Preparation of Calcium Silicate Nanobelts and the In Vitro Behavior in a Simulated Body Fluid

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Single-crystalline $CaSiO_3$ nanobelts were prepared via a simple solvothermal routine. The synthesized material revealed bioactive response when immersed in a simulated body fluid (SBF) solution, suggesting its potential application as biomedical materials.

Silicates are widely employed in industries because of their important properties, such as high strength, creep resistance, chemical inertness, thermal stability, low thermal expansion, and low thermal conductivity.[1,2] Calcium silicates are important for the construction industry, in which millions of tons of calcium silicate cement are consumed every year. Beside this, calcium silicates are also employed to strengthen polymeric materials.[3–5] Recently, an apatite layer was observed on plasma-sprayed calcium silicate coatings when they were exposed to an SBF, suggesting a potential application of calcium silicate in biotechnology.[6] Shortly after the report, some other studies reported the preparation of calcium silicate materials with the evaluation of their bioactivity both in vitro and in vivo.[7–9] In several cases, wollastonite ceramics was found to be useful in biomedical industry for artificial bone and dental root, since the material showed good bioactivity and biocompatibility.[7,8] Furthermore, it is also found that the formation of apatite on $CaSiO_3$ ceramics is much faster than that on other bioglass or glass-ceramics in SBFs.[7,9] Beside the coating and bulk materials, the bioresponse of granular $CaSiO_3$ powders in SBF solutions was also reported.[10,11] Up to now, calcium silicates with such granular shapes have been obtained mostly through chemical precipitation or hydrothermal methods with grain size at a micron scale,[12,13] and the method to synthesize the material in other shapes, such as nanorod, nanowire, or nanobelt, has not been developed yet. These one-dimensional materials are of special interests in promoting the bioactivity and enhancing the fracture strength of biodegradable polymers, such as poly(lactic acid) (PLA), poly(glycolic acid) (PGA), and their copolymers, for artificial scaffolds in bone tissue engineering. In this study, β-$CaSiO_3$, with a novel nanobelt shape, has been successfully synthesized via calcination of Xonotlite nanobelts obtained through solvothermal route at 120 °C. In vitro test, the compacted nanobelts soaked in an SBF showed good bioactivity, implying that the β-$CaSiO_3$ nanobelts prepared possess potential application as bioactive materials.

A solvothermal method was employed to prepare the Xonotlite precursor. A Ca solution (0.1 mol/L) and an Si solution (0.1 mol/L) were separately prepared by dissolving $Ca(NO_3)_2 \cdot 4H_2O$ and $Na_2SiO_3 \cdot 9H_2O$ in deionized water. The Na_2SiO_3 solution (20 mL) was slowly added to the $Ca(NO_3)_2$ solution (20 mL) with stirring. White precipitate appeared immediately. The precipitate was filtered, washed three times with deionized water, then dispersed in acetone, and transferred into a Teflon-linked autoclave. The autoclave was sealed and heated at 120 °C for 72 h. The solution was finally cooled down to room temperature. The resulting powder obtained by this solvothermal process was collected by filtration, dried at 80 °C for several hours, and calcinated at 850 °C to obtain the final β-$CaSiO_3$ nanobelts.

Phase identification was conducted by X-ray diffraction (XRD) method. As shown in Figure 1, the XRD pattern of the

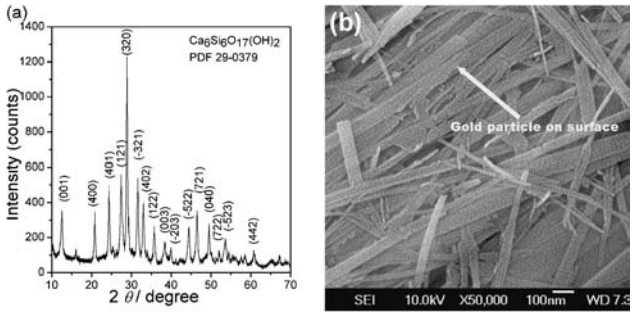

Figure 1. XRD pattern (a) and SEM micrograph (b) of the Xonotlite precursor.

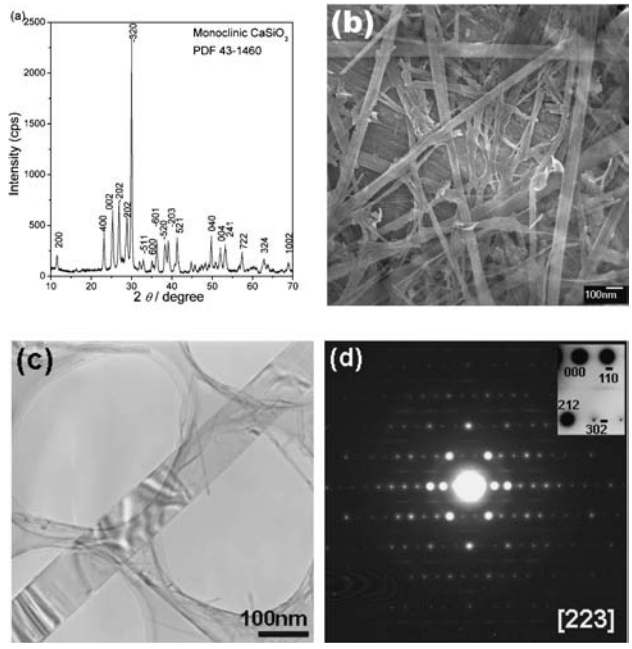

Figure 2. XRD pattern and SEM/TEM micrographs of β-$CaSiO_3$ nanobelts. (a) XRD pattern, (b) SEM micrograph, (c) TEM micrograph, and (d) SAED for the single crystal.

