



Ultrasound-assisted/biosurfactant-templated size-tunable synthesis of nano-calcium sulfate with controllable crystal morphology



Chinmay Hazra^a, Sarang Bari^b, Debasree Kundu^a, Ambalal Chaudhari^a, Satyendra Mishra^b, Aniruddha Chatterjee^{b,*}

^a School of Life Sciences, North Maharashtra University, Jalgaon 425 001, India

^b University Institute of Chemical Technology, North Maharashtra University, Jalgaon 425 001, India

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ABSTRACT

Nano-sized crystals of alpha calcium sulfate hemihydrate (α -HH) with considerable morphology-dependent properties find promising applications in the clinical fields as a cementitious material. Towards this end, ultrasound-assisted rhamnolipid and surfactin biosurfactant-template route is explored to control the morphology and aspect ratio of nano- CaSO_4 by adjusting the mass ratio of rhamnolipid/ H_2O , surfactin/ H_2O and rhamnolipid/surfactin. The change in the molar ratio of $[\text{SO}_4^{2-}]:[\text{Ca}^{2+}]$ results in modification in variable morphology and size of nano- CaSO_4 including long, short rods and nanoplates. With increase in the rhamnolipid/ H_2O ratio from 1.3 to 4.5, the crystal length decreases from 3 μm to 600 nm with the corresponding aspect ratio reduced sharply from 10 to 3. Similarly, the crystal morphology gradually changes from submicrometer-sized long rod to hexagonal plate, and then plate-like appearance with increase in surfactin concentration. The preferential adsorption of rhamnolipid on the side facets and surfactin on the top facets contributes to the morphology control. The process using 50% amplitude with a power input of 45.5 W was found to be the most ideal as observed from the high yields and lower average l/w aspect ratio, leading to more than 94% energy savings as compared to that utilized by the conventional process. As a morphology and crystal habit modifier, effects of Mg^{2+} and K^+ ions on α -HH growth were investigated to find an optimal composition of solution for α -HH preparation. Mg^{2+} ions apparently show an accelerating effect on the α -HH growth; however, the nucleation of α -HH is probably retarded by K^+ ions. Thus, the present work is a simple, versatile, highly efficient approach to controlling the morphology of α -HH and thereby, offers more opportunities for α -HH multiple applications.

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1. Introduction

Calcium sulfate (CS), an important family of minerals used in rubber, plastics, pigments and paper-making and biomedical (orthopaedic and dental) industries, exists in three forms including calcium sulfate dihydrate/gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; DH/CSD), hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$; HH/CSH; β -HH and α -HH) and anhydrite (CaSO_4) [1–6]. While the clinical application of β -HH is usually strictly restricted by its too fast resorption rate to match the growth rate of new bones, α -HH is widely used as dental impression and implant material, bone graft substitute, ceramic matrix, scaffold or carrier for delivering growth factors for osseous regeneration and to immobilize fracture zones due to biocompatibility, bioabsorbability, osteoinduction and osteoconduction [7,8]. Needless to say, the performance of α -HH in various applications is closely associated with the crystal size and morphology and morphological control of α -HH is therefore a prerequisite to

obtaining the appropriate performance to meet the targeted application [2,9–12].

Thus so far, α -HH nanoparticles [2], rods [2,9,13], long columns [11], whiskers [10,14,15], wires [16] and nanosheets [10] are commercially produced by (i) autoclave method [17], (ii) the salt solution [4,13], (iii) organic-water system [10], (iv) flame spray synthesis [18], (v) w/o microemulsion or reverse microemulsion methods [1,19], (vi) microwave-assisted route [20], and (vii) electrochemical deposition [21]. Besides, a number of strategies have been employed to control the α -HH morphology, including the manipulation of the pH [4], the electrolyte concentration [13], and the use of crystal growth modifiers [22–24]. However, the crystal size of α -HH prepared by these methods usually varies from dozens to hundreds of μm ; particles are relatively larger with a wider particle size distribution; are still confined in the synthesis of DH/CSD and the aspect ratio can be adjusted only within a narrow range [2,19,25]. Nevertheless, in spite of extensive efforts to produce nanostructured CaSO_4 of various dimensions, the actual molecular mechanism of crystal formation and how to control or alter their size remains unclear.

* Corresponding author. Tel.: +91 257 2258420; fax: +91 257 2258403.

E-mail address: aniruddha_chatterjee2006@yahoo.co.in (A. Chatterjee).

Aiming to improve the precipitation of CaSO_4 through stabilization of the metastable polymorphs, soluble additives [organic acids, carboxyl-rich polymers, phosphonate and phosphate-based species, sulfonic acids, poly-(acrylic acid), poly-(sodium-4-styrene sulfonate), sodium triphosphate, MgCl_2 , metal ions etc.] [3,9] and chemosynthetic surfactants (CTAB, SDS, CPC, alkyl benzene sulfonate etc.) [2,26] have been widely used to inhibit the precipitation of CaSO_4 , to stabilize intermediate phases, and also to some extent to modify the morphology of gypsum. However, the long reaction time and the tendency for particle aggregation, which results in particles with different shapes, are the main drawbacks of the conventional surfactant-template synthesis [1,13,17,19,25,27]. Moreover, such batch reactions are potentially unsuitable for biomedical application as these surfactants or polymers may elicit an adverse response *in vivo*.

