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A novel hydrothermal route to the synthesis of xonotlite nanofibers and investigation on their bioactivity

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Abstract Xonotlite nanofibers were synthesized under hydrothermal condition by controlling reaction time and the temperature combined with cationic surfactant as templates. The result showed that long reaction time and low reaction temperature favored the formation of xonotlite nanofibers. The nanofibers obtained at 180 °C for 30 h in the presence of cationic surfactant have high aspect ratios more than 100 with diameters of 50–200 nm. The formation mechanism of xonotlite nanofibers was assumed to be a template-based synthesis and cationic surfactants could be used as templates. The evaluation of bioactivity revealed that bonelike apatite could be formed on the surface of xonotlite nanofibers after soaking in simulated body fluid (SBF) for 7 days and xonotlite nanofibers could be potential candidate as reinforcement reagents for preparation of bioactive composites.

Introduction

Because of their promise as advanced materials and in advanced technologies, one-dimensional nanoscale building blocks, such as nanotubes, nanofibers and nanorods with uniform sizes and aspect ratios, have been intensively explored. The preparation of nanofibers from cheap and commonly available materials is of interest since nanofibers might find applications in fabricating nanodevices and in nanoscale electronic transportation, and could be used as additive of nanostructured materials to improve material properties on the basis of their structures and properties.

Preparation of calcium silicate hydrate fibers, especially xonotlite and tobermorite, has been attracting attention in recent years. This arises from the fact that these fibers are widely required in modern industry [1, 2]. Previous studies suggested that various biomaterials containing calcium silicate component such as Bioglass [3, 4], $CaSiO_3$ [5] and Ca_2SiO_4 ceramics [6, 7] were bioactive and could induce the formation of the bonelike apatite in the simulated body fluid (SBF). Therefore, as a hydrate calcium silicate, we supposed that, xonotlite could be bioactive and the nanofibers could be potential candidate as reinforcement reagents for preparation of bioactive composites. Xonotlite fibers are usually prepared from suspension of silica and calcium hydroxide by hydrothermal treatment. However, the synthesis of the nanofibers has not been reported.

Investigations on hydrothermal synthesis of calcium silicate hydrate fibers at high temperature (250–350 °C), long time (72–200 h) and using special instrument (continuous-type or multichamber autoclave) have been reported in literatures [8–10]. According to these studies, high hydrothermal temperature results in the increase of the size of the prepared fibers. Therefore, in order to obtain nanosized xonotlite fibers, we used a cationic surfactant, cetyltrimethylammonium bromide (CTAB), as the template and highly reactive reagents (tetraethyl orthosilicate (TEOS) and newly synthesized $Ca(OH)_2$) to reduce the synthesis temperature. The bioactivity of the xonotlite nanofibers was also evaluated by soaking in SBF.

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Experiment

Synthesis and characterization of xonotlite nanofibers

The procedure employed for the synthesis of xonotlite nanofibers is as follows. 0.3 g CTAB was dissolved in 60 ml distilled water and 4 ml TEOS was added. The solution was stirred for 5 min using a magnetic stirrer and then dispersed by ultrasonic until TEOS/water emulsion formed. 3.68 g $Ca(NO_3)_2 \cdot 4H_2O$ and 1.24 g NaOH were dissolved in 20 ml distilled water respectively. NaOH solution was then dropped into $Ca(NO_3)_2$ solution to obtain $Ca(OH)_2$ suspension. The $Ca(OH)_2$ suspension was homogenously mixed with the TEOS/water emulsion. The pH of the final suspension is 11.8. The suspension was then transferred into stainless steel autoclaves, and heated at 180 °C for 5, 10, 30 h respectively, followed by cooling to room temperature naturally. In order to determine the influence of temperature, the hydrothermal reaction was also performed at 200 °C for 30 h with addition of CTAB. In addition, the reaction was performed at 180 °C for 30 h without CTAB to determine the effect of CTAB. After the hydrothermal reaction, the obtained suspension was filtrated and washed with distilled water and anhydrous ethanol for three times, respectively. The resultant powders were dried at 60 °C for 72 h. The products were characterized by X-ray diffraction (XRD, D_{max} 2550V, Rigaku Co., Japan) with monochromated Cu K_α radiation ($\lambda = 0.154178$ nm). A scan rate of 0.02 s^{-1} was applied to record the patterns in the 2θ range of 20–60°. The morphology and sizes of the powders were characterized by a field emission scanning electron microscope (SEM; JSM-6700F, JEOL Co., Japan).

