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The growth mechanism of needle-like aragonite crystal

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Calcium carbonate ($CaCO_3$) is one of the most studied minerals among the barely soluble substances, since precipitation of $CaCO_3$ is a widely occurring process in biomineralization as well as in manufacturing process of industrial materials. For example, its needle-like crystals with high aspect ratios have been used as fillers to improve mechanical properties of paper and polymer materials [1]. To control the morphology or polymorph of $CaCO_3$ crystal, the effect of additives on the crystallization of $CaCO_3$ has been studied [2]. However, the growth mechanism of calcium carbonate crystals has been poorly understood yet. Understanding of the growth mechanism is important for constructing materials with morphology and function as we aim.

With respect to the needle-like crystals, two types of crystallization mechanism have been considered. One is VLS (vapor-liquid-solid) mechanism, which has been observed in formation of Si whisker [3]. Another is Frank mechanism with spiral dislocation, which is considered as a formation mechanism of NaCl whisker from solutions [4]. In this study, we synthesized needle-like aragonite crystals from solution. In order to understand the growth process of the needle-like aragonite crystal, we observed the tip of it in details by using electron microscopy.

We synthesized needle-like aragonite crystal by pouring Na_2CO_3 solution into the 40 ml of $CaCl_2$ solution with the rate of 1 mL min^{-1}. We stopped the inflow when the total volume of poured Na_2CO_3 solution reached 40 ml. The mixed solution was stirred at 300 rpm for about 3 h. The concentrations of $CaCl_2$ and Na_2CO_3 solutions are the same; we considered two cases of 0.005 and 0.05 mol/l. We controlled the temperature of solution at constant as 25, 50 and 80 deg C during precipitation. The morphology and the size of the precipitates were observed by scanning electron microscopy (SEM), and their crystalline phases were identified by X-ray diffraction (XRD).

The crystals obtained in the experiment were mainly needle-like aragonite and spherules of vaterite. The length of needle-like aragonite was about 2 -20 micrommeters. The aspect ratio was estimated from 5:1 to 20:1. For vaterite, the size was about 2-5 micrometers. The total amount of precipitated crystals definitely depended on the concentration of initial solutions: many precipitates for higher concentration and few precipitates for lower concentration. The reaction temperature obviously affected the crystalline phases; aragonite was mainly crystallized at 80 and 50 deg C, on the other hand, vaterite particles appeared at 50 and 25 deg C. The morphologies were also affected by the reaction temperature. Vaterite changed from circular disc to sphere according to the decrease of reaction temperature from 50 deg C to 25 deg C. It was also seen that the higher the reaction temperature, the larger the aspect ratio of needle-like aragonite.

By detailed SEM observation, we showed that the needle-like aragonite has multi-step on the tip, which seemed higher than monomolecular step. Based on the experimental results, possible growth mechanism of needle-like aragonite was proposed.

Reference:
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