

Growth of calcium bilirubinate crystal controlled by functional polymer

Yuhua Shen*, Anjian Xie, Yongmei Yang, Fangzhi Huang, Long Chen, Jiangtao Huang

School of Chemistry and Chemical Engineering, Anhui University, Hefei 230039, China

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Abstract

Calcium bilirubinate (CaBR) particles were synthesized in three systems, such as pure water, glucan and polyethylene glycol (PEG) aqueous solutions, respectively. The polymorph and morphology of the particles were investigated using Fourier transform infrared spectroscopy (FT-IR), transmission electron microscope (TEM) and X-ray diffraction spectroscopy (XRD). The results revealed that the CaBR formed in pure water was amorphous and quasi-spherical with a mean diameter of about 80 nm. The glucan in solutions made the size of spheric CaBR particles increased obviously, but the crystallinity of particles was not improved apparently. The oriented growth of fusiform CaBR crystals was induced by PEG successfully. The average length of the crystals was 170 nm and the diameter 26 nm. The formation mechanism of CaBR crystal controlled by PEG was also discussed in this article.

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1. Introduction

Pigment gallstone, one of the abnormal biominerals, formed in bile duct and has recently attracted considerable attention because of its insolubility, difficult surgical treat and high rate of recrudescence [1–6]. CaBR has been proved the principal component of pigment gallstones [7–11]. Therefore, the formation mechanism of the pigment gallstone is not yet completely understood through decades of research [12,13]. Bilirubin (H_2BR) is a kind of

inner-toxin as well as a kind of inner-antioxidant in human body [14,15]. When metabolism is abnormal, the surplus H_2BR will be combined with metal ions and some functional polymers, consequently resulting in the CaBR deposition that forms gallstones. Some researches through infrared spectroscopy and fluorescence spectrum has shown that BR^{2-} ions could coordinate with Ca^{2+} ions to form nonstoichiometric compounds [1–7,16], because there were several polar groups ($-COOH$ and $-NH-$) in a H_2BR molecule which resulted in complicated and multiform coordination of BR^{2-} and Ca^{2+} . Up to now, the crystal structure of CaBR has not been determined because of the difficulty in synthesizing the single crystal of CaBR [17,18].

* Corresponding author. Tel.: +86 551 5107042; fax: +85 551 5108090.

E-mail address: s_yuhua@163.com (Y. Shen).

Compared with some charged polymers, the bio-compatible functional polymer PEG is often found to be an inexpensive, nontoxic, environmentally friendly reaction medium [19,20], and carriers for calcitonin delivery [21]. Here, in order to simulate the process of abnormal biomineralization, we use the reactive and functional polymer, such as glucan and PEG, as templates to induce the formation of CaBR crystals for the first time. In this study, the nucleation and oriented growth mechanism of the CaBR crystal was discussed, which was important for us to understand the formation of gallstones.

2. Experimental details

2.1. Materials and instruments

H₂BR, PEG and Glucan were all purchased from Institute of Biological Products of Shanghai (Shanghai, China). They were biochemical reagents. Anhydrous CaCl₂ and NaOH were obtained commercially and were analytically pure. All reagents above were used without further purification.

The samples were characterized by FT-IR spectroscopy (Nicolet 870) using KBr pellets over the wave number range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹ and XRD (rigakvD/Max RA) with a scan speed of 10(2θ)/min and a scan step of 0.020. The morphologies of obtained particles were routinely observed by TEOLTEM-100sx TEM. Conductance measurements were carried out to characterize the interaction between Ca²⁺ ions and PEG. The conductivity of the mixed solution was measured with a DDSJ-308A model conductivity meter (Shanghai Precision & Scientific Instrument Co., Ltd).

2.2. Experimental procedures

At first, the 0.1 mmol/L Na₂BR solution was prepared by adding appropriate H₂BR into 0.2 mmol/L NaOH solution and stirring constantly till the complete dissolution of the H₂BR. Then, we divided the solution, which was 150 ml, into three equal parts. The first part was used as system I. Glucan and PEG were added into the other two parts, followed by stirring until the solids were dissolved completely (both concentrations were 1.5 wt%). After an overnight incubation, the two solutions were used as system II and III, respectively. 50 mL of 0.1 mmol/L CaCl₂ solution was added dropwise into the systems I–III, with constant mechanical stir

(stirring rate, 1000 rpm) for 3 h. Then the three solutions were respectively kept in sealed glass vials for 48 h to make the reaction complete and then were centrifuged at 15000 rpm to obtain the solids, which were washed three times with double-distilled water, ethanol, chloroform, respectively, and then vacuum dried, brown solids were obtained, named CaBRs I–III. All experiments above proceeded at 18 °C in the absence of light.

The Ca²⁺-PEG aqueous solution was dropped on KBr solids, dried and characterized by FT-IR spectroscopy.

3. Results and discussion

3.1. FT-IR spectroscopy

The FT-IR spectra of H₂BR and CaBRs I–III were shown in Fig. 1a–d. The major corresponding FT-IR bands and assignments were listed in Table 1. The main bands of H₂BR were observed at 3411, 1691, 1647, 1612, 1571, and 1439 cm⁻¹ in Fig. 1a, which were respectively assigned to stretching vibration of N–H of pyrrole ring, C=O of carboxyl, C=O, N–C, C=C of lactam, C=C, C=O, N–C of lactam, C=C of lactam and pyrrole ring, C–C, C=O of carboxyl. The C=O vibration peaks of the carboxyl groups at 1691 cm⁻¹ disappeared as shown in Fig. 1b–d, indicating that salt bilirubinate was not acidic. The pyrrole ring vibration peaks round 3410 cm⁻¹ shifted to higher frequency. The coincidence vibration peaks 1647 cm⁻¹ of C=O, N–H and C=C in lactam, 1612 cm⁻¹ of C=C, C=O and N–C in lactam, 1439 cm⁻¹ of C–C and C=O in carboxyl blue-shifted by 18 cm⁻¹, 7–9 cm⁻¹, 15–17 cm⁻¹, respectively. These alterations indicated that there were coordination interactions

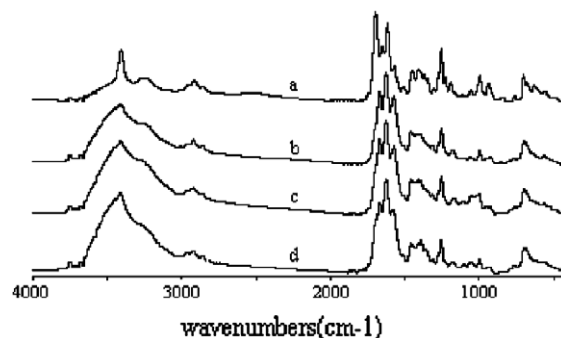


Fig. 1. FT-IR spectra of H₂BR (a) and CaBR formed in pure water (b), glucan solution (c) and PEG solution (d).

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