Evaluation of in vitro bioactivity

The bioactivity of the xonotlite nanofibers was evaluated by examining the apatite deposition on the nanofibers in SBF, which was prepared as previously described by Kokubo and had similar ion concentrations to those in human blood plasma (BP) [11] The nanofibers were soaked in the SBF at 37 °C for 7 days at a solid/liquid ratio of 1.5 mg/ml. After soaking, the nanofibers were filtered and washed in distilled water for three times, and finally dried at 60°C. The formation of apatite on the nanofibers was characterized by XRD and the morphology of the samples was observed using SEM.

Results and discussion

Synthesis and characterization of xonotlite nanofibers

TEOS is an active reagent which could hydrolysis to alcohol and silicic acid in water, so we used TEOS as Si source and newly synthesized $Ca(OH)_2$ as highly reactive Ca supplier. The high reactivity of TEOS and $Ca(OH)_2$ ensure the synthesis of xonotlite nanofibers at relative lower temperature.

The effect of varying hydrothermal reaction time from 5 h to 30 h was investigated. All products were identified as xonotlite by XRD diffraction (Fig. 1). It is clear to see from Fig. 1 that the products hydrothermal treated for 5 and 10 h showed poor crystallinity, and good crystallinity was obtained when the hydrothermal reaction increased to 30 h, and the peaks become sharper with increase of the hydrothermal treatment time, which indicated that the xonotlite crystal grew bigger and this was confirmed by the SEM analysis (Fig. 2). Figure 2a shows the SEM micrograph of products after 5 h hydrothermal treatment, it could be seen that no fibers formed (Fig. 2a). With the hydrothermal treatment prolonged to 10 h, a little xonotlite nanofibers with diameter in 100 nm were observed (Fig. 2b). When hydrothermal treatment prolonged to 30 h, the final product was composed of xonotlite nanofibers (Fig. 2c) which have a diameter from 50 nm to 200 nm and 10–15 μm in length. The result suggests that long hydrothermal treatment favors the formation of fibrous structure.

The hydrothermal treatments were performed with addition of CTAB for 30 h at 200 and 180 °C respectively to investigate the effect of the temperature. It could be seen that the size of the fibers synthesized at 200 °C was bigger compared with the products synthesized at 180 °C and some fibers aggregated to bundles with 500 nm in diameter (Fig. 2d). The result suggests that low temperature favors the decrease of fiber size.

In order to investigate the effect of CTAB, the hydrothermal treatment was performed at 180 °C for 30 h without CTAB. The product was composed of granules and fibers (Fig. 3a, b), and most of the fibers are 500 nm in diameter, suggesting that CTAB was critical for the synthesis of xonotlite nanofibers.

As for the effect of CTAB, one is the emulsification in TEOS/water system, which facilitates the homogenously mixing of the raw materials. In addition, CTAB can inhibit

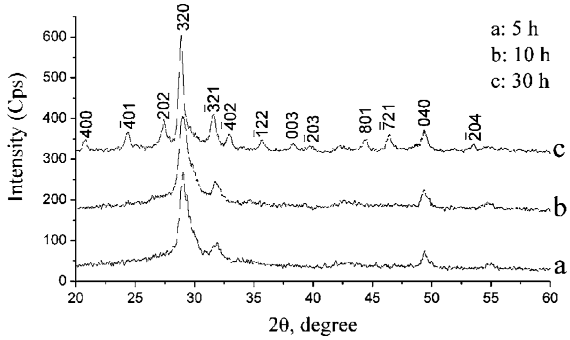

Fig. 1 XRD patterns of xonotlite fibers hydrothermal treatment for different time

