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Biomimetic growth of flower-like calcite morphology

Satya Vani Chinnamaneni¹, Saratchandra Babu Mukkamala^{1*}, Rambabu Chintala², Sethuram Kavuri³

¹Department of Chemistry, GITAM Institute of Science, GITAM University,
Visakhapatnam -530045, Andhra Pradesh, (INDIA)

²Department of Chemistry, Acharya Nagarjuna University P.G. Centre, Nuzvidu-521201, Andhra Pradesh (INDIA)

³Member, American Association of Pharmaceutical Scientists, 4714 Golden Ridge Trl, Portage, MI-49024 (USA)

E-mail : mscbabu@yahoo.com

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ABSTRACT

The crystal growth of calcium carbonate was investigated in presence of *para*-Aminobenzoic acid (PABA) at different experimental conditions. Calcite phase with new flower-like morphology was obtained biomimetically at room temperature after 24 hrs of crystal growth at pH 8.0 and 0.2mM concentration of PABA. On the other hand complex bundles of plate-like nano subunits were dominant at pH 3.0. PABA played an important role in directing the crystal phase and growth morphology of calcium carbonate. The products were characterized by Scanning Electron Microscopy (SEM) and Powder X-ray diffraction (XRD) analysis.

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KEYWORDS

Biominalisation;
Calcium carbonate;
Calcite flowers;
Vaterite nano plates;
para-Aminobenzoic acid.

INTRODUCTION

In Nature, organisms fabricate fascinating structures such as shells, bone, and teeth specifically designed to provide mechanical support and protection via biomineralisation^[1]. Biomineralisation is a highly complex phenomenon involving molecular interactions occurring at the interface between the inorganic mineral and the macromolecular organic matrix for fine tuning the deposition of biominerals^[2-4]. Much attention has been paid during recent years to adapt the biomineralisation processes to generate new materials with controlled morphologies and unique structural complexity^[5-8]. Calcium carbonate is one of the mostly studied biominerals, because of its high abundance and rich polymorphism, and it has been widely used as a model

mineral in biomimetic chemistry. Applications of calcium carbonate have been focussed on biomedical fields^[9,10] such as drug delivery, treatment of dry eye etc in addition to use in coatings, plastics, alloys and catalysts. Calcium carbonate occurs in three main crystalline polymorphs (calcite, vaterite, and aragonite), two hydrated crystal forms (calcium carbonate monohydrate and calcium carbonate hexahydrate), and also as amorphous material.

In literature, different biomimetic approaches to control the morphology of calcium carbonate using a variety of additives such as amino acids^[11] peptides^[12], proteins^[13], biopolymers^[14] carboxylate rich carbonaceous material^[15], lecithin liposome organic template^[16] and biomolecules of lotus root^[17] have been reported. It is now well established that the additives with carboxy-

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late moities can effectively control the morphology of calcium carbonate by occupying carbonate sites during crystal growth under different reaction conditions^[18-20].

Previously we have reported the synthesis of different polymorphs of calcium carbonate using various carboxylate additives (malonate, succinate, glutarate and adipate etc) by varying the reaction conditions, such as temperature and concentration^[21]. Specifically, the use of a polycarboxylate template namely 1,3-diamino-2-hydroxypropane-*N,N,N',N'*-tetraacetate has generated calcite microtrumpets^[22] which are mimicking the coccoliths of an unicellular algae, *Discosphaera tubifera*. In this manuscript, we demonstrate the role of *para*-Aminobenzoic acid (PABA) as an additive during mineralisation of calcium carbonate. In continuation of our efforts in the process of biomineralisation, we found new flower-like morphology by the influence of PABA. PABA is a naturally occurring compound, found in liver, kidney, wheat germ, bran, and yogurt. Furthermore, PABA is involved in different biochemical reactions in living systems^[23]. Hence, we have opted PABA for biomimetic growth of calcium carbonate. Since PABA is consisting of both carboxylate and amino functionalities analogous to aromatic amino acids, a similar function is expected to control the nucleation and growth of calcium carbonate mineral.

EXPERIMENTAL

The mineralization was carried out by a slow CO₂ gas diffusion technique. 2.0 mmol of CaCl₂ (0.294g) in 10ml distilled water was taken along with different proportions of *para*-Aminobenzoic acid (0.02mM, 0.04mM, 0.1mM and 0.2mM) in a cell culture dish. The dishes were covered with parafilm and 2 to 3 holes were made, so that the carbon dioxide could be introduced to the solution via vapour diffusion. The dishes were then placed in the desiccator containing ammonium carbonate (CO₂ source) for 24 hours at room temperature (25±1°C). The crystal growth process in the solutions was initiated at three different pH values of 3.0, 6.0 and 8.0. 0.1M NaOH solution was used to maintain the pH. Further, at each pH value the growth process was monitored by using different concentrations of PABA (0.02mM to 0.2mM). After completion of the reaction, the crystals were filtered, washed sev-

eral times with distilled water and dried at ambient temperature. Powder X-ray diffraction (STOE system operating with monochromated Cu K α_1 radiation) and Scanning Electron Microscopy were used for characterization of products.