In recent years, considerable efforts have been focused on using surfactant-template/ultrasound-assisted synthesis as an emerging technique with the advantages of simple reaction steps, greater control of particle size, uniform mixing, less preparation time, and less energy usage. While surfactant, sonochemistry and biomimetic route has been used for synthesizing nano-calcite and vaterite [28], the use of biosurfactant-templating strategies is still limited to brushite [29] and imogolite [30] nanotubes. In an ongoing effort, we have synthesized nano- CaCO_3 particles with diameters in the range of 10–50 nm by the solution spray process [31,32] and used them to prepare nano- CaCO_3 /polystyrene (PS) [33] and nano- CaCO_3 /poly(methyl methacrylate) (PMMA) [34] core-shell particles, by SDS assisted atomized polymerization technique, and the isolated core-shell nanoparticles were incorporated in a polypropylene matrix [33,35]. Similarly, PS (core)-biosurfactant (shell) bionanocomposites [36] and rhamnolipid biosurfactant capped zinc sulfide nanoparticles [37] were synthesized for protein drug release and photocatalytic applications, respectively. Using a cheap and eco-friendly approach, Sivakumar et al. have prepared various inorganic oxide nanocrystals like zinc ferrite [38,39], zinc oxide [40], and manganese zinc ferrite [41] utilizing the sonochemical emulsification and evaporation processes. Towata et al. have described a sonochemical process utilizing paraffin emulsion droplets as a template for the synthesis of macroporous zirconia [42]. However, to the best of our knowledge, no study has ever been reported about the synthesis of α -HH using biosurfactant-templated/ultrasonication assisted route. This has motivated us for using this soft green chemistry route and the objective of this work was, therefore, to explore size-tunable synthesis of CaSO_4 nanoparticles through biosurfactant-templated/ultrasonication assisted route. Herein, we report anionic biosurfactants (rhamnolipids and surfactin)-template method to develop α -HH nano- CaSO_4 , with the goal of gaining control over the crystal polymorph, size and shape. The effects of the main process parameters, i.e., molar ratios

of $(\text{NH}_4)_2\text{SO}_4/\text{CaCl}_2$, biosurfactant/water, ultrasonication (time, frequency, amplitude as well as intensity), pH of the reaction medium and Mg^{2+} and K^+ ions were investigated in detail to determine the domain for α -HH synthesis. Finally, the formation process is discussed, and a possible mechanism is proposed.

2. Experimental

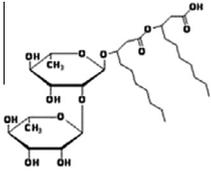
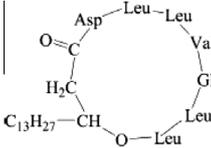
2.1. Materials

Two anionic biosurfactants i.e., rhamnolipids and surfactin were isolated and purified from *Pseudomonas aeruginosa* BS01 and *Bacillus clausii* BS02, respectively, as reported elsewhere [36,37]. Their chemical formulae, molecular weights, structures and other properties are shown in Table 1. All other chemicals used in this work were procured from Sigma Aldrich (U.S.A) and used without further purification. Double distilled and deionized water was used as a medium for all syntheses and characterizations. All syntheses were carried out at room temperature.

2.2. Biosurfactant templated sonochemical synthesis of nano- CaSO_4

The synthesis was carried out in a 100 ml beaker at a constant rate of 250 rpm. The temperature of the solution was maintained constant at ambient temperature with a deviation of $\pm 0.5^\circ\text{C}$ by a water bath. The nanosized CaSO_4 were synthesized by a modified *in situ* deposition technique. Briefly, 11.1 g (0.1 M) CaCl_2 (pH ~ 6.64) was added into 100 ml double distilled water. For experiments carried out in the presence of the two biosurfactants, these were introduced into the calcium solution prior to mixing with the sulfate solution. Each biosurfactant was added in varying amount to the aqueous calcium solution having a rhamnolipid/ H_2O or surfactin/ H_2O mass ratio ranging from 1.3 to 4.5 (step 1 solution) while rhamnolipid/surfactin mass ratio was fixed at 0.2, 0.3, and 0.4. After subjecting the aqueous calcium solution containing the biosurfactant(s) for 10 min irradiation, it was transferred to the ultrasonic reactor. Another solution of $(\text{NH}_4)_2\text{SO}_4$ (13.2 g; 0.1 M; pH ~ 6.68) dissolved in 100 ml of distilled water (step 2 solution) was introduced into the step 1 solution and ultrasound irradiation was produced with a high-intensity ultrasonic processor (Vibra Cell, Sonics, USA) for 1.0 h to form the CaSO_4 particles. The specifications of the ultrasonic horn are as follows: operating frequency, 22 kHz; rated output power, 750 W; diameter of stainless steel tip, 1.3×10^{-2} m, surface area of ultrasound irradiating face, 1.32×10^{-4} m², expected ultrasound intensity, 3.4×10^5 W/m² and the horn was operated at 50% amplitude. The energy and power input was varied while investigating the effect of amplitude (power density) variation. Overall temperature was kept constant

Table 1
Physical properties of the biosurfactants.

Biosurfactant	Molecular formula	Structure	Molecular weight (g/mol)	CMC (mM)	Interfacial tension (mN/m)
Rhamnolipid	$\text{C}_{32}\text{H}_{58}\text{O}_{13}$		650	0.1	1.2
Surfactin	$\text{C}_{53}\text{H}_{93}\text{N}_7\text{O}_{13}$		1036	0.04	1.0

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