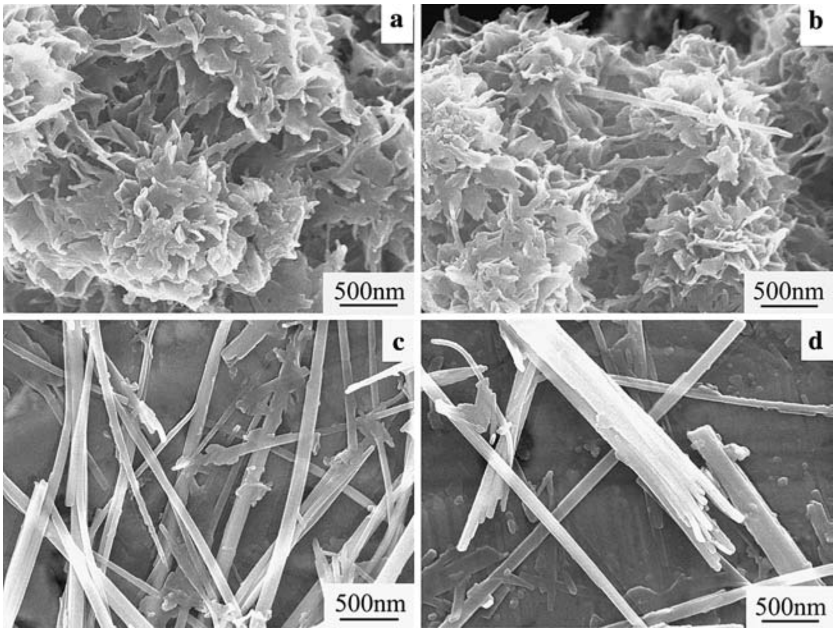

Fig. 2 SEM images of xonotlite hydrothermally synthesized under different conditions (**a**) 5 h at 180°C with CTAB, (**b**) 10 h at 180°C with CTAB, (**c**) 30 h at 180°C with CTAB, (**d**) 30 h at 200°C with CTAB

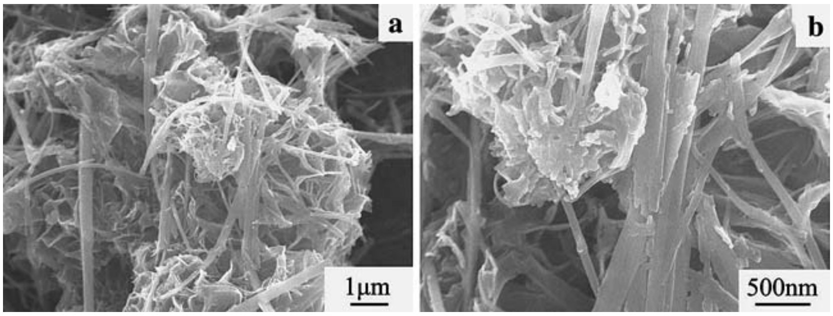

Fig. 3 SEM images of xonotlite after hydrothermal treatment for 30 h at 180°C without CTAB

the excess aggregation of nanofibers through its adsorption on the surface of the nanofibers. But the most important is, similar to other surfactants, that CTAB was thought to be able to act as a template [12]. CTAB is a cationic surfactant and its critical micelle concentration (CMC) is 0.03% (0.9–1.0 mM) [13]. Above the CMC, transition from spherical micelles to rod-like micelles occurred, and the size of micelles increased with the increase of CTAB concentration, eventually resulting in long, flexible wormlike micelles [14]. In our system, with CTAB concentration of 0.3%, CTAB could easily form rod-like micelles.

According to the mechanism suggested by Yao and Xiong on the synthesis of nanostructured hydroxyapatite and CdS [15, 16], the formation of xonotlite nanofibers might be explained as the following: The CTAB formed rod-like micelles in which TEOS oil phase was enwrapped. Because of the concentration difference between the inside (TEOS oil phase) and outside (water phase) of the rod-like micelles, the SiO_3^{2-} transferred to the surface of the micelles and CTAB-SiO_3^{2-} rod-like micelles formed. In the presence of Ca^{2+}, calcium silicate hydrate clusters were preferentially condensed on the rod-like micellar surface. The micelles act as nucleating sites for the growth of xonotlite crystals. During the hydrothermal stage, CTAB-xonotlite complexes formed and coalesced to form a stable three-dimensional fibrous structure.

