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Biomimetic synthesis of calcium carbonate with different morphologies and polymorphs in the presence of bovine serum albumin and soluble starch

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Calcium carbonate has been synthesized by the reaction of Na_2CO_3 and $CaCl_2$ in the presence of bovine serum albumin (BSA) and soluble starch. Effects of various bovine serum albumin (BSA) and soluble starch on the polymorph and morphology of $CaCO_3$ crystals were investigated. Crystallization of vaterite is favored in the presence of BSA and soluble starch, respectively, while calcite is favored in the presence of a mixture of BSA and soluble starch. The morphologies of $CaCO_3$ particles in the presence of mixture of BSA and soluble starch are mainly rod-like, suggesting that the BSA, soluble and their assemblies play key roles in stabilizing and directing the $CaCO_3$ crystal growth.

1. Introduction

Nature has succeeded in producing a number of inorganic functional structures with designed morphology, polymorph, orientation of inorganic minerals, sizes and arranged them into highly ordered and hierarchically organized structures from nanoscale to macroscale [1,2] for specific purposes, such as structural support [3], protection [4], navigation [5], and photosensitivity [6,7] through a process named biomineralization. The mild condition, high efficiency and environmentally friendly process of the biomineralization have attracted considerable attention recently to mimic it in vitro using a variety of biomolecules including proteins, nucleic acids, and polysaccharides to build functional inorganic materials, for example, bone, egg shell, and seashell [8,9]. It is important to understand this process for the controlling mineralization, which may lead to the development of new strategies in the synthesis of inorganic nanophases. Recently, much effort has gone into this field by applying this strategy in the bioinspired preparation of advanced inorganic materials. Researches have found that biological macromolecules were closely related to the mineralization process, which build and control inorganic materials through supramolecular preorganization, interfacial molecular recognition, and assembly process [10].

Calcium carbonate is one of the most abundant minerals in the natural world. It forms scales, geological deposits, ocean sediments and biominerals such as pearl, nacre of mollusc shell and otolith [11–13], which can be found in soils, marine and fresh waters [14]. On the other hand, calcium carbonate polymorphs are also important in geological, environmental and bio-sciences [15–17]. It exists as three anhydrous crystalline polymorphs of increasing thermodynamic stability: vaterite (hexagonal), aragonite (orthorhombic) and calcite (rhombohedral) [18,19].

Calcium carbonate is also one of the most useful and versatile chemical materials with broad industrial applications, for example, as filler in paint, rubber, and paper [20,21]. But the application of $CaCO_3$ is mainly determined by a number of parameters, for example, polymorph, morphology, size, chemical purity, and so on. It can also be used as a precursor, a new template [22–24], and as novel carriers for drug delivery [25–28]. Among these factors, controlling of polymorphism, morphology and crystal size distribution is the most important [29]. As a result, controllable synthesis of calcium carbonate particles with special polymorph and morphology has been attracting considerable attention [30,31].

The morphology, polymorph and morphology of the $CaCO_3$ precipitate were reported to be affected by biomolecule [32–35]. Therefore, biomacromolecules or organic matrices extensively used to induce and adjust the as-synthesized $CaCO_3$ particles. Biomimetic synthesis of calcium carbonate with various phases, sizes and morphologies by using organic substrates has become an interesting topic in recent years [36].

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Table 1
Experimental conditions.

Number	1	2	3	4	5	6	7	8	9
Soluble starch/g	0	0.6	1.2	1.8	2.3	0	0	0	0
BSA/mg	0	0	0	0	0	4.0	6.0	8.0	10.0

Number	10	11	12	13	14	15	16	17
Soluble starch/g	0.6	1.2	1.8	2.3	1.2	1.2	1.2	1.2
BSA/mg	6.0	6.0	6.0	6.0	4.0	6.0	8.0	10.0

One way for the organic matrices to influence the shape of the mineral is by chemical interaction [37]. Clearly, organic matrices are the key to controlling biomineralization since various organic biomolecules can induce formation of the precursors to biominerals or construct inorganic-organic composites [38–40]. L. Yang et al. have reported using pepsin as calcium carbonate growth adjustor. The results indicate that the pepsin can direct the nucleation and crystallization of the calcium carbonate. The vaterite with regular spheres was formed in the presence of pepsin [41]. Interestingly, those regulatory biomacromolecules always contain specific functional groups to facilitate organic-inorganic interaction [42]. Therefore, an important aspect in biomineralization processes is the role played by functional groups at the surface of biomolecule matrix, for example carboxyl, hydroxyl group et al., at the surface of organic matrix, which may influence mineralization by binding calcium ions or adsorption on the crystal surface [43–46].

Starch, a polysaccharide, may be used to facilitate particle formation because of hydroxyl groups, which can coordinate to Ca^{2+} and control the nucleation and crystallization of $CaCO_3$ [47]. Q. Liu et al. have employed the amylopectin in sticky rice as an additive in the growth medium to prepare calcium carbonate. The rhombohedral calcium carbonate crystals with lamellar texture have been obtained. The results indicate that sticky rice polysaccharide, amylopectin, not only provide nucleation sites for $CaCO_3$ crystals but also regulates their growth shapes [48].

