TEM images of silica helices under quiescent conditions for 2 h. The molar ratio of  $H_2O:HNO_3:CTAB:TEOS$  was 100:3.6:0.0113:0.45. (A) silica helices with 50–80 nm in diameter and several to tens of micrometers in length, inserted is the corresponding EDX spectrum; (B) and (C) single helix with different pitch distance; (D) double helix; (E) hollow helix; (F) hollow helix and single helix at different area of a helix; (G) amplified image of (F).



Fig. 2. TEM images of silica helices under quiescent conditions at various reaction time: (A) 1 h; (B) 2 h; (C) 3 h; (D) 8 h. The molar ratio of  $H_2O:HNO_3:CTAB:TEOS$  was 100:3.6:0.0113:0.45.

Stirring and ultrasonic were also used in the experiments (Fig. 3). No obvious change was observed for the formation of helices. When ultrasonic was used, some hollow helices and nanotubes could be found in the products in lower power (<100 W) as shown in Fig. 3C and D, and

no helical structure were obtained when the sonication power was further increased.

The use of acids is crucial to the formation of shapecontrolled silica helices. Besides  $HNO_3$ , the helices were also obtained in HBr (Fig. 4) media. Especially, beautiful



Fig. 3. TEM images of silica helices obtained at stirring and ultrasonic condition for 2 h. (A) stirring; (B) ultrasonic by a B5-E Ultrasonic Cleaner ( $55 \pm 6\%$  kHz, 21 W cm<sup>-2</sup>); (C) and (D) hollow helices and nanotubes obtained by ultrasonic using a JY92-2D Sonifier with a high-intensity ultrasonic probe (10 mm diameter, Ti horn, 20 kHz, 0–1000 W cm<sup>-2</sup>). The molar ratio of H<sub>2</sub>O:HNO<sub>3</sub>:CTAB:TEOS was 100:3.6:0.0113:0.45 in (A) and (B) and 100:3.6:0.09:0.45 in (C) and (D).



Fig. 4. Typical TEM images of silica helices obtained when HBr was used. (A) helix from stirring, (B) double helices obtained by B5-E Ultrasonic Cleaner The molar ratio of  $H_2O$ :HBr:CTAB:TEOS was 100:3.6:0.025:0.45.

double helices were obtained under sonication with the B5-E Ultrasonic Cleaner (Fig. 4b). However, no silica helices are obtained if  $H_2SO_4$ , HCl and HAc were used in the reaction. It was reported that  $NO_3^-$  and  $Br^-$  anions have greater attraction to integrate with the aggregates of CTAB (e.g. micelles) than  $SO_4^{2-}$  and Cl<sup>-</sup> and promote the formation of more complex surfactant structures [11]. This might be the reason why helical silica only formed in HNO<sub>3</sub> and HBr media.

It was found that no helix formed without the participation of surfactant CTAB. We also tried other surfactants including dodecylamine, Triton X-100, Span 40, AOT, Tween 20 and dodecyl sulphonic acid sodium

salt. However, no helix was found with these surfactants. This proves that the use of CTAB is essential to the formation of helical silica. Temperature is also another parameter influencing the formation of Silica helices. At higher temperature (e.g.  $50 \,^{\circ}$ C), no helices were got.

The products were further treated by calcination or solvothermal process (Fig. 5). The helices of silica were shortened after calcination at 560 °C for 6 h. Many pores appeared in the helices after solvothermal process using ethanol as solvent at 150 °C for 63 h. Though the morphology of the silica changed a little, however, the helical structure preserved after the treatment.



Fig. 5. (A) and (B) Silica helix after calcination at 560 °C for 6 h; (C)–(E) Silica helix after solvothermal process using ethanol as solvent at 150 °C for 63 h. The molar ratio of  $H_2O:HNO_3:CTAB:TEOS$  in (A) and (B) was 100:3.6:0.0113:0.45.

Based on the above experimental results and discussion, although the exact formation mechanism is not clear, a possible process of silica helices can be proposed. The critical micelle concentration  $C_{\rm min}$  of CTAB is  $9.2 \times 10^{-4} \text{ mol dm}^{-3}$  [12], which is lower than the CTAB concentration used in the reaction system. Thus, the CTAB tend to self-assemble and form some aggregations. When HNO<sub>3</sub> and HBr are used, NO<sub>3</sub><sup>-</sup> and Br<sup>-</sup> anions have greater affinity to the ammonium ions and they can combine with micelle of CTAB to promote the formation of the complex surfactant structure. The complex surfactant structure may act as the templates of helical silica. Furthermore, as the hydrolysis of TEOS is complicated, the reciprocity of CTAB and TEOS may cause the formation of silica with helical structure. Further research is needed to investigate the formation mechanisms in detail.

## 4. Conclusion

Amorphous silica helices have been synthesized with the help of CTAB in acidic aqueous solutions. The formation of silica with helical structure may come from the reciprocity of CTAB and TEOS. The use of CTAB and HNO<sub>3</sub> or HBr is essential to the formation of helical structure. Growth time and temperature and molar ratio of CTAB and TEOS are also important. The method demonstrated here could be extended to the synthesis of other nanomaterials.

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