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Dendritic crystallization of inorganic salts in the presence of nanocrystalline cellulose

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ABSTRACT

Crystallization of inorganic salts (NaCl, $CuSO_4 \cdot 5H_2O$, and $NiSO_4 \cdot 6H_2O$) in the presence of nanocrystalline cellulose results in dendritic growth. The dendritic crystals obtained with nanocrystalline cellulose as an additive are pure inorganic salts.

1. Introduction

The recent emphasis of materials science on the design of hierarchically self-assembled and organized nanomaterials has triggered an unprecedented input of biological concepts including building blocks, functions and mechanisms into the synthesis of materials with advanced sustainable properties [1,2]. It is a promising route to use organic templates to control the nucleation, growth, and alignment of inorganic materials, which has received much attention in recent years [3]. Taking advantage of the morphological features of nanocelluloses and their ability to self-organize, these nanosized particles have been investigated as renewable templates to control the size, structure and organization of inorganic materials as well [4]. Moreover, studies on nanocellulose and its biocomposites indicate that nanocellulose-based materials have the potential for bone tissue regeneration and healing applications [5]. The properties and applications of inorganic materials strongly depend on their morphology, structure, particle size and chemical purity. Compared with size control, morphology control by means of classical procedures of colloid chemistry is more difficult to achieve. Although various organic compounds have been used to synthesize inorganic crystals with various morphologies, polymorphs, and metastable phases, it is still very difficult to reveal the real manipulation mechanism of organics in biomineralization [6].

The aim of the present article is to study the crystallization of some inorganic salts (NaCl, $CuSO_4 \cdot 5H_2O$, and $NiSO_4 \cdot 6H_2O$) in the presence of nanocrystalline cellulose.

2. Experimental

Materials: Powder of commercial microcrystalline cellulose (~20 μm, Aldrich) has been used as a starting material. Aqueous dispersion of nanocrystalline cellulose was prepared by the acid hydrolysis of microcrystalline cellulose as described previously [7]. The hydrolysis was carried out in sulfuric acid solution (62 wt%) at 50 °C during 180 min under vigorous agitation [8].

Analytical grade NaCl, $CuSO_4 \cdot 5H_2O$ and $NiSO_4 \cdot 6H_2O$ are commercially-available, they had a purity of more than 99.9% and were used without further purification. Crystals of NaCl, $CuSO_4 \cdot 5H_2O$ and $NiSO_4 \cdot 6H_2O$ were grown for 2–3 days by slow evaporation of saturated aqueous solutions of the respective salts.

Methods: Diffraction patterns of powder samples were obtained by means of a D8 Advance (Bruker BioSpin GmbH) diffractometer using the Bragg–Brentano scheme of Mo-Kα-radiation ($\lambda = 0.71072$ Å). The angular scanning range was 2–20° with a step of 0.01°. A Super Speed Vantec-1 counter was used. The pulse acquisition time at each scanning point was 0.5 s.

FTIR spectra were produced by an Avatar 360FT-IR ESP spectrophotometer ("Nicolet", USA) in the range of frequencies 4000–400 cm^{-1}. The samples were pressed in the form of tablets containing 1 mg of the substance being analyzed and 100 mg of potassium bromide. The FTIR measurements were carried out at 25.0 ± 0.1 °C.

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Thermogravimetric analysis was performed on a TG 209F1 Iris thermo-microbalance (Netzsch Geratebau GmbH, Germany) using platinum crucibles in an atmosphere of dry argon at a flow rate of 30 ml min^{-1} and a heating rate of 10 K min^{-1}. The accuracy of the sample mass measurement was 1×10^{-7} g.

3. Results and discussion

Concentrations of aqueous dispersion of nanocrystalline cellulose were 1–10 g/l. At ratio of NCC to a salt from 0.015 to 0.3, crystallization of the inorganic salts results in dendritic growth. A crystal dendrite is a crystal that develops with a typical multi-branching tree-like form. X-ray powder diffraction patterns for the samples under study revealed that crystallization of NaCl, $CuSO_4 \cdot 5H_2O$ and $NiSO_4 \cdot 6H_2O$ in the presence of nanocrystalline cellulose occurs with formation of halite, chalcanthite and retgersite, respectively (Figs. 1–3) [9].

From the images in Figs. 1–3, it can be clearly seen that in the presence of nanocrystalline cellulose the branched structures of the inorganic salts are formed. Each dendrite of the crystal consists of a pronounced trunk with two groups of side branches growing on the trunk. Compared with the plate-like shaped crystals of the salts, in the presence of nanocrystalline cellulose the dendrite-shaped rod-like leaves or sub-branches can grow on the side branches, resulting in the formation of a dendritic structure.