Evaluation of in vitro bioactivity

Figure 4 shows the SEM micrograph of the xonotlite nanofibers after soaking in SBF for 7 days. It was obvious that a layer of nanocrystals with a fine structure of apatite overgrew on the surface of the xonotlite nanofibers. Figure 5 shows XRD patterns of xonotlite nanofibers after soaking in SBF for 7 days. It can be seen that, broad diffraction patterns ascribed to low crystalline apatite were observed at 2θ of 25.9° and 31.7° and the peaks of xonotlite weakened.

It is obvious from the results described above that the xonotlite nanofibers could develop an apatite layer on the surface when soaked in SBF. It is considered that an apatite layer, which precipitates on the surface of a bioactive material in human body, plays an essential role in forming the chemical bond to the living bone. The apatite layer can

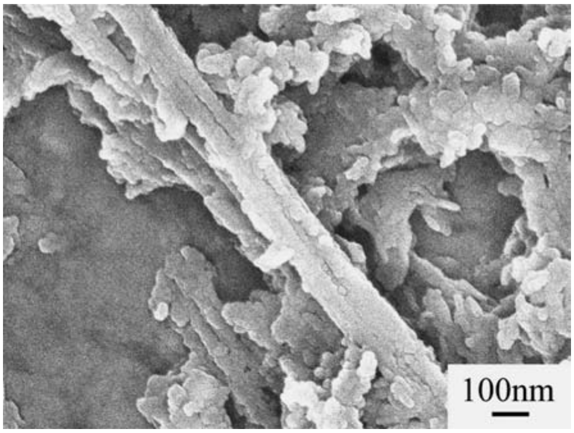

Fig. 4 SEM images of xonotlite nanofibers after soaking in SBF for 7 days

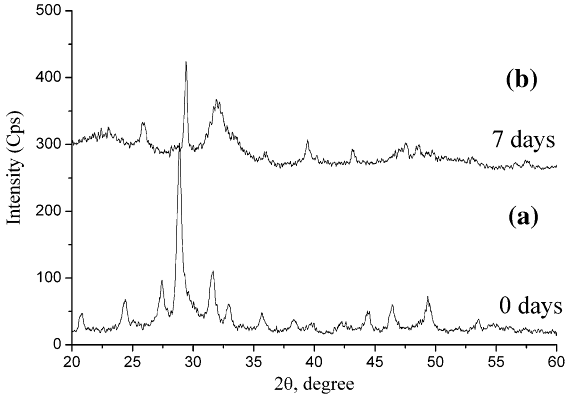

Fig. 5 XRD patterns of xonotlite nanofibers before (**a**) and after (**b**) soaking in SBF for 7 days

be reproduced in vitro in SBF and previous studies showed that, calcium silicate could induce the apatite deposition when soaking in SBF and could be used as bioactive component for preparation of bioactive composites [17]. However, calcination at high temperature (above 800°C) is required for the preparation of calcium silicate ceramic powders. In our study, we showed that xonotlite, a hydrate calcium silicate, could induce the apatite deposition in SBF, while the preparation temperature was much lower as compared to that for preparation of calcium silicate. This result suggests that xonotlite might be a more economic reinforcement reagent for preparation of bioactive composites.

Conclusion

Xonotlite nanofibers were synthesized through a novel hydrothermal route by controlling reaction time and temperature. The synthesized xonotlite nanofibers had a length of 10–15 μm and 50–200 nm in diameter. Long reaction time, low reaction temperature and the presence of CTAB favored the synthesis of xonotlite nanofibers. The xonotlite nanofibers have excellent in vitro bioactivity as shown by the formation of apatite in SBF and could be potential candidate as reinforcement reagents for preparation of bioactive composites.

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