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Synthesis and characterization of aragonite whiskers by a novel and simple route

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A novel and simple synthetic method for the preparation of aragonite whiskers has been developed, whereby aqueous solutions of $CaCl_2$ and Na_2CO_3 are combined in the presence of a suitable surfactant, poly(ethylene glycol)-20 000 (abbreviated as PEG), under ambient reaction conditions. The whiskers have high aspect ratios ranging from 20 to 80 with diameters in the range 0.50–1 μm. They were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. The formation of aragonite whiskers is due to the soft template effect of PEG.

1 Introduction

The control of the crystal shape or morphology of $CaCO_3$ is important to its industrial uses. Ground or synthesized $CaCO_3$ granules are now used in structural engineering applications as fillers for fabrication of polymer composite materials. Recently, needle-like $CaCO_3$ crystals with high aspect ratios have been in great demand for the improvement of mechanical properties of polymer materials. Many researchers have been concentrating on the synthesis of needle-like $CaCO_3$ crystals.[1–9]

Synthesis of $CaCO_3$ was followed by two basic synthetic routes: (1) the solution route[9,10] through a double decomposition reaction, wherein aqueous $CaCl_2$ and Na_2CO_3, or $CaCl_2$ and $(NH_4)_2CO_3$, or $Ca(NO_3)_2$ and Na_2CO_3 are combined in an equal molar ratio; and (2) the carbonation method,[11] in which CO_2 gas is bubbled through an aqueous slurry of $Ca(OH)_2$. The latter is preferred in terms of environment preservation and the effective use of mineral resources. The carbonation method is an industrially useful method, but it is difficult to control the crystal shape and modification of $CaCO_3$. Granular calcite is usually easy to precipitate.

Tanaka *et al.*[5] synthesized needle-like aragonite by reaction of the milk of lime-containing aragonite seed crystal with CO_2-containing gas. However, the reaction must be regulated within pH 8–9 by careful addition of CO_2-containing gas to obtain the needle-like aragonite.

Here, we report a novel and easy approach for the synthesis of $CaCO_3$ (aragonite) whiskers. The preparation involves double decomposition of an aqueous solution of $CaCl_2$ and Na_2CO_3 in the presence of a suitable surfactant, PEG, at about 90 °C, without use of complex apparatus. Aragonite whiskers can be produced easily and effectively without complicated control of the reaction conditions.

2 Experimental

All of the chemical reagents used in this experiment were of analytical grade. The procedure employed for the synthesis of $CaCO_3$ (aragonite) whiskers is as follows. 500 mg of PEG solid were added to 250 ml of 0.01 M $CaCl_2$ solution. This solution was stirred for 10–15 min using a magnetic stirrer in order to ensure that the PEG surfactant was completely dissolved. Then 250 ml of 0.01 M Na_2CO_3 solution was added to the $CaCl_2$ solution, whose temperature was maintained at 90 ± 2 °C till completion of the reaction under constant stirring. The precipitate was filtered off, washed with distilled water several times, and then dried for 3 h in an oven at 100 °C.

The crystal structure and composition of the specimens were analyzed by powder X-ray diffraction (XRD) using a Rigaku D_{max} γ_A X-ray diffractometer with Cu-Kα 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°. Powder morphology and size were characterized by transmission electron microscopy (TEM) on a JEM-200 CX transmission electron microscope, using an accelerating voltage of 200 kV. Infrared spectra were recorded by using a Nicolet 170 SX Fourier transform infrared (FTIR) spectrometer employing a KBr pellet method. Laser Raman spectra were obtained using a SPEX-1403 Ramanscope. The 514.5 nm line of the laser was the excitation source, with the capability of supplying 30 mW power.

3 Results and discussion

3.1 Characterization

Aragonite can be distinguished from the other two calcium carbonates (calcite and vaterite) on the basis of its characteristic powder X-ray diffraction (XRD) pattern and IR or Raman vibrational spectra. Fig. 1 shows the XRD pattern of a sample of aragonite whiskers as prepared by the method described above. It was compared with the data from the JCPDS file No. 5-453 and all peaks of the obtained product can be assigned to those of aragonite crystals, indicating the formation of single-phase aragonite.

Characteristic carbonate IR vibrations for aragonite are shown in Fig. 2. Aragonite displays a characteristic symmetric carbonate stretching vibration (ν_1) at 1083 cm^{-1} and a carbonate out-of-plane bending vibration (ν_2) at 853 cm^{-1} in its FTIR spectrum. While the symmetric stretching (ν_1) vibration is both IR- and Raman-active for aragonite, it is only Raman-active in the case of calcite. Therefore, the peak around 1080 cm^{-1} is sometimes used to quantify aragonite from a mixture of aragonite and calcite.[12]

The Raman spectrum for the as-prepared sample is shown in Fig. 3. Raman spectra can also be used to identify and

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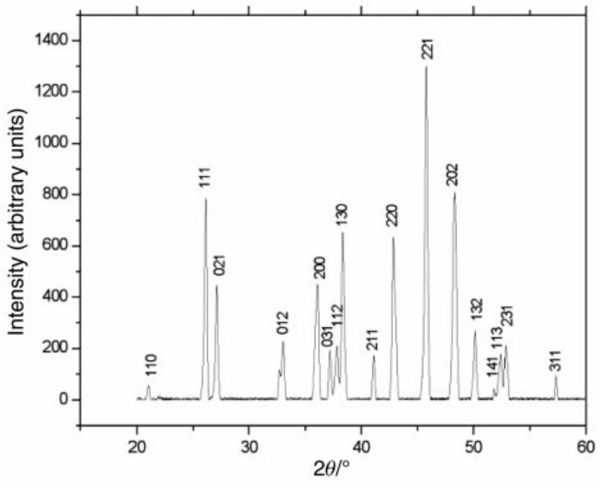

Fig. 1 XRD pattern of the as-prepared product.