Clear diffraction peaks of halite, chalcanthite and retgersite observed in the XRD patterns (Figs. 1–3) suggest that products obtained with nanocrystalline cellulose as an additive are pure inorganic salts. Therefore, the NCCs are not entrapped and distributed in the matrix of salts microparticles during crystallization. This result indicates that nanocrystalline cellulose can significantly affect the morphology of the inorganic salts crystals; however, it has no effect on the purity of the crystalline form. The FTIR and TG analyses were used to further prove the absence of any organic molecules in the salts crystals.

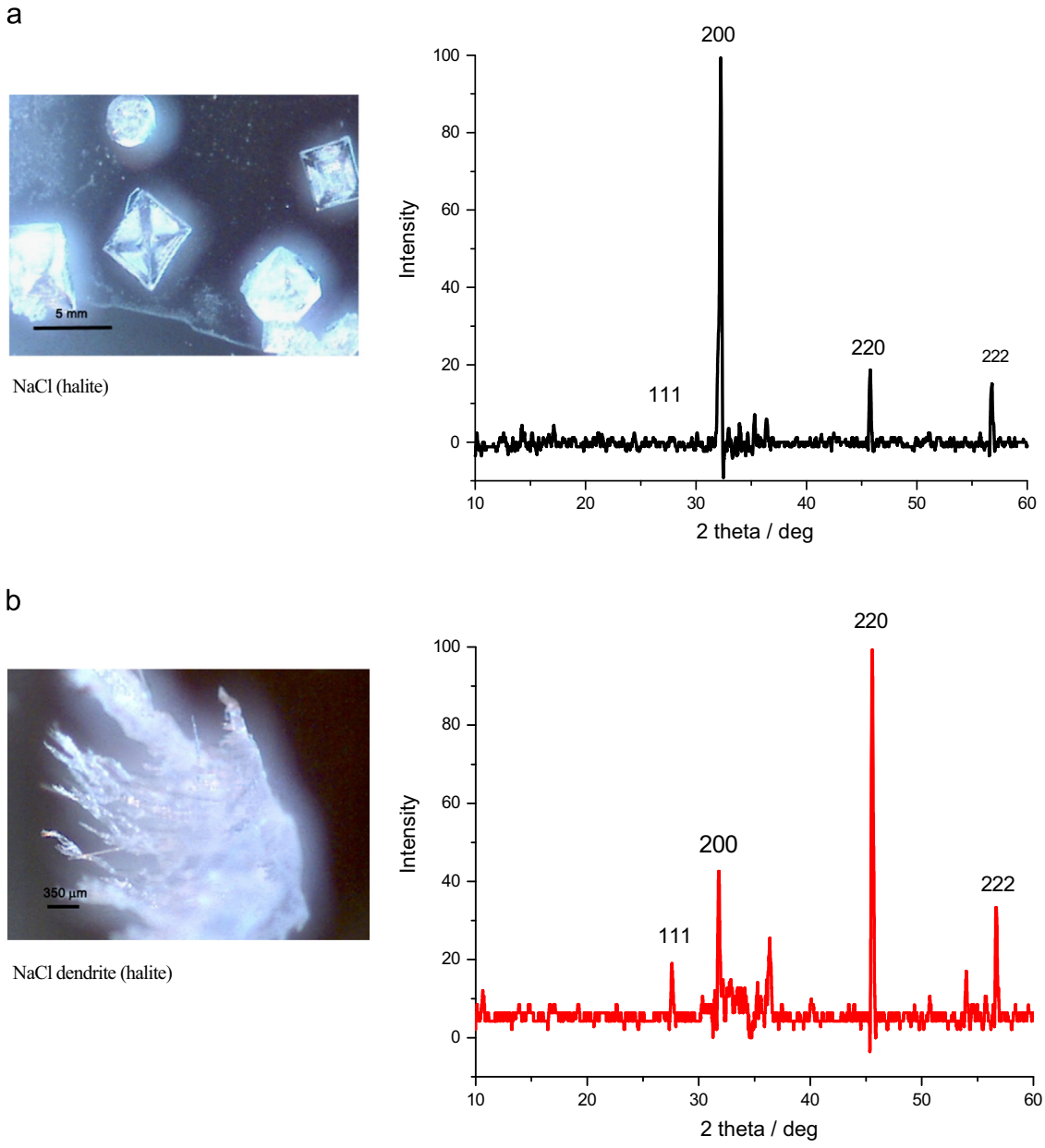

Fig. 1. Photo images and respective XRD pattern characteristics of the NaCl.