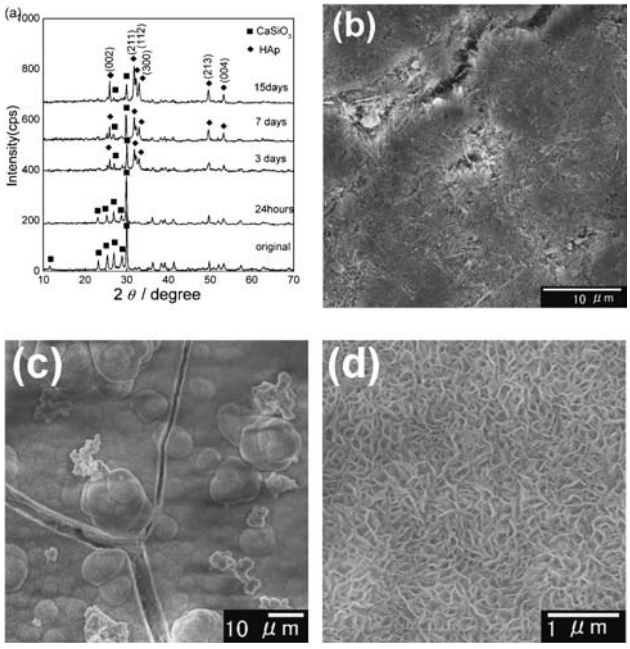

Figure 3. XRD patterns and SEM micrographs of β-$CaSiO_3$ after soaking for various duration, indicating the formation of an HAp layer. (a) XRD patterns after immersion for various durations. (b) SEI of initial surface of the pellet. (c) SEI of the sample surface after soaking for 15 days. (d) A magnified image of (c) focusing on the surface of HAp particles.

Xonotlite precursor reveals a pure phase with good crystallinity, and the peaks in the pattern can be indexed as a monoclinic structure, with the unit cell parameters $a = 17.02$, $b = 7.356$, $c = 7.007$ Å, and $\beta = 90.34^\circ$, which are in good agreement with those of Xonotlite (JCPDS card: No. 29-0379). The slight broadness of the peaks also indicates that very fine crystals were obtained by the present solvothermal routine. A second electron image (SEI) by scanning electron microscopy (SEM) of the synthesized material shows belt-like textures (Figure 1b). The fine particles on the nanobelts are gold particles, which were sputtered onto the surface of the nanobelts to prevent the charge-up effects. Although it is hard to tell the accurate size of such nanobelts, the average width of the nanobelts can be estimated to be 100–200 nm.

The β-$CaSiO_3$ nanobelts were obtained simply by calcination of the precursor under 850 °C for 4 h. The XRD pattern for the calcinated product shown in Figure 2a was indexed into another monoclinic structure, with $a = 15.42$, $b = 7.325$, $c = 7.069$ Å and $\beta = 95.38^\circ$, which is in good agreement with the crystal structure of β-$CaSiO_3$ (JCPDS card: No. 43-1460). The SEM and TEM micrographs, shown in Figures 2b and 2c, show that the belt-like morphology of the Xonotlite precursor was preserved even after the calcination, as well as dimension of the nanobelts ($\approx$100 nm in width). The selected area electron diffraction (SAED) viewed along [223] zone axis indicated the single crystalline nature of the nanobelts (Figure 2d).

The formation of hydroxyapatite (HAp) on the β-$CaSiO_3$ pellet after soaking in an SBF with various soaking time was investigated by XRD and SEM. After 3 days of soaking, diffractions from β-$CaSiO_3$ decreased, and some additional peaks corresponding to HAp appeared around 32 degree of 2θ in Figure 3a. With increasing soaking time, the diffraction intensities from β-$CaSiO_3$ became weaker, while those from HAp became stronger. After 15 days of soaking, β-$CaSiO_3$ was entirely covered by an HAp layer, and only the strongest diffraction peaks from β-$CaSiO_3$ could be observed. Such HAp formation on a nanobelt β-$CaSiO_3$ pellet was similarly observed in our previous study.[14] Figure 3b shows the initial surface of the pellet before soaking in an SBF solution, where a nanobelt-like structure is observed. However, after soaking in an SBF solution for 15 days, the pellet surface became smooth with some fractures, and granular HAp crystals formed on the surface of the pellet (see Figure 3c). A magnified image of the granular HAp crystals shown in Figure 3d clearly shows a fine lathlike network texture, which is very similar to that of apatite in human bone. These results suggest that such β-$CaSiO_3$ nanobelts can be utilized to develop bone-like HAp layers on its surface when exposed to SBF. It is commonly agreed that bone like HAp plays an important role in the formation and growth of tissue–biomaterial interface. Therefore, the results obtained in this study indicate that β-$CaSiO_3$ nanobelts possess high bioactivity and may be used for the preparation of bioactive materials.

In summary, single-crystalline β-$CaSiO_3$ nanobelts were obtained via a simple solvothermal routine: preparation of Xonotlite nanobelts precursor (100–200 nm of the width) through the solvothermal method and dehydration of the precursor. The in vitro test in an SBF solution revealed the formation of an HAp layer on the compacted surface, suggesting potential application of these nanobelts as bioactive materials.

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