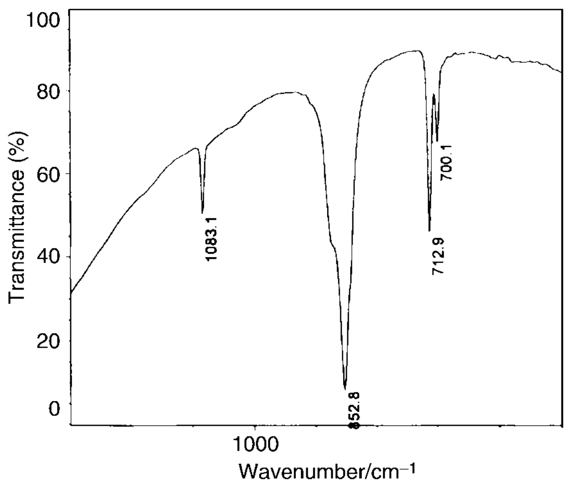

Fig. 2 FTIR spectrum of the sample showing its characteristic carbonate vibrational bands.

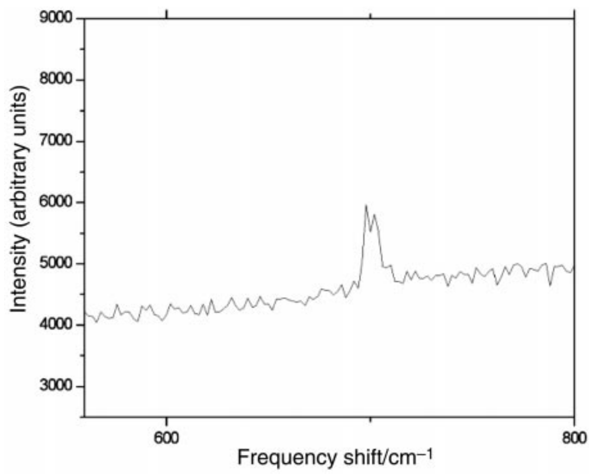

Fig. 3 Raman spectrum showing the characteristic doublet feature due to the 'in-plane' bending mode of the carbonate group in aragonite whiskers.

distinguish aragonite from the other two calcium carbonate phases. According to ref. 13, a pair of peaks at 700 and 704 cm^{-1} is characteristic of aragonite and is present in our sample. For aragonite, the site symmetry of the CO_3^{2-} ion

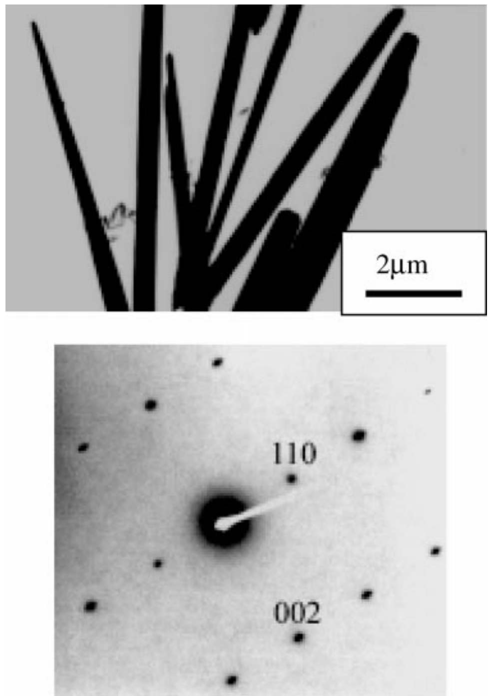

Fig. 4 TEM image (top) and SAD pattern (bottom) of the $CaCO_3$ crystal obtained.

causes the two doubly degenerate ν_4 in-plane bending modes to split into a pair of non-degenerate modes.[14]

Fig. 4 shows the TEM image and the selected area diffraction (SAD) pattern of a needle-like crystal of aragonite. The TEM images of aragonite whiskers revealed that these materials have a smooth surface and a rod-like shape, of 0.5–1 μm in diameter and 10–50 μm in length. The SAD pattern demonstrates that the fibrous product obtained is a single crystal consisting of an aragonite phase. Therefore, the TEM image and the SAD pattern of aragonite whiskers indicate that the crystallization quality of the whiskers is very good.

3.2 Effect of the surfactant PEG

The present study demonstrates that it is possible to prepare aragonite whiskers by using double decomposition of an aqueous solution of $CaCl_2$ and Na_2CO_3 in the presence of the surfactant PEG at about 90 °C. We believe that the PEG plays an important role in controlling the aragonite shape due to the following reasons: PEG is a non-ionic surfactant; and according to recent reports,[15–18] the PEG monomer (CH_2–CH_2–O) can easily form long chain structures in aqueous solution. $CaCO_3$ may therefore be grown along these long chains when Ca^{2+} ions meet with CO_3^{2-} ions, and hence PEG may be used as a soft template in the synthesis of aragonite whiskers.

4 Conclusions

We have described a novel and easy method to synthesize aragonite whiskers which have high aspect ratios from 20 to 80 with diameters of 0.5–1 μm by using the double decomposition reaction of $CaCl_2$ and Na_2CO_3 in the presence of the surfactant PEG. This method requires no complex apparatus and techniques. Aragonite whiskers can be produced easily and effectively without complicated control of the reaction conditions. We attribute the formation of aragonite whiskers to the soft template effect of PEG.

Acknowledgements

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