RESULTS AND DISCUSSION

The crystal growth process of calcium carbonate was initiated at three different pH values of 3.0, 6.0 and 8.0 by PABA additive. In addition, at each pH value the growth process was further monitored by using different concentrations of PABA (0.02mM, 0.04mM, 0.1mM and 0.2mM). Three polymorphs of calcium carbonate i.e., calcite, aragonite and vaterite were observed under the above mentioned experimental conditions. However, in the absence of PABA, the thermodynamically most stable regular rhombohedral calcite was the only phase observed. In all the above experiments a reaction period of 24 hrs was found to be appropriate to note the changes in the crystal growth of calcium carbonate.

Remarkable effects on the evolved morphologies were observed by varying both the concentration of PABA and pH. When the solution starting pH was 3.0 and PABA concentration was 0.04mM, truncated rhombohedral calcite morphology (Figure 1a) was obtained. On the other hand, at same pH, when the concentration of PABA was increased to 0.2mM, beautiful bundles of vaterite nano plates along with traces of calcite were produced (Figure 2b). Mixed phases of calcite and aragonite were resulted at pH 6.0 with different concentrations of PABA.

Interesting transitions in the crystal morphology of calcium carbonate were noted in the experiments carried out at pH 8.0. At lower concentrations of PABA (0.04mM), the growth of flower shaped calcite was initiated from elongated truncated calcite crystals as shown in figure 2a, which however was not completed. Presumably, the concentration is not sufficient to convert the truncated rhombohedral calcite to fully grown flower-like calcite. Whereas at higher concentrations of PABA (0.2mM), completely grown calcite flowers were seen (Figure 2b & 2c). A stepwise growth of petals of calcite flower was also recorded in SEM study and depicted in figure 2d.

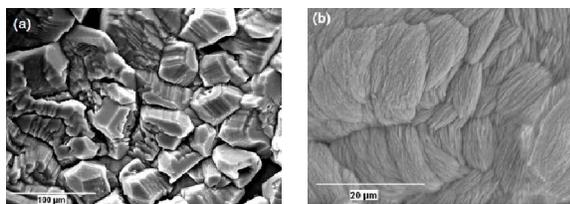


Figure 1 : SEM images of various phases of calcium carbonate found at pH 3.0. (a) truncated calcite crystals at PABA concentration 0.04mM, (b) vaterite nano plates PABA concentration 0.2mM

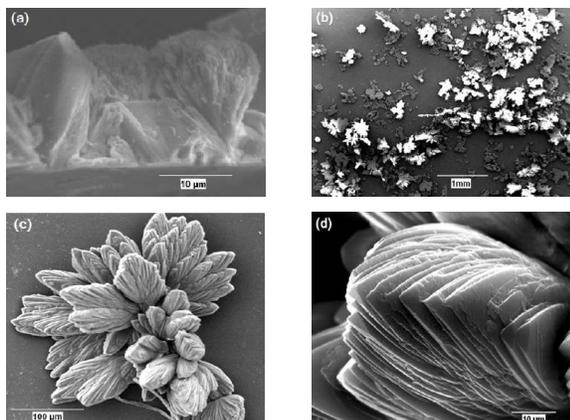


Figure 2 : SEM images of flower-shaped calcite superstructures (a,b,c). Stepwise growth on petals of calcite flower(d)

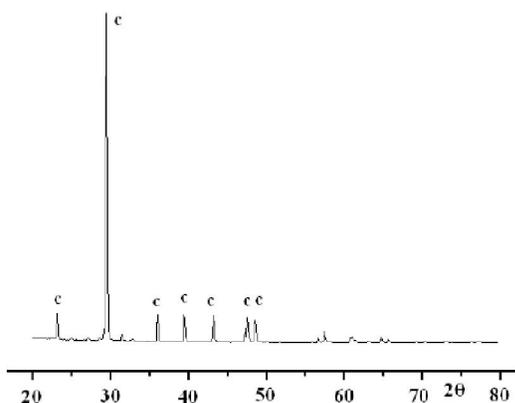


Figure 3 : X-ray powder patterns of the calcium carbonate (c=calcite)

In general, organic additives or templates interact with the reacting species either in solution or at the step edge during the crystal growth process and direct the crystal morphology^[19,24]. However, the growth of flower-like calcite structures appear to be a complex phenomenon. The ionisation of both carboxylic and amino groups mainly depends on the pH value of the reacting medium. The ionisation constant, pK_a of PABA is 4.65. So at higher pH the carboxylate group from

PABA was effectively complexed with Ca²⁺[25]. In a similar way carboxylate group of PABA interacts with calcium and occupy the carbonate sites in the growing calcium carbonate crystals. Presumably, this could be due to the accumulation of PABA molecules from all {104} faces and eventually extends the growth outward from all the edges, therefore it gradually grows like a petal with time, leading to the final flower-like crystals. Figure 3 shows the Powder XRD patterns of crystalline flower-like calcite phase.

CONCLUSION

In conclusion, *para*-Aminobenzoic acid used in the present study could be an effective organic additive in mimicking the biomineralisation. In addition to the pH, the concentration of PABA was also found to control the crystal growth process of calcium carbonate. At any given pH, better crystal growth process was observed by using higher concentrations of PABA. While the crystal growth initiated at lower pH (3.0) produced dominant vaterite phase of bundles of plate-like nano subunits, a fully grown flower-like calcite was developed only at higher pH value (8.0). It is well-known that the acidic proteins in living systems can direct and modify the crystal growth and morphology. Since PABA is having carboxylate and amino functionalities, a similar function could be possible during the crystal growth of calcium carbonate. However, further efforts are necessary to better understand the growth of the mechanism mentioned above in the presence of PABA.

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