BSA can also use its —NH—CO— (peptide bond) groups to coordination interact with Ca^{2+} and control the nucleation and crystallization of $CaCO_3$ [36,49–54]. Xue et al. have prepared the BSA Langmuir film, and studied the influence of bovine serum albumin (BSA) on the polymorph, morphology and growth orientation of calcium carbonate in the process of the biomineralization. The results show that the polymorph of calcium carbonate initially formed is calcite, while the morphologies of calcium carbonate particles are different at different time. In the beginning of crystallization, the morphology of calcium carbonate particles is global [55]. Xue et al. have used bovine serum albumin Langmuir monolayer as template to synthesize $CaCO_3$ nanocrystals at room temperature. Spindle-like calcite has been synthesized under BSA Langmuir monolayers [56].

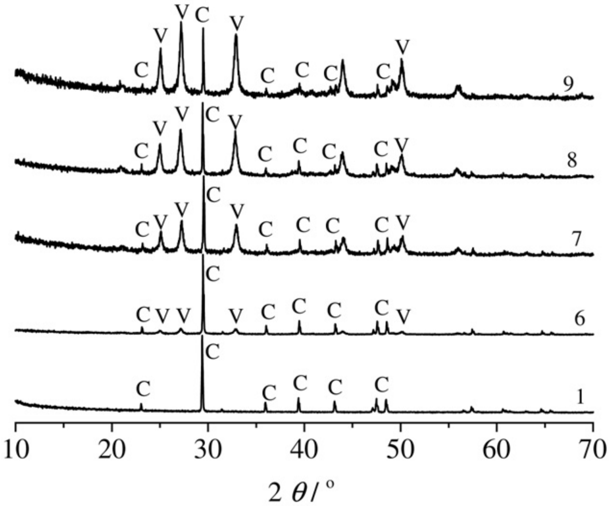

Fig. 2. XRD patterns of the as-prepared samples in the presence of BSA (mg): 1: 0, 6: 4.0, 7: 6.0, 8: 8.0, 9: 10.0.

Therefore, soluble starch and BSA were selected as the model organic additives of polysaccharide and protein to influence the crystallization and growth of calcium carbonate. But in living organism, there may be simultaneous protein and polysaccharide. The polymorph and morphology of $CaCO_3$ are not regulated only by protein or only by polysaccharide. In fact, it may be influenced by the assembly of protein and polysaccharide, resulting from H-bonding et al. interactions [57]. In this paper, we not only research the influence of BSA and soluble starch on polymorph and morphology of $CaCO_3$, respectively, but also study the influence of assembly of BSA and soluble starch on polymorph and morphology of $CaCO_3$.

2. Experimental

2.1. Materials and characterization

All commercially available chemicals were of reagent grade and used as received without further purification. Powder X-ray diffraction

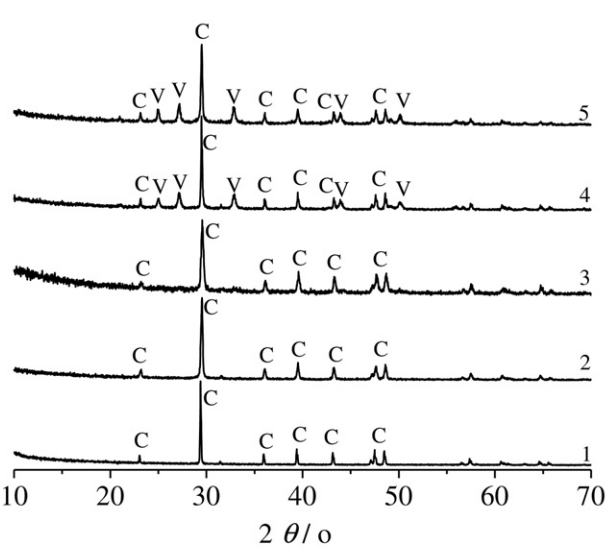

Fig. 1. XRD patterns of the as-prepared samples in the presence of soluble starch (g): 1: 0, 2: 0.6, 3: 1.2, 4: 1.8, 5: 2.3.

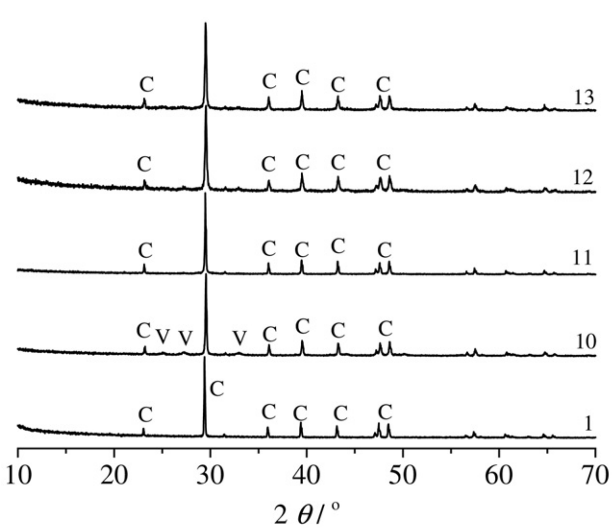

Fig. 3. XRD patterns of the as-prepared samples in the presence of BSA (fixed: 6.0 mg) and soluble starch (g): 1: 0, 10: 0.6, 11: 1.2, 12: 1.8., 13: 2.3.